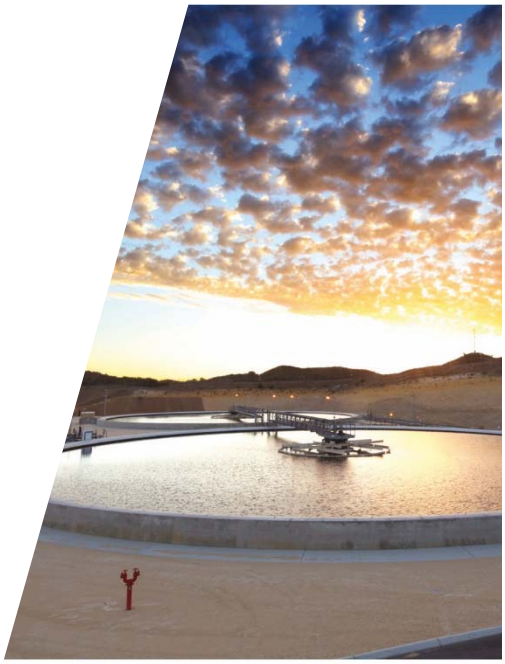
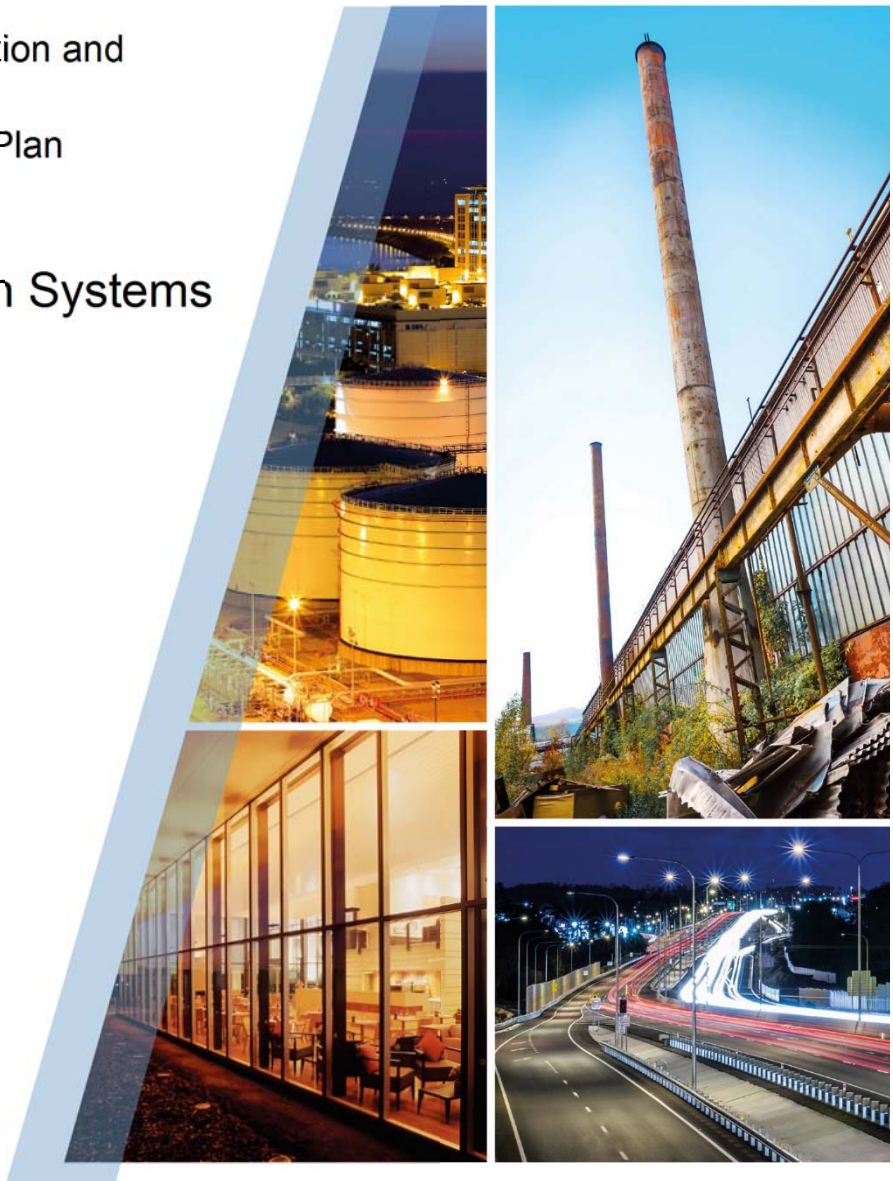


Quality Assurance Project Plan (QAPP)

for the Resource Conservation and Recovery Act (RCRA)
Facility Investigation Work Plan

GM Global Propulsion Systems
Bedford Facility
Bedford, Indiana



USEPA ID Number: IND 006036099
Revision Number 0
January 2019
Prepared by: GHD
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1. Project Description

The following outlines the scope of the Resources, Conservation and Recovery Act (RCRA) Facility Investigation (RFI), and any subsequent events, to be performed in accordance with the requirements of the RCRA Administrative Order on Consent (AOC) (effective August 4, 2014) between the United States Environmental Protection Agency (USEPA) and General Motors LLC (GM) for the GM Global Propulsion Systems-Bedford Facility (Docket No. RCRA 005-2014-0011) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) AOC (upon execution), but does not apply to any sampling associated with state or local permit requirements.

This Quality Assurance Project Plan (QAPP) presents the organization, objectives, planned activities, and specific quality assurance/quality control (QA/QC) procedures associated with the specific phases of RFI and Operation, Maintenance, and Monitoring (OMM) activities for the GM Global Propulsion Systems-Bedford Facility. Protocols for sample collection, sample handling and storage, chain-of-custody (COC) procedures, and laboratory and field analyses are described or specifically referenced to related investigation documents.

This QAPP addresses the QA/QC elements in the USEPA's QA-R5 document (March 2001) and other relevant guidance documents. The QA/QC procedures described in this QAPP are consistent with USEPA guidance in general.

1.1 Introduction

This QAPP has been prepared on behalf of GM. The QAPP is a component of the overall project scope including the RFI Work Plan and Interim Measures (IM) Work Plans, including the applicable Field Sampling Plan (FSP), Project Management Plan (PMP), Data Management Plan (DMP), Health and Safety Plan (HASP), and Waste Management Plan (WMP and the Final Corrective Measures for the Facility). This QAPP is also a component of Long-Term Operations, Maintenance, and Monitoring (OMM) programs associated with RCRA Interim or Final Corrective Measures implementation plans.

1.1.1 Project Objectives and Decision Statement

The primary objectives for data collection activities include:

i) Define the nature and extent of releases of hazardous wastes and/or hazardous constituents in environmental media (soil, sediment, groundwater, and/or surface water) at the GM Global Propulsion Systems-Bedford Facility.

ii) Collect sufficient data and information to evaluate the risk to human health and the environment, if any, associated with any releases of hazardous waste and/or hazardous constituents.

iii) Collect groundwater and measurement data in support of the CA750 Environmental Indicator.

iv) Collect sufficient data to properly characterize waste samples and to meet disposal criteria.

v) Collect sufficient data to meet requirements of OMM Plans and treatment permit requirements.

The Decision Statement for the investigation work is as follows:

i) Determine whether interim or final remedial actions are necessary to control current unacceptable risks, if any, to human health or the environment.

ii) Provide data for the development of a study of appropriate corrective measures (if warranted) to control current and future unacceptable risks to human health and the environment.

Associated specific objectives for field and laboratory data collection are discussed in Section 1.4 of this plan.

1.1.2 Project Status/Phase

The project status and investigation approach is presented in the RFI Work Plan and subsequent amendments or sampling programs. Sections 1.2 and 1.3 summarize the GM Global Propulsion Systems-Bedford Facility description and site history, respectively. Section 1.5 describes the GM Global Propulsion Systems-Bedford Facility sampling programs covered under this QAPP. Section 8 describes how the data evaluation procedures for this project will be conducted.

1.1.3 QAPP Preparation Guidelines

As previously noted, this QAPP has been prepared to present the project specific QA/QC elements in the EPA's QA-R5 document (March 2001).

1.2 Facility Description

The general Facility description is provided and is incorporated here by reference to the following draft RCRA Facility Investigation (RFI) Report (GHD, September 30, 2015) sections

Land Use	RFI Report Section 2.1
Climate	RFI Report Section 2.2
Topography	RFI Report Section 2.6
Surface Water Hydrology	RFI Report Section 2.8
Local Geology and Hydrology	RFI Report Sections 2.6 and 2.7

1.3 Site History

The GM Global Propulsion Systems-Bedford Facility history is provided in Section 3 of the RFI Report and incorporated here by reference:

Current and Historical Operations	RFI Report 3.1
Current Conditions Report Summary	RFI Report Section 3.2
RFI Objectives and Strategy	RFI Report Section 3.3 Pre-RFI Activities
	RFI Report Section 3.4
Results of RFI Investigations	RFI Report Section 7

1.4 Project Objectives and Intended Data Use

1.4.1 Target Parameter List

The investigative and OMM programs include the sampling and analysis of environmental media for the presence of organic and inorganic constituents based on historical operations at the Facility. The field and laboratory parameters are summarized below and presented in Table 1.1. This table may be updated when the Long Term OMM programs are developed/finalized.

1.4.1.1 Field Parameters

Concurrent with sample collection, several field parameters will be determined by the field sampling personnel. For soils and solid matrices, these field parameters will include visual observations, odor identification, and volatile organic compound (VOC) screening using handheld monitoring equipment. For aqueous samples (surface water and groundwater), at a minimum, the following parameters will be determined with field testing equipment: pH, specific conductivity, temperature turbidity, dissolved oxygen, and oxidation/reduction potential (ORP). Field parameter measurements will be dependent upon the requirements of the applicable sampling program.

1.4.1.2 Laboratory Parameters

Polychlorinated biphenyls (PCBs) are the primary target analytes. Other possible target parameters (primarily for disposal profiling) include organic compounds, metals and general/physical parameters. The basis for the selected parameter list is provided in the RFI Work Plan.

Tables 1.2-1.4 presents the estimated quantitation limits (EQL) for each compound or analyte. Method detection limit (MDL) studies have been performed by Eurofins TestAmerica, Pace and Merit in accordance with the procedures established in the Federal Register, Title 40, Part 136, August 28, 2017. MDLs are updated on an annual basis; the most recent results will be furnished upon request. Eurofins TestAmerica (North Canton, Ohio and Pittsburgh, Pennsylvania) and Pace Analytical (Indianapolis, Indiana) will be used as assigned primary project laboratories. Merit Labs (East Lansing, Michigan) will serve as a backup to project laboratories.

1.5 Sampling Locations

The RFI Work Plan and subsequent amendments or sampling programs provide a summary and rationale for the sample locations at the GM Global Propulsion Systems-Bedford Facility. It is possible, however, that depending on the nature of encountered field conditions, sampling locations may change. The person responsible for making such decisions will be the Field Quality Assurance (QA) Officer whose responsibilities are described in Section 2 of this QAPP. Any change of the sampling strategy will only be implemented after approval from the GHD Director and GM Project Manager. Current sample collection activities include: soil/water investigative sampling, groundwater monitoring, surface water monitoring, waste characterization, and OMM including wipe sampling and water treatment systems.

1.6 Project Schedule

The schedule and projected milestones are presented in the RFI Report and any additional work plans.

2. Project Organization and Responsibilities

The GM Project Manager with assistance from the designated GHD Project Director, will have the primary responsibility for the implementation of the RFI Work Plan. One or more of the following laboratories listed in Appendix A will perform the analyses of environmental samples collected at the Facility. This section defines the roles and responsibilities of the individuals who will perform the RFI and subsequent activities.

Figure 1 provides the organization chart for the project team.

2.1 Management Responsibilities

A description of the project organization and responsibilities of key personnel is presented in detail in the PMP. Management responsibilities are as follows:

Peter Ramanauskas (U.S. EPA RCRA Corrective Action Project Manager)

The Regulatory Agency Project Coordinator has the overall responsibility for oversight of all phases of the Investigation.

Ed Peterson – GM Project Manager

The GM Project Manager is responsible for implementing the project, and has the authority to commit the resources necessary to meet project objectives and requirements. The GM Project Manager's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully. The GM Project Manager will provide the major point of contact and control matters concerning the project and represent the project team at regulatory agency meetings and public hearings. The Project Manager will define project objectives and develop a detailed project schedule. The GM Project Manager will oversee project policy and procedures to address the specific needs of the project as a whole, as well as the objectives of each task.

Katie Kamm - GHD Project Director

The GHD Project Director will provide final review of significant work products and may participate in technical meetings with the USEPA or State Agency. The GHD Project Director will ensure that overall technical quality is maintained. The GHD Project Director will be actively involved in the direction of the project. The GHD Project Director has overall responsibility for ensuring that the project meets RFI objectives. The GHD Project Director will:

i) Acquire and apply technical and other resources as needed to ensure performance within budget and schedule restraints.

ii) Review work performed on each task to ensure quality, responsiveness, cost effectiveness, and timeliness.

iii) Be responsible for the preparation and quality of interim and final reports.

iv) Communicate with GM about the progress of the project.

Bill Steinmann – GHD Project Manager

The GHD Project Manager is responsible for managing the implementation of the RFI Work Plan and other RCRA activities and coordinating the collection of data pertaining to the Investigation or OMM stages. The GHD Project Manager is responsible for technical QC and project oversight. The GHD Project Manager also reviews, understands and provides approval of the QAPP.

Julie Luzwick - GHD Project Coordinator

The GHD Project Coordinator will assist the GHD Project Director and the GHD Project Manager in day-to-day project management. The GHD Project Coordinator is responsible for coordinating field activities and the procurement of project subcontractors. Additional responsibilities include:

i) Assisting in monitoring the RFI progress and quality

ii) Preparing and reviewing RFI reports

iii) Providing technical support of project activities

iv) Review and understand the QAPP

2.2 Quality Assurance Responsibilities

The QA team will consist of a QA Officer and the GHD Project Manager. QA responsibilities are described as follows:

Ruth Mickle – GHD Quality Assurance Officer

The GHD QA Officer reports directly to the GHD Project Manager and will be responsible for ensuring that all QA/QC procedures are being followed. The GHD QA Officer will be responsible for overseeing the review of all field and laboratory data. Additional responsibilities include:

i) Assuring the application and effectiveness of the QAPP by the analytical laboratory and the project staff

ii) Conducting internal QA/QC of the investigation activities

iii) Providing input to the GHD Project Director, the GHD Project Manager, and the GHD Project Engineer as to corrective actions required resulting from the above-mentioned evaluations

iv) Preparation and review of data validation and audit reports

v) Approval of the QAPP

The GHD QA Officer will be assisted by the data validation staff in the evaluation and validation of field and laboratory generated data. The GHD QA Officer will monitor the performance of the laboratory to ensure that the Data Quality Objectives (DQOs) for the project are met.

Regulatory Agency Quality Assurance Officer

The Regulatory Agency QA Officer may review this QAPP. Additional Regulatory Agency responsibilities for the project may include:

i) Conducting external performance and system audits of the RFI laboratories

ii) Reviewing and evaluating field and analytical laboratory procedures

2.3 Laboratory Responsibilities

Laboratory Project Manager

The Laboratory Project Manager will report directly to the GHD QA Officer and will be responsible for ensuring all resources of the laboratory are available on an as-required basis. The Laboratory Project Manager will also be responsible for the approval of the final analytical reports and approval of the laboratory's ability to adhere to the QAPP.

Laboratory Operations Manager

The Laboratory Operations Manager will report to the Laboratory Project Manager and will be responsible for coordinating laboratory analysis, supervising in-house COC reports, scheduling sample analyses, overseeing data review, and overseeing preparation of analytical reports.

Laboratory QA Officer

The Laboratory QA Officer or designee will have sole responsibility for review and validation of the analytical laboratory data generated as part of the RFI. The Laboratory QA Officer or Project Manager will sign all final laboratory data reports provided from the analysis of the project samples and will provide Case Narrative descriptions of any data quality issues encountered during the analyses conducted by the laboratory. The Laboratory QA Officer will also define appropriate QA procedures, overview QA/QC documentation, and approve this QAPP.

Laboratory Sample Custodian

The Laboratory Sample Custodian will report to the Laboratory Operations Manager and will be responsible for the following:

i) Receiving and inspecting the incoming sample containers

ii) Recording the condition of the incoming sample containers

iii) Signing appropriate documents

iv) Verifying COC and its correctness

v) Notifying the Laboratory Project Manager and Laboratory Operations Manager of sample receipt and inspection

vi) Assigning a unique identification number and customer number and entering each into the sample receiving log

vii) Initiating transfer of samples to lab sections

viii) Controlling and monitoring access/storage of samples and extracts

Laboratory Technical Personnel

The laboratory technical staff will have the primary responsibility in the performance of sample analysis and the execution of the QA procedures developed to determine the data quality. These activities will include the proper preparation and analysis of the project samples in accordance with the contract laboratory's Quality Assurance Manual and associated Standard Operating Procedures (SOPs).

One or more of the following laboratories may provide laboratory services in support of the Correct Action including the different phases of RFI, OMM, and waste characterization:

- Eurofins TestAmerica/North Canton, Ohio/Denise Heckler
- Eurofins TestAmerica/Pittsburgh, Tennessee/Denise Heckler
- Pace Analytical/Indianapolis, Indiana/Tina Sayer
- Merit Labs/East Lansing, Michigan/Barb Ball

Data Validation Staff

The data validation staff will be independent of the laboratory and familiar with the analytical procedures performed. The validation will include a review of each validation criterion as prescribed by the guidelines presented in Section 9.2.2 of this document, based on the phase of Corrective Action activity, and be presented in a formal written report for submittal to the GHD Project Manager.

2.4 Field Responsibilities

Julie Luzwick – GHD Field QA Officer

The GHD Field QA Officer is responsible for the overall operation of the field team and reports directly to the GHD Project Director and GHD Project Manager. The GHD Field QA Officer works with the project Health and Safety Officer to conduct operations in compliance with the project HASP. The GHD Field QA Officer will facilitate communication and coordinate efforts between the GHD Project Director and the field team members. Other responsibilities include:

i) Developing and implementing field-related work plans, ensuring schedule compliance, and adhering to management-developed project requirements

ii) Coordinating and managing field staff, including sampling and drilling

iii) Performing field system audits

iv) Overseeing QC for technical data provided by the field staff

v) Preparing and approving of text and graphics required for field team efforts

vi) Coordinating and overseeing technical efforts of subcontractors assisting the field team

vii) Identifying problems in the field, resolving difficulties in consultation with the GHD Project Director, GHD Project QA Officer, and GHD Project Manager, and implementing and documenting corrective action procedures

viii) Will review and understand the QAPP

ix) Participating in preparation of the final reports

Field Team Personnel

Field Team Personnel involved in the RFI will be responsible for:

i) Performance of field activities as detailed in the RFI Work Plan and in compliance with the DQO outlined in this QAPP for the specific activity being conducted

3. Quality Assurance Objectives for Measurement Data

The RFI Work Plan and subsequent amendments or sampling programs and associated QAPP are designed to produce data of the quality necessary to achieve the project objectives for the specific phase of the project and meet or exceed the minimum standard requirements for field and analytical methods. The overall QA objective for measurement data is to develop and implement procedures for field sampling, COC, lab analyses, and reporting that will provide results which are adequate for supporting the specific Corrective Action activity objectives and legally defensible in a court of law. The QAPP program will include:

i) A mechanism for ongoing control of measurements and evaluation of data quality

ii) A measure of data quality in terms of precision, accuracy, representativeness, completeness, and comparability

The following section is a general discussion of the criteria used to measure the field and laboratory analytical data quality. The laboratory reference data and SOPs provided in Appendix B and C present the performance criteria for laboratory QC objectives.

3.1 Precision

3.1.1 Definition

Precision is defined as a quantitative measure of the degree to which two or more measurements are in agreement. Precision will be stated in terms of relative percent difference (RPD). The overall precision of measurement data is a mixture of sampling and analytical factors. Precision will be determined by collecting and analyzing field duplicate samples and by creating and analyzing

laboratory duplicates from one or more of the field samples. The analytical results from the field duplicate samples will provide data on sampling precision. The results from the laboratory created duplicate samples will provide data on analytical precision.

3.1.2 Field Precision Sample Objectives

Field precision will be assessed through collection and measurement of field duplicates of investigation samples (excluding waste samples).

3.1.3 Laboratory Precision Sample Objectives

Laboratory duplicate analyses will be performed through the use of matrix spike/matrix spike duplicates (MS/MSD) for organic parameters and matrix duplicate (MD) analyses for certain inorganic parameters. The analytical data will be presented in summary table format. The precision criteria for laboratory MS/MSD/MD analyses are provided in the laboratory reference data provided in Appendix C.

3.2 Accuracy

3.2.1 Definition

Accuracy relates to the bias in a measurement system. Bias is the difference between the observed and the "true" value. Sources of error are the sampling process, field contamination, preservation techniques, sample handling, sample matrix, sample preparation, and analytical procedure limitations.

3.2.2 Field Accuracy Objectives

Sampling bias will be assessed by evaluating the results of field equipment rinsate and trip blanks. Field equipment rinsate and trip blanks will be collected as appropriate for each sampling effort.

Field equipment rinsate blanks will be collected by passing laboratory purified water over and/or through the respective decontaminated field equipment utilized during each sampling effort if the equipment will be reused to collect several samples. Field rinsate blanks will be analyzed for each target parameter for the respective sampling effort for which environmental media have been collected. (Note: If dedicated or disposable sampling equipment is used, equipment rinsate samples will not be collected as part of that field effort).

Trip blank samples will be prepared or purchased by the laboratory and provided with each cooler that includes VOC analysis containers. Trip blank samples will be analyzed for each VOC for which environmental media have been collected for analysis.

3.2.3 Laboratory Accuracy Sample Objectives

Analytical bias will be assessed through the use of known laboratory control samples (LCS) and GM Global Propulsion Systems-Bedford Facility specific MS sample analyses. LCS and MS/MSD sample analysis will be performed as prescribed by the analytical method SOPs. LCS analyses will be performed with each analytical batch of project samples to determine the accuracy of the analytical system.

The results of the LCS and MS/MSD analyses will be presented in a summary table reporting format and evaluated versus the acceptance criteria presented in the laboratory analytical reports. Current acceptance criteria are presented in the laboratory reference data provided in Appendix C.

The accuracy of organic parameter analyses is also monitored through the analysis of system monitoring or surrogate compounds. Surrogate compounds are added to each sample, standard, blank, and QC samples prior to the sample preparation and analysis. Surrogate compound percent recoveries provide information on the effect of the sample matrix on the accuracy of the analyses and are evaluated against the acceptance criteria presented in laboratory analytical reports. Current acceptance criteria are presented in the laboratory reference data provided in Appendix C.

3.3 Representativeness

3.3.1 Definition

Representativeness expresses the degree to which sample data accurately and precisely represents a characteristic of a population, a parameter variation at a sampling point, or an environmental condition. Representativeness is a qualitative parameter that is dependent upon the design of the sampling program. The representativeness criterion is satisfied by proper selection of sampling locations and quantity of samples collected.

3.3.2 Measures to Ensure Representativeness of Field Data

Representativeness will be addressed by describing sampling techniques and the rationale used to select sampling locations. Sampling locations may be biased (based on existing data, instrument surveys, observations, etc.) or unbiased (completely random or stratified-random approaches).

For this project, sampling will be biased; that is, sampling associated with the soil and groundwater will be based on the observed or known presence/absence of GM Global Propulsion Systems-Bedford Facility specific contaminants, and/or GM Global Propulsion Systems-Bedford Facility knowledge of a release. Specific sampling technique descriptions, which allow consistency, repetitiveness, and thus representativeness, are provided as SOPs in the FSP.

3.3.3 Measures to Ensure Representativeness of Laboratory Data

Representativeness in the laboratory is ensured by using proper analytical procedures, and analyzing field duplicate samples. By definition, field duplicate samples are collected to be representative of a given point in space and time. Thus, sample duplicates provide both precision and representativeness information.

3.4 Completeness

3.4.1 Definition

Completeness is a measure of the amount of valid (usable) data obtained from a measuring system compared to the amount that was expected to be obtained under normal conditions. The completeness goal for all data uses is that a sufficient amount of valid data be generated so that determinations can be made related to the intended data use with a high degree of confidence.

3.4.2 Field Completeness Objectives

Completeness is a measure of the amount of valid measurements obtained from all measurements taken in this project. Field completeness objective for this project will be 90 percent.

3.4.3 Laboratory Completeness Objectives

Laboratory data completeness objective is a measure of the amount of valid data obtained from all laboratory measurements. The evaluation of the data completeness will be performed at the conclusion of each sampling and analysis effort. Corrective actions such as revised sample handling procedures will be implemented if problems are noted.

The completeness of the data generated will be determined by comparing the amount of valid data, based on independent validation, with the total data set. The completeness objective will be 90 percent.

3.5 Comparability

3.5.1 Definition

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another.

3.5.2 Measures to Ensure Comparability of Field Data

Sample data should be comparable with other measurement data for similar samples and sample conditions. This goal is achieved through using SOPs to collect, preserve, store, and analyze representative samples and the reporting of analytical results. The field SOPs for the various activities to be conducted during this investigation provide guidelines to generate reproducible results.

3.5.3 Measures to Ensure Comparability of Laboratory Data

Comparability of laboratory data will also be measured with the results from the analysis of Standard Reference Materials (SRM) obtained from either USEPA Cooperative Research and Development Agreement (CRADA) suppliers or the National Institute of Standards and Technology (NIST) (formerly National Bureau of Standards) for instrument initial and continuing calibration verification. The reported analytical data will be presented in standard units of mass of contaminant within a known volume or mass of environmental media.

- **Solid Matrices** - micrograms (µg) contaminant per kilogram (kg) for organic analyses, and milligrams (mg) contaminant per kg for inorganic analyses of media (Dry Weight)
- **Aqueous Matrices** – µg contaminant per liter (L) of media for organic analyses, and mg per L for inorganic analyses
- **Non-Aqueous Phase Liquids (NAPL)** – µg contaminant per kg of media
- **Wipe samples** - µg contaminant per 100 cubic centimeter (cm^3) of surface area

Additional guidance on analytical data reporting is contained in the laboratory SOPs.

3.6 Decision Rules

3.6.1 Definition

The decision rule is a statement that prescribes a course of action or non-action to be taken based on assumptions to test its logical and empirical consequences.

3.6.2 Decision Rule Objective

The rationale for sample locations, sample number, and analytical parameters is provided in the main text of the RFI Work Plan and subsequent amendments or sampling programs. The decision rule for the sampling and analysis data collected is also provided in the RFI Work Plan, and supplemented as follows:

i) Define statistical parameters characterizing the population (e.g., mean, maximum, and percentile) and incorporate the scale of decision making (i.e., AOI size). Samples will be collected discreetly and biased towards locations with the highest likelihood to encounter maximum contaminant levels to provide an indication of impacted zones.

ii) Identify action levels (e.g., Risk-based Screening Levels; Regional Screening Levels [RSLs]); or a reference-based standard based on a GM Global Propulsion Systems-Bedford Facility Conceptual Model that will be developed as part of the RFI process.

iii) The maximum contaminant concentration or the 95th percent Upper Confidence Limit of the valid data set for each parameter detected within an AOI will be used to conduct a preliminary baseline human health and ecological risk assessment for the determination of appropriate corrective actions.

3.7 Level of Quality Control Effort

Equipment rinsate (if required), trip (if required by the type of contaminant), method blank samples, field duplicate samples, laboratory control, and MS/MSD samples will be prepared and analyzed to determine the data quality provided by the sampling and analysis activities conducted during the execution of the investigative program.

Equipment rinsate blanks will be prepared by field personnel and submitted for analysis of target parameters. Equipment rinsate blanks will provide the means to assess the quality of data resulting from the field program. Equipment rinsate blank samples will be analyzed to check for cross-contamination of equipment introduced during sampling at the GM Global Propulsion Systems-Bedford Facility. One equipment rinsate blank, if required by use of non-disposable or non-dedicated equipment, will be collected for every 20 investigative samples or 1 per sampling phase. However, a minimum of one will be collected each day of sampling activities for each type of non-dedicated or non-disposable equipment.

Trip blanks are used to assess the potential for contamination during sample storage and shipment. The trip blank consists of laboratory purified water that has been purged with an inert gas by the laboratory and provided with the sample containers to be used for the sampling of VOCs. The trip blanks may be purchased or prepared by the lab. Trip blanks will be preserved and handled in the

same manner as the investigation samples. One trip blank will be included along with each shipment cooler containing project samples to be analyzed for VOCs.

Method blank samples will be prepared by the laboratory and analyzed concurrently with all project samples to assess potential contamination introduced during the analytical process. Method blanks will be prepared and/or analyzed at a frequency required by the analytical method.

Field duplicate samples are analyzed to check for sampling and analytical reproducibility. One field duplicate will be collected for every 10 or fewer investigative samples collected during sampling activities, excluding waste samples and wipe samples.

MS will provide information to assess the precision and accuracy of the analysis of the target parameters within the environmental media collected at the GM Global Propulsion Systems-Bedford Facility. MS will be performed in duplicate for all TCL/TAL parameters. Initially, one MS/MSD will be collected for every 20 or fewer investigative samples per sample matrix (e.g., soil, groundwater). Based on the Corrective Action sampling reason, the frequency of MS/MSD samples may be reduced to every 20 investigative samples collected during the year or at a minimum, once per year. Soil MS/MSD samples usually only require triple sample volume for VOCs. Aqueous MS/MSD samples require triple the normal sample volume for all requested analysis.

4. Special Training/Certification Sampling Procedures

Consultant field personnel all hold current hazardous waste site operation (HAZWOPER) certification required by 29 CFR 1910.120. Consultant field personnel also undergo an extensive training program. Field personnel must first read the SOPs and attend a series of live seminars and CD-ROM courses on fieldwork topics that need to be monitored. A practical demonstration of skills learned must be demonstrated in order for field personnel to be able to work independently. These training requirements pertain to sampling procedures and the calibration/operation of field instrumentation. Field training records are stored electronically per the consultant quality systems.

5. Sampling Procedures

Samples of groundwater, surface water, soil, and sediment will be obtained throughout all the Corrective Action sampling activity phases. The sampling procedures will be consistent for the objectives of the project and the particular phase of the Corrective Action and as agreed to between GM and the regulatory agency. The FSP describes each of the sampling tasks and objectives.

Refer to the FSP for the field investigation SOPs.

5.1 Sample Containers

Sample containers for each sampling task will be provided by the project laboratory. The containers will be cleaned by the manufacturer to meet or exceed the analyte specifications established in the USEPA, "Specifications and Guidance for Obtaining Contaminant-Free Sample Containers", April 1992, OSWER Directive #9240.0-0.5A. Certificates of analysis for each lot of sample

containers used during the Corrective Action sampling activity will be maintained by the laboratory and will be available upon request.

The appropriate sample containers, preservation method, maximum holding times, and shipping information for each target parameter and sampling task are provided in Table 5.1.

5.2 Sample Labeling

Each sample will be labeled with a unique sample number that will facilitate tracking and cross-referencing of sample information. Field blank and field duplicate samples also will be numbered with a unique sample number to prevent analytical bias of field QC samples.

Refer to the FSP for the sample labeling procedures.

5.3 Field QC Sample Collection

5.3.1 Equipment Rinsate Blank Sample Collection

Equipment rinsate blank samples will be collected when non-dedicated or non-disposable sampling equipment is used to collect samples. Equipment rinsate blanks consist of laboratory purified water that has been routed through decontaminated sampling equipment and collected into the appropriate containers. The containers will be filled in order of decreasing analyte volatility (i.e., VOCs first, SVOCs second, which are followed by the containers for the remaining analyses).

5.3.2 Field Duplicate Sample Collection

5.3.2.1 Water Samples

Field duplicate samples will be collected concurrently with the investigative sample alternating the filling of each sample container using the procedures identified in the FSP.

5.3.2.2 Soil and Sediment Samples

Soil and sediment field duplicates will be collected concurrently with the investigative sample using the procedures identified in the FSP.

5.3.3 MS/MSD Sample Collection

MS/MSD sample collection for aqueous samples requires triple the sample volume. The sampling procedure specified in Section 5.3.2.1 is used to collect aqueous samples. Soil MS/MSD samples require triple volume for VOC analyses. No additional volume is required for remaining soil parameters. Section 5.3.2.2 describes the sampling procedures for soil sample collection.

6. Custody Procedures

Custody is one of several factors necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for admissibility: relevance and authenticity. Sample custody is addressed in three parts: field sample collection,

laboratory analysis, and final evidence files. Final evidence files, including all originals of laboratory reports, are maintained under document control in a secure area.

Custody of a sample begins when it is collected by or transferred to an individual and ends when that individual relinquishes or disposes of the sample. A sample or evidence file is under your custody if:

- The item is in actual possession of a person
- The item is in the view of the person after being in actual possession of the person
- The item was in actual possession but is stored to prevent tampering
- The item is in a designated and identified secure area

6.1 Field Custody Procedures

Field personnel will be required to keep written records of field activities on applicable preprinted field forms, in a bound field notebook, or in an electronic format. The records provide the means of recording data collecting activities. Non-electronic records will be written legibly in ink and will contain pertinent field data and observations. Written entry errors or changes will be crossed out with a single line, dated, and initialed by the person making the correction. The records will be periodically reviewed by the GHD Field QA Officer. Each member of the field team will be assigned a record or logbook. Alternatively, the team may have one record or logbook (or electronic record) for the team, which is kept as the project record. If this is the project standard, all samplers must record their findings in the same record location/logbook. Each title page should include field team member's name, project name, project start date, project end date, and unique page number.

The beginning of each entry in the record will contain the following information:

- Date
- Start time
- Weather
- Names of field personnel (including subcontractors)
- Level of personal protection used at the Facility
- Names of all visitors and the purpose of their visit

For each measurement and sample collected the following will be recorded:

- Detailed description of sample point
- Equipment used to collect sample or make measurement and the date equipment was last calibrated
- Time sample was collected
- Sample description
- Depth sample was collected
- Volume and number of containers

- Sampler identification

6.1.1 Field Procedures

The data quality can be affected by sample collection activities. If the integrity of collected samples is questionable, the data, regardless of its analytical quality, will also be questionable.

The following procedure describes the process to maintain the integrity of the samples:

i) Upon collection, samples are placed in the proper containers. In general, samples collected for organic analysis will be placed in pre-cleaned glass containers, and samples collected for inorganic analysis will be placed in pre-cleaned plastic (polyethylene) bottles. The sample container, preservation methods, shipping, and packaging requirements are presented in Table 5.1.

ii) Samples will be assigned a unique sample number and will have a sample label affixed to the sample container. The information to be placed on the sample label will include the sample ID number, the sample type, the sampler's name, date collected, preservation technique, and analytical parameter and method to be performed. Information on the labels will be completed with a ballpoint pen or indelible marker, or pre-printed labels may be available, which would contain most of the required information. The remaining information would then need to be added.

iii) Samples will be properly and appropriately preserved by field personnel in order to minimize loss of the constituent(s) of interest due to physical, chemical, or biological mechanisms. Sample bottles for aliquots that require preservation (pH adjustment) will be pre-preserved by the laboratory before sending (each bottle will have the appropriate preservative already added).

iv) Appropriate volumes will be collected to ensure that the EQLs can be successfully achieved and that the required QC Sample Analyses can be completed.

6.1.2 Transfer of Custody and Shipment Procedures

i) A COC record will be completed during sample collection and will accompany each shipment identifying the contents of the shipment. The COC record will accompany the samples to the laboratory. The field personnel collecting the samples will be responsible for the custody of the samples until the samples are relinquished to the laboratory. Sample transfer will require the individuals relinquishing and receiving the samples to sign, date, and note the time of sample transfer on the COC record. As few people as possible should handle the samples.

ii) Samples will be shipped or delivered in a timely fashion to the laboratory so that holding times and/or analysis times as prescribed by the methodology can be met.

iii) Samples will also be transported in containers (coolers) packed with ice to maintain the temperatures prescribed in Table 5.1. Samples will be packaged for shipment and shipped to the appropriate laboratory for analysis. The samples will be packed to prevent breakage and movement during shipping. If one COC is used and there are multiple coolers, copies of the COC should be placed in all coolers. The number of coolers must be written on the COC. If one COC per cooler is completed and if coolers split up samples, copies of the

original COC may be placed in all coolers related to that sample ID with page numbers (i.e., 1 of 3) on the batched COCs and coolers to alert the lab of the common sample delivery group (SDG). VOC samples will be placed in bubble wrap bags or foam bottle holders. The remaining samples in glass containers will be wrapped in bubble wrap or other lab-supplied packaging material and placed in the sample cooler. Samples in polyethylene containers will be placed upright directly in the sample cooler. All samples will be placed in an upright position and limited to one layer of samples per each cooler. Additional bubble wrap or packaging material will be added to fill the cooler. Shipping containers will be secured with strapping tape and custody tape for shipment to the laboratory.

iv) When samples are split with a regulatory agency and GM Global Propulsion Systems-Bedford Facility representatives, a separate COC will be prepared for the samples and marked to indicate to whom the samples are being split. The person relinquishing the samples to the regulatory agency or the GM Global Propulsion Systems-Bedford Facility will require the representative's signature acknowledging sample receipt.

v) If samples are sent by a commercial carrier, a bill of lading will be used. A copy of the bill of lading will be retained as part of permanent documentation. Commercial carriers are not required to sign the custody record as long as the custody record is sealed inside the sample cooler and the custody tape remains intact.

vi) Samples will be picked up by a laboratory courier or transported overnight by a courier to the laboratory. In cases where there is more than one day in a given sampling event, samples may be stored in a secure location under proper chain of custody until shipping or delivery to the lab. This cost saving effort would reduce the number of laboratory batches and, in most cases, reduce the amount of associated QC samples/data reporting from the lab. Additional ice will be added to the cooler as needed to maintain proper preservation temperatures.

6.2 Laboratory Chain of Custody Procedures

A full-time sample custodian will be assigned the responsibility of sample control. It will be the responsibility of the sample custodian to receive all incoming samples. Once received, the custodian will document that the custody tape on the coolers is unbroken, that each sample is received in good condition (e.g., unbroken, cooled, etc.), that the associated paperwork, such as COC forms, have been completed, and will sign the COC forms. In special cases, the custodian will document from appropriate sub-samples that COC with proper preservation has been accomplished. The custodian will also document that sufficient sample volume has been received to complete the analytical program. The sample custodian will then place the samples into secure, limited access storage (refrigerated storage, if required). The sample custodian will assign a unique number to each incoming sample for use in the laboratory. The unique number will then be entered into the sample-receiving log. The laboratory date of receipt will also be noted.

Consistent with the analyses requested on the COC form, analyses by the laboratory's analysts will begin in accordance with the appropriate methodologies. Samples will be removed from secure storage only after internal COC sign-out procedures have been followed.

6.3 Storage of Samples

Sample containers with volume remaining will be returned to secure and limited access storage. Upon completion of all laboratory analyses for each sample submittal and generation of the laboratory report, samples will be stored by the sample custodian. The length of time that samples are held will be at least 30 days after reports have been submitted. Disposal of remaining samples will be completed in compliance with all Federal, State, and local requirements.

Laboratory custody procedures and document control for those samples analyzed by the project laboratory will be carried out using the laboratory's SOPs.

6.4 Final Project Files Custody Procedures

The final project file will be the central repository for all documents with information relevant to sampling and analysis activities as described in this QAPP. The GHD Project Manager will be the custodian of the project file. The project files for the Corrective Action sampling activity, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews will be maintained in a secured, limited access area and under custody of the GHD Project Manager or their designee.

The final project file will include:

- Project plans and drawings
- Field data records
- Sample identification documents and soil boring/monitoring well logs
- All COC documentation
- Correspondence
- References, literature
- Laboratory data deliverables
- Data validation and assessment reports
- Progress reports, QA reports
- Final reports

The laboratory will be responsible for maintaining analytical logbooks, laboratory data, and sample COC documents, both hard copy and electronic. Raw laboratory data files and copies of hard copy reports will be inventoried and maintained by the laboratory for a period of 6 years, at which time the laboratory will contact GHD QA Officer regarding the disposition of the project related files. Lab and field records will be stored for 10 years in GHDs electronic filing system.

7. Calibration Procedures and Frequency

This section describes procedures for maintaining the accuracy for all the instruments and measurement equipment, which will be used for conducting field tests and laboratory analyses.

These instruments and equipment will be calibrated prior to each use or according to a periodic schedule.

7.1 Field Instrument Calibration Procedures

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated as specified in the field SOPs.

The field instruments are likely to include dissolved oxygen meters, pH meters, turbidity meters, specific conductance meters, and photoionization detectors (PIDs). Field instruments will be used for real-time sample measurement during monitoring well sampling and organics screening for both on-Facility screening of soil samples and for health and safety air monitoring, as described in the HASP. On-Facility air monitoring for health and safety purposes and the screening of soil samples may be accomplished using PIDs. On-Facility air monitoring for PCBs and dust will be conducted during intrusive construction activities to characterize potential to site workers and evaluate fugitive dust emissions. Dustrak aerosol monitors or equivalent will be used for real-time air monitoring, as described in the project work plan.

Field instruments will be calibrated prior to use and the calibration will be verified after a maximum of ten measurements or at a minimum beginning of the day, middle of the day, and end of day. Specific information concerning calibration frequency, acceptance criteria, and the conditions that require more frequent calibration is contained in the field SOPs in Appendix D.

Satisfactory completion of the pre-operation inspection will be noted on the Field Sampling Record, along with the results of each field measurement.

7.2 Laboratory Instrument Calibration Procedures

Calibration procedures for a specific laboratory instrument will consist of initial calibration, initial calibration verification, and continuing calibration verification. The SOPs in Appendix B present the specific calibration procedures for each method of analysis. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria, and the conditions that will require calibration. In all cases, the initial calibration will be verified using an independently prepared calibration verification solution.

The use of materials of known purity and quality will be utilized for the analysis of environmental samples. The laboratory will carefully monitor the use of all laboratory materials including solutions, standards, and reagents through well-documented procedures.

All solid chemicals and acids/bases used by the laboratory will be reagent grade or better. All gases will be high purity or better. All SRMs or Performance Evaluation (PE) Materials will be obtained from approved vendors of the NIST, the USEPA Environmental Monitoring Support Laboratories (EMSL), or reliable CRADA certified commercial sources.

All materials including standards or standard solutions will be dated upon receipt, and will be identified by material name, lot number, purity or concentration, supplier, receipt/preparation date, recipient/preparer's name, expiration date, and all other pertinent information.

8. Analytical Procedures

Analytical procedures to be utilized for analysis of environmental samples will be based on referenced USEPA analytical protocols and the laboratory SOPs that implement these methods. These project-specific SOPs are provided in Appendix B and D to this QAPP.

8.1 Field Analytical Procedures

Field analytical procedures include the measurement of pH/temperature, specific conductivity, dissolved oxygen, turbidity, and ORP during sampling of groundwater, and the qualitative measurement of VOC(for areas of known, suspected or unknown VOC impacts) during the collection of soil samples at the GM Global Propulsion Systems-Bedford Facility. Specific guidance in the measurement of these parameters is presented in the SOPs provided in Appendix D of this QAPP.

8.2 Laboratory Analytical Procedures

Laboratory preparation and analytical SOPs and the methods upon which they are based are presented in Tables 8.1-8.3. The referenced SOPs provided in Appendix B of this document are based on the USEPA methodology requirements promulgated in:

i) "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846 EPA, USEPA Office of Solid Waste, 3rd Edition and promulgated updates, 1986

ii) "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983

iii) "Standard Methods for the Examination of Water and Wastewater", APHA, AWWA, and WEF, 22th Edition, 2009 (with subsequent editions)

The EQLs for the target analytes and compounds for the environmental media to be analyzed as part of the investigation are presented in Tables 1.2-1.4.

8.2.1 List of Project Target Compounds and Laboratory Detection Limits

A complete listing of project target compounds and project EQLs for each analyte group are listed in Tables 1.2-1.4. MDLs have been experimentally determined by the project laboratory using the procedure identified in 40 CFR, Part 136 Appendix B. The laboratory's most recent MDLs will be provided upon request.

8.2.2 List of Method Specific Quality Control Criteria

The laboratory SOPs include a section that presents the minimum QC requirements for the project analyses. Section 9 references the frequency of the associated QC samples for each sampling effort and matrix.

9. Internal Quality Control Checks

This section presents the internal QC checks that will be employed for field and laboratory measurements.

9.1 Field Quality Control

QC procedures for pH/temperature, turbidity, and conductivity of water samples and PID screening soil samples will include calibrating the instruments as described in Section 6.1 of this QAPP, measuring duplicate samples and checking the reproducibility of the measurements by taking multiple readings on a single sample or the measurement reference standards. The QC information for field equipment is stated in Section 3 of this QAPP. Assessment of field sampling precision and bias will be made by collecting field duplicates and equipment rinsate blanks for laboratory analysis. Collection of the samples will be in accordance with the applicable procedures in Section 4.3 of this QAPP.

9.1.1 Equipment Rinsate Blanks

Internal QC checks will include analysis of equipment rinsate blanks to validate successful equipment cleaning activities if the equipment is used and decontaminated between sampling locations. Whenever possible, dedicated equipment (no rinsate blank necessary) will be employed to reduce the possibility of cross-contamination of samples.

The frequency of non-disposable equipment rinsate blank sample preparation will be 1 for every 20 investigative samples. However, at a minimum, one will be collected each day for each type of sampling equipment on which decontamination procedures have been performed.

9.1.2 Trip Blanks

Trip blanks samples will be prepared by the project laboratory using laboratory purified water placed within pre-cleaned 40-milliliter (mL) VOC vials equipped with Teflon septa.

Trip blanks will accompany each SDG of environmental samples collected for analysis of VOCs.

Trip blank samples will be placed in each cooler which stores and transports project samples to be analyzed for VOCs along with the project samples.

9.1.3 Field Duplicate Samples

Field duplicate samples are collected in a similar fashion to investigative samples at a minimum frequency of 1 duplicate per 10 investigative samples by matrix. Based on the Corrective Action sampling reason, the frequency of field duplicate samples may be reduced to every 20 investigative samples collected during the year or at a minimum, once per year. Field duplicate samples are analyzed by the laboratory to evaluate matrix, sample, and analytical reproducibility.

9.2 Laboratory Procedures

The laboratories identified in Section 7 of this QAPP have QC programs to ensure the reliability and validity of the analysis performed at the laboratory. All analytical procedures are documented in writing as SOPs and each SOP includes a QC section, which addresses the minimum QC requirements for the procedure. The internal QC checks may vary slightly for each individual procedure but, in general, will include the following QC requirements:

- Calibration Standards

- Instrument Performance Checks – Organics
- Initial and Continuing Calibration Checks
- Internal Standard Performance
- Method Blank Samples
- LCSs and QC Check Samples
- MS/MSD
- Surrogates
- Inductively Coupled Plasma (ICP) Interference Check Samples (ICS)
- ICP Serial Dilution
- ICP and ICP/MS QC Analyses
- Reagent Checks
- Blind Check Samples

All data will be properly recorded. The data package will include a summary of QC data as presented in Section 9.3.2. Any samples analyzed in nonconformance with QC criteria will be reanalyzed by the laboratory, if sufficient volume is available.

10. Data Reduction, Validation, and Reporting

All data generated through in field activities or by the laboratory operation shall be reduced and validated prior to reporting in accordance with the following procedures.

10.1 Data Reduction

10.1.1 Field Data Reduction Procedures

Field data reduction procedures will be minimal in scope compared to those implemented in the laboratory setting. Only direct read instrumentation will be employed in the field. The pH, conductivity, temperature, turbidity, and HNU readings collected in the field will be generated from direct read instruments following calibration per manufacturer's recommendations. Such data will be written into field logbooks immediately after measurements are taken. If errors are made, results will be legibly crossed out, initialed, and dated by the field member, and corrected in a space adjacent to the original entry. Later, when the results forms required for this study are being filled out, the GHD Project Coordinator will proof the forms to determine whether any transcription errors have been made by the field crew.

10.1.2 Laboratory Data Reduction Procedures

For this project, the equations that will be employed in reducing data are found in the appropriate chapter of SW-846, Third Edition. Two of these equations, expressing analytical accuracy and precision, are presented in Section 3 of this QAPP. Such formulae make pertinent allowances for matrix type. All calculations are checked at the conclusion of each operating day. Errors are noted;

corrections are made, but the original notations are crossed out legibly. Analytical results for soil samples shall be calculated and reported on a dry weight basis.

QC data (e.g., laboratory duplicates, surrogates, MS, and MSD) will be compared to the method acceptance criteria or laboratory acceptance criteria when no method criteria are available. Data considered to be acceptable will be entered into the laboratory computer system. Data summaries will be sent to the Laboratory QA Officer for review. If approved, data are logged into the project database format. Unacceptable data shall be appropriately qualified in the project report. Case narratives will be prepared, which will include information concerning data that fell outside acceptance limits and any other anomalous conditions encountered during sample analysis.

10.2 Data Validation

Data validation procedures shall be performed for both field and laboratory operations as described below.

10.2.1 Procedures Used to Evaluate Field Data

Procedures to evaluate field data for this project will include review of field logbooks and checking for transcription errors to project specific documents. This task will be the responsibility of the GHD Field QA Officer.

10.2.2 Procedures to Validate Laboratory Data

The GHD QA Officer or designee will perform analytical data validation using the following documents as guidance for the review process.

"National Functional Guidelines for Superfund Organic Methods Data Review", EPA 540-R-2016-002, September 2016 and "National Functional Guidelines for Inorganic Superfund Methods Data Review", EPA 540-R-2016-001, September 2016

The specific data qualifiers used will be as presented and defined in the Contract Laboratory Program (CLP) National Functional Guidelines. The level of validation will depend on the stage or phase of the Project. The stages of data validation and review is defined in "Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use", 2009.

A Stage 2A data validation will be performed on 100 percent of the laboratory data for Spring 18, CA 750 groundwater monitoring semi-annual samples and trench monitoring samples. Investigative samples used for risk assessment purposes analyzed by Eurofins TestAmerica will be validated initially using the Stage 3 validation process. Then, further analytical data collected for risk assessment will undergo Stage 2A validation. The Stage 2A deliverables will consist of the following components:

Organic Analysis

- Technical holding times
- Method, trip and field blanks
- System monitoring compounds (surrogate spikes)

- MS/MSD results
- LCS
- Field duplicate samples

Inorganic Analysis

- Technical holding times
- Blanks
- LCS
- MS/MSD and MD results
- Field duplicate

The laboratory data package will include sample COC forms, analytical results, QC summaries, and supporting raw data from instrument printouts. If QC issues are suspected during the Stage 2a validation, a higher stage of validation, Stage 3, may be performed on the data.

The Stage 3 deliverables will consist of the following components:

Organic Analysis

- Technical holding times
- GC/MS instrument performance check
- Initial and continuing calibration
- Internal standard performance
- Method, trip and equipment rinsate blanks
- System monitoring compounds (surrogate spikes)
- MS/MSD results
- Laboratory control samples
- Field duplicate samples

Inorganic Analysis

- Technical holding times
- Initial calibration
- Initial and continuing calibration verification
- Calibration and method blanks
- ICP interference check samples
- ICP/MS internal standards
- ICP serial dilutions
- Laboratory control samples

- MS/MSD results
- Field duplicate

A Stage 1 validation will be performed on the remaining current water, soil, sediment and waste scope. The laboratory data package will include sample COC forms, analytical results, and QC summaries. The data will be reviewed for completeness.

The Data Validator will evaluate the completeness of each data package. Completeness checks will be administered on all data to determine whether deliverables specified in the QAPP are present. At a minimum, deliverables will include sample COC forms, analytical results, QC summaries, and supporting raw data from instrument printouts. The review will determine whether all required items are present and request copies of missing deliverables.

10.3 Data Reporting

Data reporting procedures shall be carried out for field and laboratory operations as indicated below.

10.3.1 Field Data Reporting

Field data reporting shall be conducted principally through the transmission of report sheets containing tabulated results of all measurements made in the field and documentation of all field calibration activities.

10.3.2 Laboratory Data Reporting

The laboratory data reporting package will be sufficient to perform a data validation in accordance with protocols described in Section 9.2.2. The task of reporting laboratory data by GM will be initiated after the completion of data validation.

The Laboratory Project Manager will perform a final review of the QC data summary packages and case narratives to determine whether the report meets the project requirements. In addition to the record of the COC, the final laboratory data report format shall consist of the following:

i) Title Page

- Project name and number
- Laboratory project or lot number
- Signature of the Laboratory QA Officer or his designee
- Date issued

ii) Table of Contents - Laboratory Report Contents

iii) Case Narrative

- Number of samples and respective matrices
- Laboratory analysis performed
- Any deviations from intended analytical strategy
- Definition of data qualifiers used
- QC procedures utilized and references to the acceptance criteria
- Condition of samples "as received"
- Discussion of whether or not sample holding times were met
- Discussion of technical problems or other observations which may have created analytical difficulties
- Discussion of laboratory QC checks which failed to meet project criteria

iv) Analytical Methods Summary - Methods of Sample Preparation and Analyses for Samples

v) Analytical Sample Summary - Cross-Reference Table of Laboratory Sample to Project Sample Identification Numbers

vi) Shipping and Receiving Documents

- Sample container documentation
- Sample reception information and original COC record

vii) Chemistry Data Package by Analysis

- Sample Results
  - Sample quantitation reporting limit (RL), reporting MDL, and estimated values between the RL and MDL
  - Methods of sample preparation and analyses for samples
  - Raw data for sample results (dated chromatograms, parameter specific quantitation reports, mass spectra, and instrument printouts (not required for OMM and waste samples)
- QC Summary Data with Current Control Limits
  - MS/MSD recoveries, LCS, method blank results, and surrogate recoveries
  - GC/MS tuning results and internal standards (organics) (not required for OMM and waste samples)
  - MS recoveries and MD RPDs, LCS, method blank results
  - Serial dilutions, reagent blank results, and interference check standards (inorganics) (not required for OMM and waste samples)
- Standard Data (not required for OMM and waste samples)
  - Initial calibration data, initial calibration checks, continuing calibration verification/check standards
  - Initial and continuing calibration blanks

- Raw data for calibration data (dated chromatograms, parameter specific quantitation reports, mass spectra, and instrument printouts

- Raw QC Data (not required for OMM and waste samples)
  - Dated chromatograms, parameter specific quantitation reports, mass spectra, and instrument printouts of QC samples
- Miscellaneous Data (not required for OMM and waste samples)
  - Instrument Run Logs
  - Sample preparation records
  - Instrument conditions

Note: Only the TCL parameter list identified in Tables 1.2 and 1.4 shall be included in the laboratory chromatographic quantitation reports.

The project laboratory will provide electronic data deliverables (EDDs) in an EQuIS® 4-file format. The laboratory data will be downloaded into the EDDs directly from the laboratory information management system (LIMS). The EDDs are imported into EQuIS, and the data are maintained in the database for manipulation and presentation in accordance with the project DMP.

The GHD QA Officer will verify the correctness of the analytical database by comparing the data from the database to the analytical reports for a minimum of 10 percent of the sample results. If discrepancies between the database and analytical reports are detected, a complete verification of the database will be performed.

11. Performance and System Audits

A performance audit is an independently obtained quantitative comparison with data routinely obtained in the field or the laboratory. Performance audits include two separate, independent parts: internal and external audits.

11.1 Field Performance and System Audits

11.1.1 Internal Field Audit Responsibilities

Internal audits of field activities include the review of sampling and field measurements conducted by the GHD Field QA Officer. The audits will verify that all procedures are being followed. Internal field audits will be conducted once during each phase (or once per year for routine repetitive sampling) of the sampling and at the conclusion of the project. The audits will include examination of the following:

i) Field sampling records, screening results, instrument operating records

ii) Sample collection

iii) Handling and packaging in compliance with procedures

iv) Maintenance of QA procedures

v) COC reports

Follow-up audits will be conducted to correct deficiencies and to verify that procedures are maintained throughout the investigation. The field audit checklist will be included in Appendix E.

11.1.2 External Field Audit Responsibilities

External audits may be conducted by the Regulatory Agency Project Coordinator at any time during the field operations. These audits may or may not be announced and are at the discretion of the regulatory agency. The external field audits can include (but are not limited to) the following:

i) Sampling equipment decontamination procedures

ii) Sample bottle preparation procedures

iii) Sampling procedures

iv) Examination of HASPs

v) Procedures for verification of field duplicates

vi) Field screening practices

11.2 Laboratory Performance and System Audits

11.2.1 Internal Laboratory Audit Responsibilities

The laboratory system audits will be conducted by the Laboratory Project QA Officer or designee and performed on an annual basis. Laboratory performance audits will be conducted prior to field activities or on an annual basis, depending on the duration of the project.

The system audit will include an examination of laboratory documentation including: sample receiving logs, sample storage, COC procedures, sample preparation and analysis, and instrument operating records.

The performance audits will include submittal of blind performance evaluation samples along with project samples. The Laboratory Project QA Officer will evaluate the analytical results to ensure the lab is maintaining acceptable QC performance. The laboratory audit checklist is provided in Appendix F.

System audits, as opposed to performance audits, are strictly qualitative and consist of an on-Facility review of a laboratory's QA system and physical facilities for calibration and measurement.

At the conclusion of internal or external system audits, reports are provided to the laboratory's operating divisions for appropriate comment and remedial/corrective action where necessary. Written response to internal as well as external audits will be required. Records of audits and corrective actions are maintained by the Laboratory QA Officer.

11.2.2 External Laboratory Audit Responsibilities

External audits may be conducted as required, by appropriate QA personnel of the regulatory agency and may be conducted at least once prior to sampling and analysis activities.

External audits may include any of the following:

i) Review of laboratory analytical procedures

ii) Laboratory on-Facility visits

iii) Submission of performance evaluation samples for analysis

Failure of any of the above audit procedures may lead to laboratory disqualification, and another suitable laboratory may have to be chosen. An on-Facility review can consist of:

i) Sample receipt procedures

ii) Custody, sample security, and log-in procedures

iii) Review of instrument calibration logs

iv) Review of QA procedures

v) Review of logbooks

vi) Review of analytical SOPs

vii) Personnel interviews

A review of a data package from samples recently analyzed by the laboratory can include (but not be limited to) the following:

i) Comparison of resulting data to the SOP or method

ii) Verification of initial and continuing calibrations within control limits

iii) Verification of surrogate recoveries and instrument timing results

iv) Review of extended quantitation reports for comparisons of library spectra to instrument spectra, where applicable

v) Assurance that samples are run within holding times

12. Preventative Maintenance

12.1 Field Instrument Preventative Maintenance

The field equipment preventative maintenance program ensures the effective completion of the sampling effort and is designed to minimize equipment downtime. Program implementation is concentrated in three areas:

- Maintenance responsibilities
- Maintenance schedules
- Inventory of critical spare parts and equipment

The maintenance responsibilities for field equipment will be assigned to the task leaders in charge of specific field operations. Field personnel will be responsible for daily field checks and calibrations and for reporting any problems with the equipment. The maintenance schedule will follow the manufacturer's recommendations. In addition, the field personnel will be responsible for determining

that critical spare parts are included with the field equipment. An adequate inventory of spare parts will be maintained. The inventory will primarily contain parts that are subject to frequent failure, have limited useful lifetimes, and/or cannot be obtained in a timely manner.

12.2 Laboratory Instrument Preventative Maintenance

Analytical instruments at the laboratory will undergo routine and/or preventative maintenance. The extent of the preventative maintenance will be a function of the complexity of the equipment.

Generally, annual preventative maintenance service will involve cleaning, adjusting, inspecting, and testing procedures designed to deduce instrument failure and/or extend useful instrument life. Between visits, routine operator maintenance and cleaning will be performed according to manufacturer's specifications by laboratory personnel.

Maintenance records will be placed on file at the laboratory and can be made available upon request.

13. Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness

The following sections include the procedures and formulae utilized to assess the levels of precision, accuracy, and completeness achieved during the associated sample analyses.

13.1 Field Measurements

Field generated information such as pH and specific conductance data will be reviewed for validity. The review will be performed by the GHD Field QA Officer and typically includes electronic or bound logbooks/forms, data entry, and calculation checks. Field data will be assessed by the GHD Project Field QA Officer who will review the field results for compliance with the established QC criteria that are specified in Section 3 of this QAPP. The accuracy of pH and specific conductance will be assessed using daily instrument calibration, calibration check, and blank data.

13.2 Laboratory Data

Laboratory results will be assessed for compliance with required precision, accuracy, and completeness detailed in the following subsections.

13.2.1 Precision

The precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSD analyses. The RPD will be calculated for each pair of duplicate analyses (laboratory MS/MSDs and field duplicates).

13.2.1.1 Accuracy

The accuracy of laboratory results will be assessed for compliance with the established QC criteria that are described in Sections 3 and 8 of the QAPP using the analytical results of method blanks,

reagent/preparation blank, SRMs or QC check samples, and MS/MSD samples. The percent recovery (%R) of MS samples and SRMs will be calculated.

13.2.2 Completeness

Completeness will be assessed by comparing the number of valid (usable) results (as determined by the GHD QA Officer) to the total possible number of results using the formula presented in Section 12.1.

13.3 Statistical Evaluations

In the examination of data and determination of their precision and accuracy, standard statistical formulae will be used. Further details are provided in the following subsections.

13.3.1 Percent Recovery

The percent recovery of a parameter is calculated by dividing the amount recovered by the true amount added and multiplying by 100. The percent recoveries of spiked samples are evaluated to establish the analytical accuracy of a measurement. Percent recovery is calculated using the following formula:

$$\%R = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Spiked Sample Result
SR = Sample Result or Background
SA = Spike Added

13.3.2 Relative Percent Difference

The RPD is calculated by dividing the absolute value of the difference between two numbers by their arithmetic mean and multiplying by 100. The RPD is used to evaluate the analytical precision of two replicate measurements (i.e., MS/MSD). RPD is calculated using the following formula:

$$RPD = \frac{(R_1 - R_2)}{R_1 + R_2} \times 200$$

where:

R_1 = value of first result

R_2 = value of second result

14. Corrective Action

14.1 Field Corrective Action

Corrective action is intended to address problems that arise by identification, recommendation, approval, and implementation of measures that counter unacceptable procedures or deficient QC performance. The GHD Field QA Officer and GHD QA Officer will be responsible for ensuring the quality of the sampling procedures and environmental data and as such, will be responsible for initiating corrective action when appropriate.

The corrective action procedures will be as follows:

i) Identify/define the problem.

ii) Assign responsibility for investigating the problem.

iii) Investigate/determine the cause of the problem.

iv) Determine an appropriate corrective action to eliminate the problem.

v) Implement the corrective action.

vi) Evaluate the effectiveness of the corrective action.

vii) Verify that the corrective action has eliminated the problem.

viii) Prepare a written record detailing the problem, corrective action utilized, and solution of the problem.

ix) Submit the Corrective Action Record (CAR) to whoever initiated the corrective action and the GHD Project QA Officer, GHD Project Manager and GM Project Manager.

The above procedures may be implemented through the use of the Systems Audit as described previously. Any Field Team member of the project may initiate corrective action procedures by reporting in writing the nature of the suspected problem to the GHD Project Manager or GHD QA Officer. The GHD Project Manager will begin corrective action by relating the problem to appropriate personnel.

14.2 Laboratory Corrective Action

The following paragraphs define the corrective action decision process relative to possible noncompliant events encountered during laboratory analysis of the project samples. Corrective actions will be initiated by the laboratory QA personnel and will be implemented by laboratory staff chemists under the oversight of the laboratory QA personnel. As with field corrective actions, the laboratory QA personnel will document the problem, the corrective action undertaken, and the resolution of the problem. The corrective actions will be performed prior to release of the data from the laboratory.

Documentation will be provided to the Laboratory QA Officer, GHD QA Officer, GHD Project Manager, and GM Project Manager.

14.3 Corrective Action During Data Validation and Data Assessment

The GHD QA Officer may identify the need for corrective action during either the data validation or data assessment processes. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory (if possible).

These actions are dependent upon the ability to mobilize the field team, whether the data to be collected is necessary to meet the required QA objectives (i.e., the holding time for samples is not exceeded). When the GHD QA Officer identifies a corrective action situation, the GM Project Manager will be responsible for approving the implementation of corrective action, including resampling, during data assessment. All corrective actions will be documented by the GHD Project Manager.

15. Quality Assurance Reports

Critically important to the successful implementation of the QA Plan is a reporting system that provides the means by which the program can be reviewed, problems identified, and programmatic changes made to improve the plan.

QA reports to management include:

- Audit reports, internal and external audits with responses
- Performance evaluation sample results; internal and external sources
- Daily QA/QC exception reports/corrective actions

QA/QC corrective action reports will be prepared by the GHD QA Officer when appropriate and presented to the project and/or laboratory management personnel so that performance criteria can be monitored for all analyses from each analytical department.

16. References

- United States Environmental Protection Agency, (2001). EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations. EPA QA/R-5, March 2001
- United States Environmental Protection Agency (1991). Preparation Aids for the Development of Category I Quality Assurance Project Plans. USEPA/600/8-91/003, Risk Reduction Engineering Laboratory, Office of Research and Development, Cincinnati, Ohio, February 1991
- United States Environmental Protection Agency, (1993). Data Quality Objectives Process for Superfund Interim Final Guidance. USEPA/540/R-93-071, Office of Solid Waste and Emergency Response (OSWER), September 1993
- United States Environmental Protection Agency, (1992). Specifications and Guidance for Contaminant-Free Sample Containers. OSWER Directive 9240.0-05A, April 1992
- United States Environmental Protection Agency. USEPA National Functional Guidelines for Superfund Organic Methods Data Review. USEPA 540-R-2016-002

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- United States Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Office of Solid Waste, USEPA, SW-846, November 1986, with updates
- United States Environmental Protection Agency. Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use Office of Solid Waste, USEPA 540-R-05-005

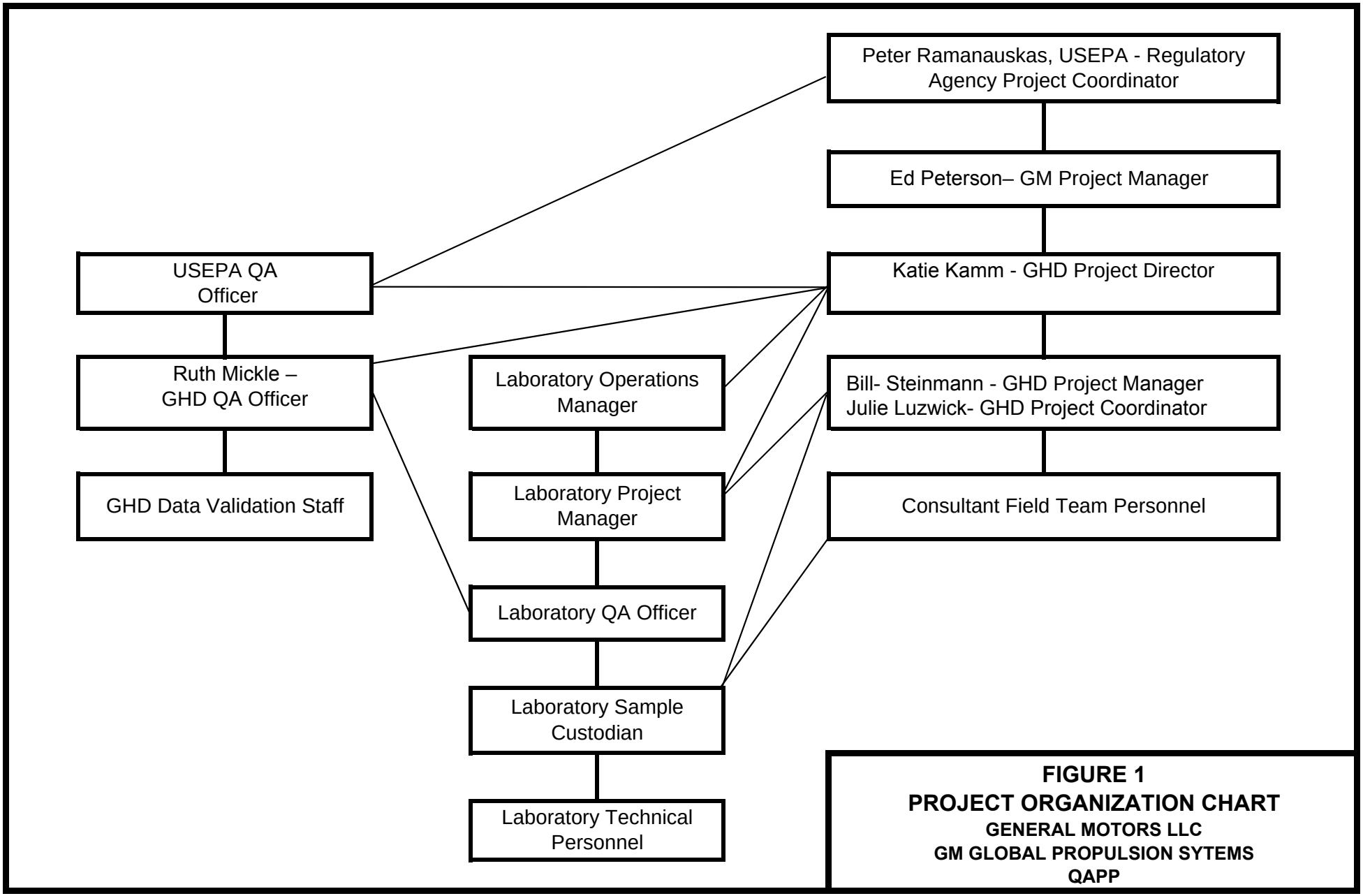

FIGURE 1
PROJECT ORGANIZATION CHART
GENERAL MOTORS LLC
GM GLOBAL PROPULSION SYTEMS
QAPP

Table 1.1

Summary of Sampling and Analysis Program
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Lab	Sample Description	Sample Matrix	Field Parameters	Laboratory Parameters	No. of Annual Samples	Quality Control Samples [1]			Total
						Field Blanks [2]	Field Duplicates	MS/MSD [3]	
TA	Pilot Trench Monitoring	Water	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	PCB-total & dissolved	70 (1st year)/36 (2nd year & beyond)	1/20	1/10	1/20	[4]
				Select/TCL VOC, Select/TCL SVOC, Total PCB	12	1/20	1/10	1/20	[4]
				chloride, conductivity, pH	6	1/20	1/10	1/20	[4]
TA	RFI CA 750 Groundwater Sampling	Water	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	PCB-total & dissolved	55	1/20	1/10	1/20	[4]
				Select/TCL VOC, Select/TCL SVOC, Total PCB	12	1/20	1/10	1/20	[4]
				chloride, conductivity, pH	6	1/20	1/10	1/20	[4]
TA	Spring 18 Semi-annual Sampling	Water	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	PCB, TSS	5	1/20	1/10	1/20	[4]
Pace	Spring 18 Semi-annual Sampling	Water	Temperature, Turbidity	PCB	1	1/20	1/10	1/20	[4]
TA	Characterization	Soil/Water	--	TCL VOC/SVOC, TAL Metals, TCLP VOC/SVOC/Metals, PCBs, pH, reactivity, ignitability, paint filter	20	-	-	-	20
TA	Water Treatment Filter Media	Solid	--	TCLP VOC/SVOC/Metals, PCBs, paint filter	12	-	-	-	12
		Solid	--	TCLP VOC/SVOC/Metals, PCBs, paint filter, ignitablity, corrosivity, particle size reduction	4	-	-	-	4

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Table 1.1

Summary of Sampling and Analysis Program
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Lab	Sample Description	Sample Matrix	Field Parameters	Laboratory Parameters	No. of Annual Samples	Quality Control Samples (1)			
						Field Blanks (2)	Field Duplicates	MS/MSD (3)	Total
TA	East Plant Area Vault Monitoring	Water	pH/Temperature, DO, Specific Conductivity, Turbidity, ORP	PCBs	24	-	-	-	24
				VOCs	12				12
TA	GWTP Compliance & Operational	Water	ph/Temperature, conductivity, Turbidity,ORP	Permit compliance:PCB, TSS, HEM	12	-	-	-	12
				Operational system: PCB, TSS, HEM	84	-	-	-	6

Notes:

(1) - A laboratory trip blank will be submitted with each shipment of samples for TCL VOC analysis.
(2) - Field blank samples will not be required if dedicated or disposable sampling equipment is used.
(3) - Matrix Spike/Matrix Spike duplicate (MS/MSD) analyses are required for samples submitted for organic and inorganic analyses are to be analyzed at a frequency of one per group of twenty (20) or fewer investigative samples and will be combined based on event.
(4) - The total sample quantity will vary depending on which scope the QC samples are collected from.

TCL = Target Compound List
TCLP = Toxicity Characteristic Leaching Procedure
TAL = Target Analyte List
Laboratores=Pace Analytical and TestAmerica (TA)

VOC = Volatile Organic Compounds
SVOC = Semi-volatile Organic Compounds
PCB = Polychlorinated Biphenyls
DO = Dissolved Oxygen

ORP = Oxidation-Reduction Potential
TSS = Total Suspended Solids
HEM = Hexane Extractable Material

TA = Eurofins TestAmerica

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TestAmerica - North Canton					
General/physical Parameters- water					
	Anions, Ion Chromatography	Chloride	1.00	0.407	mg/L
	Conductance	Conductance	1.0		umho/cm
	HEM and SGT-HEM	HEM	5.00	1.02	mg/L
	pH	pH	0.100		SU
	Solids, Total Suspended (TSS)	Total Suspended Solids	4.00	2.22	mg/L
	Ignitability, Pensky-Martens Closed-Cup Method	Flashpoint	1.00		Degrees F
	Cyanide, Total	Cyanide, Total	0.500	0.256	mg/Kg
	Sulfide, Acid soluble and Insoluble (Titrimetric)	Sulfide	30.0	14.7	mg/Kg
	Paint Filter	Free Liquid	0.100		NONE
Chlorinated Organic VOC-water	(GC/MS)	1,1,1-Trichloroethane	1.00	0.230	ug/L
		1,1,2,2-Tetrachloroethane	1.00	0.320	ug/L
		1,1,2-Trichloroethane	1.00	0.340	ug/L
		1,1-Dichloroethane	1.00	0.250	ug/L
		1,1-Dichloroethene	1.00	0.270	ug/L
		1,2-Dichlorobenzene	1.00	0.260	ug/L
		1,2-Dichloroethane	1.00	0.300	ug/L
		1,2-Dichloropropane	1.00	0.300	ug/L
		1,3-Dichlorobenzene	1.00	0.320	ug/L
		1,4-Dichlorobenzene	1.00	0.230	ug/L
		2-Chloroethyl vinyl ether	10.0	0.650	ug/L
		Benzene	1.00	0.280	ug/L
		Bromoform	1.00	0.430	ug/L
		Bromomethane	1.00	0.420	ug/L
		Carbon tetrachloride	1.00	0.350	ug/L
		Chlorobenzene	1.00	0.320	ug/L
		Chloroethane	1.00	0.410	ug/L

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Table 1.2

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GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
Chlorinated Organic VOC-water	(GC/MS)	Chloroform	1.00	0.310	ug/L
		Chloromethane	1.00	0.430	ug/L
		cis-1,3-Dichloropropene	1.00	0.260	ug/L
		Bromodichloromethane	1.00	0.300	ug/L
		Dichlorodifluoromethane	1.00	0.500	ug/L
		Ethylbenzene	1.00	0.260	ug/L
		Methylene Chloride	1.00	0.530	ug/L
		Tetrachloroethene	1.00	0.300	ug/L
		Toluene	1.00	0.230	ug/L
		trans-1,2-Dichloroethene	1.00	0.290	ug/L
		trans-1,3-Dichloropropene	1.00	0.310	ug/L
		Trichlorofluoromethane	1.00	0.500	ug/L
		Vinyl chloride	1.00	0.450	ug/L
		Dibromochloromethane	1.00	0.250	ug/L
TCL VOC - water	(GC/MS)	Acetone	10.0	1.76	ug/L
		Benzene	1.00	0.280	ug/L
		Dichlorobromomethane	1.00	0.300	ug/L
		Bromoform	1.00	0.430	ug/L
		Bromomethane	1.00	0.420	ug/L
		2-Butanone (MEK)	10.0	1.02	ug/L
		Carbon disulfide	1.00	0.340	ug/L
		Carbon tetrachloride	1.00	0.350	ug/L
		Chlorobenzene	1.00	0.320	ug/L
		Chloroethane	1.00	0.410	ug/L
		Chloroform	1.00	0.310	ug/L
		Chloromethane	1.00	0.430	ug/L
		1,1-Dichloroethane	1.00	0.250	ug/L
		1,2-Dichloroethane	1.00	0.300	ug/L
		1,1-Dichloroethene	1.00	0.270	ug/L
		1,2-Dichloropropane	1.00	0.300	ug/L

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC - water	(GC/MS)	cis-1,3-Dichloropropene	1.00	0.260	ug/L
		trans-1,3-Dichloropropene	1.00	0.310	ug/L
		Ethylbenzene	1.00	0.260	ug/L
		2-Hexanone	10.0	1.23	ug/L
		Methylene Chloride	1.00	0.530	ug/L
		4-Methyl-2-pentanone (MIBK)	10.0	0.710	ug/L
		Styrene	1.00	0.230	ug/L
		1,1,2,2-Tetrachloroethane	1.00	0.320	ug/L
		Tetrachloroethene	1.00	0.300	ug/L
		Toluene	1.00	0.230	ug/L
		Trichloroethene	1.00	0.330	ug/L
		Vinyl chloride	1.00	0.450	ug/L
		Xylenes, Total	2.00	0.240	ug/L
		1,1,1-Trichloroethane	1.00	0.230	ug/L
		1,1,2-Trichloroethane	1.00	0.340	ug/L
		Cyclohexane	1.00	0.440	ug/L
		1,2-Dibromo-3-Chloropropane	2.00	0.470	ug/L
		Ethylene Dibromide	1.00	0.230	ug/L
		Dichlorodifluoromethane	1.00	0.500	ug/L
		cis-1,2-Dichloroethene	1.00	0.300	ug/L
		trans-1,2-Dichloroethene	1.00	0.290	ug/L
		Isopropylbenzene	1.00	0.210	ug/L
		Methyl acetate	10.0	1.43	ug/L
		Methyl tert-butyl ether	1.00	0.270	ug/L
		1,1,2-Trichloro-1,2,2-trifluoroethane	1.00	0.410	ug/L
		1,2,4-Trichlorobenzene	1.00	0.270	ug/L
		1,2-Dichlorobenzene	1.00	0.260	ug/L
		1,3-Dichlorobenzene	1.00	0.320	ug/L
		1,4-Dichlorobenzene	1.00	0.230	ug/L
		Trichlorofluoromethane	1.00	0.500	ug/L
		Chlorodibromomethane	1.00	0.250	ug/L

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GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC - water	(GC/MS)	Methylcyclohexane	1.00	0.450	ug/L
		m-Xylene & p-Xylene	2.00	0.240	ug/L
		o-Xylene	1.00	0.280	ug/L
TCL - SVOC - water	Semivolatile Organic Compounds (GC/MS)	1,1'-Biphenyl	1.00	0.492	ug/L
		bis (2-chloroisopropyl) ether	1.00	0.551	ug/L
		2,4,5-Trichlorophenol	5.00	1.99	ug/L
		2,4,6-Trichlorophenol	5.00	1.80	ug/L
		2,4-Dichlorophenol	2.00	0.262	ug/L
		2,4-Dimethylphenol	2.00	0.518	ug/L
		2,4-Dinitrophenol	10.0	6.21	ug/L
		2,4-Dinitrotoluene	5.00	2.07	ug/L
		2,6-Dinitrotoluene	5.00	2.13	ug/L
		2-Chloronaphthalene	1.00	0.483	ug/L
		2-Chlorophenol	1.00	0.273	ug/L
		2-Methylnaphthalene	0.200	0.111	ug/L
		2-Methylphenol	1.00	0.209	ug/L
		2-Nitroaniline	2.00	0.510	ug/L
		2-Nitrophenol	2.00	0.564	ug/L
		3,3'-Dichlorobenzidine	5.00	1.15	ug/L
		3-Nitroaniline	2.00	0.566	ug/L
		4,6-Dinitro-2-methylphenol	5.00	2.82	ug/L
		4-Bromophenyl phenyl ether	2.00	0.499	ug/L
		4-Chloro-3-methylphenol	2.00	0.296	ug/L
		4-Chloroaniline	2.00	0.316	ug/L
		4-Chlorophenyl phenyl ether	2.00	0.551	ug/L
		4-Nitroaniline	2.00	0.917	ug/L
		4-Nitrophenol	10.0	2.17	ug/L
		Acenaphthene	0.200	0.172	ug/L
		Acenaphthylene	0.200	0.125	ug/L
		Acetophenone	1.00	0.366	ug/L

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL - SVOC - water	Semivolatile Organic Compounds (GC/MS)	Anthracene	0.200	0.135	ug/L
		Atrazine	2.00	0.340	ug/L
		Benzaldehyde	2.00	0.390	ug/L
		Benzo[a]anthracene	0.200	0.171	ug/L
		Benzo[a]pyrene	0.200	0.173	ug/L
		Benzo[b]fluoranthene	0.200	0.154	ug/L
		Benzo[g,h,i]perylene	0.200	0.178	ug/L
		Benzo[k]fluoranthene	0.200	0.140	ug/L
		Bis(2-chloroethoxy)methane	1.00	0.455	ug/L
		Bis(2-chloroethyl)ether	1.00	0.402	ug/L
		Bis(2-ethylhexyl) phthalate	5.00	2.22	ug/L
		Butyl benzyl phthalate	2.00	0.666	ug/L
		Caprolactam	5.00	0.200	ug/L
		Carbazole	1.00	0.490	ug/L
		Chrysene	0.200	0.186	ug/L
		Dibenz(a,h)anthracene	0.200	0.0446	ug/L
		Dibenzofuran	1.00	0.561	ug/L
		Diethyl phthalate	5.00	3.82	ug/L
		Dimethyl phthalate	2.00	0.515	ug/L
		Di-n-butyl phthalate	5.00	1.80	ug/L
		Di-n-octyl phthalate	2.00	0.821	ug/L
		Fluoranthene	0.200	0.160	ug/L
		Fluorene	0.200	0.169	ug/L
		Hexachlorobenzene	0.200	0.161	ug/L
		Hexachlorobutadiene	1.00	0.543	ug/L
		Hexachlorocyclopentadiene	10.0	1.76	ug/L
		Hexachloroethane	1.00	0.395	ug/L
		Indeno[1,2,3-cd]pyrene	0.200	0.135	ug/L
		Isophorone	1.00	0.324	ug/L
		Naphthalene	0.200	0.109	ug/L
		Nitrobenzene	1.00	0.514	ug/L

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GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL - SVOC - water	Semivolatile Organic Compounds (GC/MS)	N-Nitrosodi-n-propylamine	1.00	0.253	ug/L
		N-Nitrosodiphenylamine	1.00	0.440	ug/L
		Pentachlorophenol	10.0	3.10	ug/L
		Phenol	1.00	0.128	ug/L
		Phenanthrene	0.200	0.167	ug/L
		Pyrene	0.200	0.175	ug/L
		3 & 4 Methylphenol	2.00	0.191	ug/L
TCL PCB - water	Polychlorinated Biphenyls (PCBs) (GC)	Aroclor-1016	0.100	0.0560	ug/L
	Compliance	Aroclor-1221	0.100	0.0570	ug/L
		Aroclor-1232	0.100	0.0740	ug/L
		Aroclor-1242	0.100	0.0760	ug/L
		Aroclor-1248	0.100	0.0500	ug/L
		Aroclor-1254	0.100	0.0400	ug/L
		Aroclor-1260	0.100	0.0460	ug/L
	Polychlorinated Biphenyls (PCBs) (GC)	Aroclor-1016	0.2	0.0560	ug/L
		Aroclor-1221	0.2	0.0570	ug/L
		Aroclor-1232	0.2	0.0740	ug/L
		Aroclor-1242	0.2	0.0760	ug/L
		Aroclor-1248	0.2	0.0500	ug/L
		Aroclor-1254	0.2	0.0400	ug/L
		Aroclor-1260	0.2	0.0460	ug/L
TAL Metals - water		Aluminum	200	47.3	ug/L
		Antimony	2.00	0.570	ug/L
		Barium	200	1.33	ug/L
		Beryllium	1.00	0.305	ug/L
		Calcium	5000	307	ug/L

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TAL Metals - water		Cadmium	2.00	0.203	ug/L
		Cobalt	10.0	0.752	ug/L
		Chromium	5.00	0.625	ug/L
		Copper	25.0	3.55	ug/L
		Iron	100	26.0	ug/L
		Potassium	5000	557	ug/L
		Magnesium	5000	776	ug/L
		Manganese	15.0	2.12	ug/L
		Silver	5.00	0.623	ug/L
		Sodium	5000	560	ug/L
		Nickel	40.0	2.20	ug/L
		Vanadium	50.0	5.56	ug/L
		Zinc	50.0	9.67	ug/L
		Arsenic	10.0	4.05	ug/L
		Lead	5.00	2.77	ug/L
		Selenium	15.0	5.96	ug/L
		Thallium	1.00	0.200	ug/L
		Mercury	0.200	0.130	ug/L
TCL VOC -soil	(GC/MS)	Acetone	20.0	3.06	ug/Kg
		Benzene	5.00	0.320	ug/Kg
		Dichlorobromomethane	5.00	0.330	ug/Kg
		Bromoform	5.00	0.400	ug/Kg
		Bromomethane	5.00	0.590	ug/Kg
		2-Butanone (MEK)	20.0	1.27	ug/Kg
		Carbon disulfide	5.00	0.210	ug/Kg
		Carbon tetrachloride	5.00	0.250	ug/Kg
		Chlorobenzene	5.00	0.330	ug/Kg
		Chloroethane	5.00	0.380	ug/Kg
		Chloroform	5.00	0.230	ug/Kg
		Chloromethane	5.00	0.380	ug/Kg
		1,1-Dichloroethane	5.00	0.330	ug/Kg
		1,2-Dichloroethane	5.00	0.290	ug/Kg

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC -soil	(GC/MS)	1,1-Dichloroethene	5.00	0.540	ug/Kg
		1,2-Dichloropropane	5.00	0.310	ug/Kg
		cis-1,3-Dichloropropene	5.00	0.260	ug/Kg
		trans-1,3-Dichloropropene	5.00	0.210	ug/Kg
		Ethylbenzene	5.00	0.270	ug/Kg
		2-Hexanone	20.0	0.580	ug/Kg
		Methylene Chloride	5.00	0.240	ug/Kg
		4-Methyl-2-pentanone (MIBK)	20.0	0.890	ug/Kg
		Styrene	5.00	0.270	ug/Kg
		1,1,2,2-Tetrachloroethane	5.00	0.260	ug/Kg
		Tetrachloroethene	5.00	0.370	ug/Kg
		Toluene	5.00	0.340	ug/Kg
		Trichloroethene	5.00	0.410	ug/Kg
		Vinyl chloride	5.00	0.280	ug/Kg
		Xylenes, Total	10.0	0.400	ug/Kg
		1,1,1-Trichloroethane	5.00	0.230	ug/Kg
		1,1,2-Trichloroethane	5.00	0.390	ug/Kg
		Cyclohexane	10.0	0.210	ug/Kg
		1,2-Dibromo-3-Chloropropane	10.0	0.680	ug/Kg
		Ethylene Dibromide	5.00	0.350	ug/Kg
		Dichlorodifluoromethane	5.00	0.350	ug/Kg
		cis-1,2-Dichloroethene	5.00	0.280	ug/Kg
		trans-1,2-Dichloroethene	5.00	0.380	ug/Kg
		Isopropylbenzene	5.00	0.200	ug/Kg
		Methyl acetate	25.0	1.17	ug/Kg
		Methyl tert-butyl ether	5.00	0.270	ug/Kg
		1,1,2-Trichloro-1,2,2-trifluoroethane	5.00	0.490	ug/Kg
		1,2,4-Trichlorobenzene	5.00	0.240	ug/Kg
		1,2-Dichlorobenzene	5.00	0.220	ug/Kg
		1,3-Dichlorobenzene	5.00	0.290	ug/Kg
		1,4-Dichlorobenzene	5.00	0.350	ug/Kg
		Trichlorofluoromethane	5.00	0.240	ug/Kg

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC -soil	(GC/MS)	Chlorodibromomethane	5.00	0.300	ug/Kg
		Methylcyclohexane	10.0	0.230	ug/Kg
		m-Xylene & p-Xylene	10.0	0.400	ug/Kg
		o-Xylene	5.00	0.220	ug/Kg
TCL SVOC - soil	Semi-Volatile Organic Compounds (GC/MS)	1,1'-Biphenyl	50.0	17.0	ug/Kg
		bis (2-chloroisopropyl) ether	100	10.0	ug/Kg
		2,4,5-Trichlorophenol	150	69.0	ug/Kg
		2,4,6-Trichlorophenol	150	64.0	ug/Kg
		2,4-Dichlorophenol	150	44.0	ug/Kg
		2,4-Dimethylphenol	150	40.0	ug/Kg
		2,4-Dinitrophenol	330	142	ug/Kg
		2,4-Dinitrotoluene	200	62.0	ug/Kg
		2,6-Dinitrotoluene	200	56.0	ug/Kg
		2-Chloronaphthalene	50.0	14.0	ug/Kg
		2-Chlorophenol	50.0	10.0	ug/Kg
		2-Methylnaphthalene	6.67	0.500	ug/Kg
		2-Methylphenol	200	31.0	ug/Kg
		2-Nitroaniline	200	40.0	ug/Kg
		2-Nitrophenol	50.0	13.0	ug/Kg
		3,3'-Dichlorobenzidine	100	43.0	ug/Kg
		3-Nitroaniline	200	49.0	ug/Kg
		4,6-Dinitro-2-methylphenol	330	80.0	ug/Kg
		4-Bromophenyl phenyl ether	50.0	14.0	ug/Kg
		4-Chloro-3-methylphenol	150	45.0	ug/Kg
		4-Chloroaniline	150	30.0	ug/Kg
		4-Chlorophenyl phenyl ether	50.0	14.0	ug/Kg
		4-Nitroaniline	200	60.0	ug/Kg
		4-Nitrophenol	330	94.0	ug/Kg
		Acenaphthene	6.67	0.760	ug/Kg
		Acenaphthylene	6.67	0.350	ug/Kg

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL SVOC - soil	Semi-Volatile Organic Compounds (GC/MS)	Acetophenone	100	11.0	ug/Kg
		Anthracene	6.67	0.780	ug/Kg
		Atrazine	200	36.0	ug/Kg
		Benzaldehyde	100	23.0	ug/Kg
		Benzo[a]anthracene	6.67	0.630	ug/Kg
		Benzo[a]pyrene	6.67	0.640	ug/Kg
		Benzo[b]fluoranthene	6.67	0.590	ug/Kg
		Benzo[g,h,i]perylene	6.67	0.350	ug/Kg
		Benzo[k]fluoranthene	6.67	0.680	ug/Kg
		Bis(2-chloroethoxy)methane	100	12.0	ug/Kg
		Bis(2-chloroethyl)ether	100	12.0	ug/Kg
		Bis(2-ethylhexyl) phthalate	70.0	51.0	ug/Kg
		Butyl benzyl phthalate	70.0	22.0	ug/Kg
		Caprolactam	330	75.0	ug/Kg
		Carbazole	50.0	19.0	ug/Kg
		Chrysene	6.67	1.10	ug/Kg
		Dibenz(a,h)anthracene	6.67	0.660	ug/Kg
		Dibenzofuran	50.0	13.0	ug/Kg
		Diethyl phthalate	70.0	31.0	ug/Kg
		Dimethyl phthalate	70.0	14.0	ug/Kg
		Di-n-butyl phthalate	70.0	22.0	ug/Kg
		Di-n-octyl phthalate	70.0	28.0	ug/Kg
		Fluoranthene	6.67	0.550	ug/Kg
		Fluorene	6.67	0.530	ug/Kg
		Hexachlorobenzene	6.67	2.10	ug/Kg
		Hexachlorobutadiene	50.0	12.0	ug/Kg
		Hexachlorocyclopentadiene	330	62.0	ug/Kg
		Hexachloroethane	50.0	9.00	ug/Kg
		Indeno[1,2,3-cd]pyrene	6.67	0.350	ug/Kg
		Isophorone	50.0	12.0	ug/Kg
		Naphthalene	6.67	0.820	ug/Kg

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL SVOC - soil	Semi-Volatile Organic Compounds (GC/MS)	Nitrobenzene	100	13.0	ug/Kg
		N-Nitrosodi-n-propylamine	50.0	11.0	ug/Kg
		N-Nitrosodiphenylamine	50.0	12.0	ug/Kg
		Pentachlorophenol	150	58.0	ug/Kg
		Phenol	50.0	8.00	ug/Kg
		Phenanthrene	6.67	0.730	ug/Kg
		Pyrene	6.67	0.440	ug/Kg
		3 & 4 Methylphenol	400	29.0	ug/Kg
TCL PCB - soil	Polychlorinated Biphenyls (PCBs) by Gas Chromatography	Aroclor-1016	50.0	22.0	ug/Kg
		Aroclor-1221	50.0	24.0	ug/Kg
		Aroclor-1232	50.0	23.0	ug/Kg
		Aroclor-1242	50.0	19.0	ug/Kg
		Aroclor-1248	50.0	24.0	ug/Kg
		Aroclor-1254	50.0	23.0	ug/Kg
		Aroclor-1260	50.0	22.0	ug/Kg
TCL PCB - wipes	Polychlorinated Biphenyls (PCBs) by Gas Chromatography	Aroclor-1016	0.500	0.240	ug/Wipe
		Aroclor-1221	0.500	0.230	ug/Wipe
		Aroclor-1232	0.500	0.160	ug/Wipe
		Aroclor-1242	0.500	0.200	ug/Wipe
		Aroclor-1248	0.500	0.170	ug/Wipe
		Aroclor-1254	0.500	0.140	ug/Wipe
		Aroclor-1260	0.500	0.180	ug/Wipe
TAL Metals - soil	Metals (ICP)	Aluminum	20.0	5.33	mg/Kg
	Mercury (CVAA)	Antimony	1.00	0.359	mg/Kg
		Barium	20.0	0.362	mg/Kg

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TAL Metals - soil	Metals (ICP)	Beryllium	0.500	0.0540	mg/Kg
	Mercury (CVAA)	Calcium	500	36.5	mg/Kg
		Cadmium	0.200	0.0480	mg/Kg
		Cobalt	1.00	0.200	mg/Kg
		Chromium	0.500	0.151	mg/Kg
		Copper	2.50	0.236	mg/Kg
		Iron	10.0	6.94	mg/Kg
		Potassium	500	36.1	mg/Kg
		Magnesium	500	46.1	mg/Kg
		Manganese	1.50	0.309	mg/Kg
		Silver	0.500	0.0810	mg/Kg
		Sodium	500	62.8	mg/Kg
		Nickel	4.00	0.233	mg/Kg
		Vanadium	5.00	0.822	mg/Kg
		Zinc	5.00	1.37	mg/Kg
		Arsenic	1.00	0.316	mg/Kg
		Lead	1.00	0.282	mg/Kg
		Selenium	1.50	0.469	mg/Kg
		Thallium	1.00	0.399	mg/Kg
		Mercury	0.100	0.0180	mg/Kg
TCLP VOC -waste	(GC/MS)	1,1-Dichloroethene	0.0250	0.000270	mg/L
		1,2-Dichloroethane	0.0250	0.000300	mg/L
		2-Butanone (MEK)	0.250	0.00102	mg/L
		Benzene	0.0250	0.000280	mg/L
		Carbon tetrachloride	0.0250	0.000350	mg/L
		Chlorobenzene	0.0250	0.000320	mg/L
TCLP VOC -waste	(GC/MS)	Chloroform	0.0250	0.000310	mg/L
		Tetrachloroethene	0.0250	0.000300	mg/L
		Trichloroethene	0.0250	0.000330	mg/L
		Vinyl chloride	0.0250	0.000450	mg/L

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCLP SVOC -waste	Semivolatile Organic Compounds (GC/MS)	1,4-Dichlorobenzene	0.00400	0.000340	mg/L
		2,4,5-Trichlorophenol	0.00400	0.000300	mg/L
		2,4,6-Trichlorophenol	0.00400	0.000240	mg/L
		2,4-Dinitrotoluene	0.00400	0.000250	mg/L
		Hexachlorobenzene	0.000800	0.0000852	mg/L
		Hexachlorobutadiene	0.00400	0.000270	mg/L
		Hexachloroethane	0.00400	0.000190	mg/L
		3 & 4 Methylphenol	0.00400	0.000800	mg/L
		2-Methylphenol	0.00400	0.000170	mg/L
		Nitrobenzene	0.00400	0.0000400	mg/L
		Pentachlorophenol	0.0160	0.000270	mg/L
		Pyridine	0.00400	0.000350	mg/L
TCLP Metals - waste	Metals (ICP)	Arsenic	0.0500	0.00330	mg/L
		Barium	0.500	0.00240	mg/L
		Cadmium	0.0500	0.000290	mg/L
		Chromium	0.0500	0.000550	mg/L
		Lead	0.0500	0.00190	mg/L
		Selenium	0.0500	0.00510	mg/L
		Silver	0.0500	0.000920	mg/L
	Mercury (CVAA)	Mercury	0.00200	0.000130	mg/L

TestAmerica - Pittsburgh

TCL PCB - water	Polychlorinated Biphenyls (PCBs) (GC)	PCB-1016	0.2	0.0688	ug/L
		PCB-1221	0.2	0.1832	ug/L
		PCB-1232	0.2	0.0668	ug/L
		PCB-1242	0.2	0.1868	ug/L
		PCB-1248	0.2	0.1372	ug/L
		PCB-1254	0.2	0.0992	ug/L
		PCB-1260	0.2	0.1146	ug/L

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Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL PCB - water	Polychlorinated Biphenyls (PCBs) (GC)	PCB-1016	0.2	0.0734	ug/L
		PCB-1221	0.2	0.1172	ug/L
		PCB-1232	0.2	0.121	ug/L
		PCB-1242	0.2	0.067	ug/L
		PCB-1248	0.2	0.064	ug/L
		PCB-1254	0.2	0.089	ug/L
		PCB-1260	0.2	0.0572	ug/L
TCL PCB - water	Polychlorinated Biphenyls (PCBs) (GC)	PCB-1016	0.1	0.0367	ug/L
	Pitt PCBs compliance samples 0.1 ppb	PCB-1221	0.1	0.0586	ug/L
		PCB-1232	0.1	0.0603	ug/L
		PCB-1242	0.1	0.0335	ug/L
		PCB-1248	0.1	0.032	ug/L
		PCB-1254	0.1	0.0445	ug/L
		PCB-1260	0.1	0.0286	ug/L
General/physical Parameters- water	HEM and SGT-HEM	HEM (Oil & Grease)	5.00	1.40	mg/L
	Solids, Total Suspended (TSS)	Total Suspended Solids	0.500	0.500	mg/L

Notes:

[1] - Please note that these are estimated quantitation limits and are presented for guidance only.
Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and

[2] - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a effect when the samples are analyzed will be used for reporting purposes.

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Table 1.3

Target Compound and Target Analyte Parameter List - Pace
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

PACE - Indianapolis Parameter	Estimated Quantitation Limits (EQL)[1]	Method Detection Limits (MDL)[2]	Units
Water			
Polychlorinated Biphenyls (PCBs) by EPA Method 8082A			
PCB-1016	0.1	0.026	ug/L
PCB-1221	0.2	0.1	ug/L
PCB-1232	0.1	0.043	ug/L
PCB-1242	0.1	0.027	ug/L
PCB-1248	0.1	0.024	ug/L
PCB-1254	0.1	0.034	ug/L
PCB-1260	0.1	0.022	ug/L
Polychlorinated Biphenyls (PCBs) by EPA Method 608			
PCB-1016	0.1	0.08	ug/L
PCB-1221	0.2	0.19	ug/L
PCB-1232	0.1	0.09	ug/L
PCB-1242	0.1	0.08	ug/L
PCB-1248	0.1	0.09	ug/L
PCB-1254	0.1	0.08	ug/L
PCB-1260	0.1	0.09	ug/L

Notes:

(1) - Please note that these are estimated quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.

(2) - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly due matrix dependent and may be elevated to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic basis MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used

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Table 1.4

Target Compound and Target Analyte Parameter List - Merit
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
Merit					
General/physical Parameters-water					
	Anions, Ion Chromatography	Chloride	1.00	0.015	mg/L
	Conductance	Conductance	1.0	NA	umho/cm
	HEM and SGT-HEM	HEM	2	NA	mg/L
	pH	pH	0.100	NA	SU
	Solids, Total Suspended (TSS)	Total Suspended Solids	3.00	NA	mg/L
	Ignitability, Pensky-Martens Closed-Cup Method	Flashpoint	1.00	NA	Degrees
	Cyanide, Total	Cyanide, Total	0.500	0.200	mg/L
	Sulfide, Acid soluble and Insoluble (Titrimetric)	Sulfide	20	6	mg/Kg
	Paint Filter	Free Liquid	0.100		NONE
TCL VOC - water	Volatile Organic Compounds (GC/MS)	Acetone	50	1.385	ug/L
		Benzene	1	0.160	ug/L
		Bromochloromethane	1	0.381	ug/L
		Bromodichloromethane	1	0.313	ug/L
		Bromoform	1	0.292	ug/L
		Bromomethane	5	0.276	ug/L
		2-Butanone	25	3.972	ug/L
		Carbon Disulfide	5	0.139	ug/L
		Carbon Tetrachloride	1	0.259	ug/L
		Chlorobenzene	1	0.229	ug/L
		Chloroethane	5	0.267	ug/L
		Chloroform	1	0.200	ug/L
		Chloromethane	5	0.165	ug/L
		Cyclohexane	1	0.152	ug/L
		Dibromochloromethane	5	0.127	ug/L

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Table 1.4

Target Compound and Target Analyte Parameter List - Merit
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC - water	Volatile Organic Compounds (GC/MS)	1,2-Dibromo-3-chloropropane	5	0.262	ug/L
		1,2-Dibromoethane	1	0.187	ug/L
		Dichlordifluoromethane	5	0.333	ug/L
		1,2-Dichlorobenzene	1	0.137	ug/L
		1,3-Dichlorobenzene	1	0.209	ug/L
		1,4-Dichlorobenzene	1	0.165	ug/L
		1,1-Dichloroethane	1	0.225	ug/L
		1,2-Dichloroethane	1	0.262	ug/L
		1,1-Dichloroethene	1	0.242	ug/L
		cis-1,2-Dichloroethene	1	0.311	ug/L
		trans-1,2-Dichloroethene	1	0.221	ug/L
		1,2-Dichloropropane	1	0.261	ug/L
		cis-1,3-Dichloropropene	1	0.198	ug/L
		trans-1,3-Dichloropropene	1	0.166	ug/L
		Ethylbenzene	1	0.224	ug/L
		2-Hexanone	50	0.377	ug/L
		Isopropylbenzene	5	0.240	ug/L
		Methyl Acetate	10	0.328	ug/L
		Methyl Cyclohexane	1	0.237	ug/L
		4-Methyl-2-pentanone	50	0.343	ug/L
		Methyl tert-butyl ether	5	0.185	ug/L
		Methylene Chloride	5	0.237	ug/L
		Styrene	1	0.194	ug/L
		1,1,2,2-Tetrachloroethane	1	0.468	ug/L
		Tetrachloroethene	1	0.213	ug/L
		Toluene	1	0.173	ug/L
		1,1,1-Trichloroethane	1	0.277	ug/L
		1,1,2-Trichloroethane	1	0.285	ug/L
		Trichloroethene	1	0.352	ug/L
		1,2,4-Trichlorobenzene	5	0.180	ug/L

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Table 1.4

Target Compound and Target Analyte Parameter List - Merit
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC - water	Volatile Organic Compounds (GC/MS)	1,2,3-Trichlorobenzene	1	0.20	ug/L
		Trichlorofluoromethane	1	0.204	ug/L
		Trifluorotrichloroethane	1	0.283	ug/L
		Vinyl Chloride	1	0.332	ug/L
		m&p-Xylene	2	0.395	ug/L
		o-Xylene	1	0.196	ug/L
TCL - SVOC - water	Semivolatile Organic Compounds (GC/MS)	Acenaphthene	5	0.238	ug/L
		Acenaphthylene	5	0.237	ug/L
		Acetophenone	5	0.24	ug/L
		Anthracene	5	0.232	ug/L
		Atrazine	5	0.267	ug/L
		1,1-Biphenyl	5	0.215	ug/L
		Benzaldehyde	5	0.243	ug/L
		Benzo(a)anthracene	1	0.235	ug/L
		Benzo(a)pyrene	1	0.216	ug/L
		Benzo(b)fluoranthene	1	0.196	ug/L
		Benzo(g,h,i)perylene	1	0.232	ug/L
		Benzo(k)fluoranthene	1	0.212	ug/L
		bis(2-Chloroethoxy)methane	5	0.207	ug/L
		bis(2-Chloroethyl)ether	5	0.214	ug/L
		bis(2-Chloroisopropyl)ether	5	0.51	ug/L
		bis(2-Ethylhexyl)phthalate	5	0.412	ug/L
		4-Bromophenyl-phenylether	5	0.22	ug/L
		Butylbenzylphthalate	5	0.234	ug/L
		Caprolactam	10	0.206	ug/L
		Carbazole	10	0.211	ug/L
		4-Chloro-3-Methylphenol	5	0.193	ug/L
		4-Chloroaniline	10	0.981	ug/L
		2-Chloronaphthalene	5	0.244	ug/L
		2-Chlorophenol	10	0.22	ug/L

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL - SVOC - water	Semivolatile Organic Compounds (GC/MS)	4-Chlorophenyl-phenylether	5	0.236	ug/L
		Chrysene	1	0.242	ug/L
		2-Methylphenol	10	0.199	ug/L
		3-, 4-Methylphenol	20	0.404	ug/L
		Di-n-Butylphthalate	5	0.349	ug/L
		Di-n-Octylphthalate	5	0.299	ug/L
		Dibenzo(a,h)anthracene	2	0.231	ug/L
		Dibenzofuran	5	0.216	ug/L
		3,3'-Dichlorobenzidine	5	0.19	ug/L
		2,4-Dichlorophenol	10	0.218	ug/L
		Diethylphthalate	5	0.678	ug/L
		Dimethylphthalate	5	0.201	ug/L
		2,4-Dimethylphenol	5	0.224	ug/L
		4,6-Dinitro-2-methylphenol	20	0.15	ug/L
		2,4-Dinitrophenol	25	0.181	ug/L
		2,4-Dinitrotoluene	5	0.183	ug/L
		2,6-Dinitrotoluene	5	0.228	ug/L
		Fluoranthene	1	0.247	ug/L
		Fluorene	5	0.198	ug/L
		Hexachlorobenzene	5	0.204	ug/L
		Hexachlorobutadiene	10	0.2	ug/L
		Hexachlorocyclopentadiene	5	0.156	ug/L
		Hexachloroethane	5	0.245	ug/L
		Indeno(1,2,3-cd)pyrene	2	0.211	ug/L
		Isophorone	5	0.24	ug/L
		2-Methylnaphthalene	5	0.255	ug/L
		Naphthalene	5	0.247	ug/L
		2-Nitroaniline	25	0.18	ug/L
		3-Nitroaniline	25	0.235	ug/L
		4-Nitroaniline	25	0.204	ug/L

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL - SVOC - water	Semivolatile Organic Compounds (GC/MS)	Nitrobenzene	5	0.219	ug/L
		2-Nitrophenol	5	0.2	ug/L
		4-Nitrophenol	25	0.183	ug/L
		N-Nitroso-di-n-propylamine	5	0.234	ug/L
		N-Nitrosodiphenylamine	5	0.244	ug/L
		Pentachlorophenol	5	0.208	ug/L
		Phenanthrene	2	0.263	ug/L
		Phenol	5	0.213	ug/L
		Pyrene	5	0.235	ug/L
		2,4,5-Trichlorophenol	5	0.224	ug/L
		2,4,6-Trichlorophenol	5	0.188	ug/L
TCL PCB - water	Polychlorinated Biphenyls (PCBs) (GC)	Aroclor-1016	0.10	0.0133	ug/L
compliance	Compliance	Aroclor-1221	0.10	0.0149	ug/L
		Aroclor-1232	0.10	0.014	ug/L
		Aroclor-1242	0.10	0.0192	ug/L
		Aroclor-1248	0.10	0.0119	ug/L
		Aroclor-1254	0.10	0.0409	ug/L
		Aroclor-1260	0.10	0.0124	ug/L
TCL PCB - water	Polychlorinated Biphenyls (PCBs) (GC)	Aroclor-1016	0.2	0.0133	ug/L
		Aroclor-1221	0.2	0.0149	ug/L
		Aroclor-1232	0.2	0.014	ug/L
		Aroclor-1242	0.2	0.0192	ug/L
		Aroclor-1248	0.2	0.0119	ug/L
		Aroclor-1254	0.2	0.0409	ug/L
		Aroclor-1260	0.2	0.0124	ug/L

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TAL Metals - water		Aluminum	5.0	0.368	ug/L
		Antimony	2.0	0.017	ug/L
		Arsenic	1.0	0.085	ug/L
		Barium	5.0	0.156	ug/L
		Beryllium	1.0	0.054	ug/L
		Cadmium	0.5	0.030	ug/L
		Calcium	1000	4.000	ug/L
		Chromium	5.0	0.041	ug/L
		Cobalt	5.0	0.014	ug/L
		Copper	1.0	0.038	ug/L
		Iron	20	2.043	ug/L
		Lead-Total	3.0	0.019	ug/L
		Magnesium	1000	2.000	ug/L
		Manganese	5.0	0.052	ug/L
		Mercury	0.2	0.009	ug/L
		Nickel	5.0	0.044	ug/L
		Potassium	1000	8.9	ug/L
		Selenium	5.0	0.480	ug/L
		Silver	0.2	0.014	ug/L
		Sodium	1000	8.2	ug/L
		Thallium	1.0	0.019	ug/L
		Vanadium	2.0	0.015	ug/L
		Zinc	5.0	0.128	ug/L
TCL VOC -soil	Volatile Organic Compounds (GC/MS)	Acetone	2500	276.7	ug/Kg
		Benzene	50	6.4	ug/Kg
		Bromochloromethane	50	12.2	ug/Kg
		Bromodichloromethane	50	8.0	ug/Kg
		Bromoform	50	12.9	ug/Kg
		Bromomethane	250	11.4	ug/Kg

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC -soil	Volatile Organic Compounds (GC/MS)	2-Butanone	1250	26.7	ug/Kg
		Carbon Disulfide	250	6.4	ug/Kg
		Carbon Tetrachloride	50	8.1	ug/Kg
		Chlorobenzene	50	11.7	ug/Kg
		Chloroethane	250	10.7	ug/Kg
		Chloroform	50	8.8	ug/Kg
		Chloromethane	250	6.4	ug/Kg
		Cyclohexane	50	12.4	ug/Kg
		Dibromochloromethane	250	8.0	ug/Kg
		1,2-Dibromo-3-chloropropane	250	43.9	ug/Kg
		1,2-Dibromoethane	50	9.5	ug/Kg
		Dichlordifluoromethane	250	10.6	ug/Kg
		1,2-Dichlorobenzene	50	10.9	ug/Kg
		1,3-Dichlorobenzene	50	9.9	ug/Kg
		1,4-Dichlorobenzene	50	9.3	ug/Kg
		1,1-Dichloroethane	50	4.9	ug/Kg
		1,2-Dichloroethane	50	8.5	ug/Kg
		1,1-Dichloroethene	50	7.1	ug/Kg
		cis-1,2-Dichloroethene	50	11.7	ug/Kg
		trans-1,2-Dichloroethene	50	7.7	ug/Kg
		1,2-Dichloropropane	50	10.9	ug/Kg
		cis-1,3-Dichloropropene	50	7.1	ug/Kg
		trans-1,3-Dichloropropene	50	8.4	ug/Kg
		Ethylbenzene	50	7.9	ug/Kg
		2-Hexanone	2500	21.3	ug/Kg
		Isopropylbenzene	250	8.9	ug/Kg
		Methyl Acetate	500	21.9	ug/Kg
		Methyl Cyclohexane	50	7.6	ug/Kg
		4-Methyl-2-pentanone	2500	19.0	ug/Kg
		Methyl tert-butyl ether	250	7.9	ug/Kg

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOC -soil	Volatile Organic Compounds (GC/MS)	Methylene Chloride	250	10.7	ug/Kg
		Styrene	50	6.1	ug/Kg
		1,1,2,2-Tetrachloroethane	50	14.5	ug/Kg
		Tetrachloroethene	50	8.2	ug/Kg
		Toluene	50	6.4	ug/Kg
		1,1,1-Trichloroethane	50	6.7	ug/Kg
		1,1,2-Trichloroethane	50	13.0	ug/Kg
		Trichloroethene	50	7.0	ug/Kg
		1,2,3-Trichlorobenzene	250	9.8	ug/Kg
		1,2,4-Trichlorobenzene	50	14.2	ug/Kg
		Trichlorofluoromethane	50	8.4	ug/Kg
		Trifluorotrichloroethane	50	12.5	ug/Kg
		Vinyl Chloride	50	8.3	ug/Kg
		m&p-Xylene	100	14.7	ug/Kg
		o-Xylene	50	8.5	ug/Kg
TCL SVOC - soil	Semi-Volatile Organic Compounds (GC/MS)	Acenaphthene	330	7.7	ug/Kg
		Acenaphthylene	330	7.6	ug/Kg
		Acetophenone	330	6.7	ug/Kg
		Anthracene	330	6.8	ug/Kg
		Atrazine	330	7.3	ug/Kg
		1,1-Biphenyl	330	5.4	ug/Kg
		Benzaldehyde	330	7.8	ug/Kg
		Benzo(a)anthracene	330	6.2	ug/Kg
		Benzo(a)pyrene	330	5.9	ug/Kg
		Benzo(b)fluoranthene	330	6.2	ug/Kg
		Benzo(g,h,i)perylene	330	6.5	ug/Kg
		Benzo(k)fluoranthene	330	5.7	ug/Kg
		bis(2-Chloroethoxy)methane	330	6.1	ug/Kg
		bis(2-Chloroethyl)ether	330	6.3	ug/Kg

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL SVOC - soil	Semi-Volatile Organic Compounds (GC/MS)	bis(2-Chloroisopropyl)ether	330	5.2	ug/Kg
		bis(2-Ethylhexyl)phthalate	330	33.2	ug/Kg
		4-Bromophenyl-phenylether	330	6.5	ug/Kg
		Butylbenzylphthalate	330	8.2	ug/Kg
		Caprolactam	330	7.1	ug/Kg
		Carbazole	330	6.6	ug/Kg
		4-Chloro-3-Methylphenol	280	5.9	ug/Kg
		4-Chloroaniline	330	8.5	ug/Kg
		2-Chloronaphthalene	330	6.0	ug/Kg
		2-Chlorophenol	330	6.6	ug/Kg
		4-Chlorophenyl-phenylether	330	7.3	ug/Kg
		Chrysene	330	6.7	ug/Kg
		2-Methylphenol	330	7.0	ug/Kg
		3-, 4-Methylphenol	330	12.0	ug/Kg
		Di-n-Butylphthalate	330	18.0	ug/Kg
		Di-n-Octylphthalate	330	11.4	ug/Kg
		Dibenzo(a,h)anthracene	330	6.4	ug/Kg
		Dibenzofuran	330	6.1	ug/Kg
		3,3'-Dichlorobenzidine	2000	9.2	ug/Kg
		2,4-Dichlorophenol	330	5.5	ug/Kg
		Diethylphthalate	330	8.0	ug/Kg
		Dimethylphthalate	330	6.0	ug/Kg
		2,4-Dimethylphenol	330	5.9	ug/Kg
		4,6-Dinitro-2-methylphenol	830	5.6	ug/Kg
		2,4-Dinitrophenol	830	2.2	ug/Kg
		2,4-Dinitrotoluene	330	15.1	ug/Kg
		2,6-Dinitrotoluene	330	20.2	ug/Kg
		Fluoranthene	330	6.6	ug/Kg
		Fluorene	330	5.3	ug/Kg
		Hexachlorobenzene	330	5.0	ug/Kg

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL SVOC - soil	Semi-Volatile Organic Compounds (GC/MS)	Hexachlorobutadiene	330	5.1	ug/Kg
		Hexachlorocyclopentadiene	330	5.5	ug/Kg
		Hexachloroethane	330	6.4	ug/Kg
		Indeno(1,2,3-cd)pyrene	330	6.2	ug/Kg
		Isophorone	330	7.1	ug/Kg
		2-Methylnaphthalene	330	6.7	ug/Kg
		Naphthalene	330	5.9	ug/Kg
		2-Nitroaniline	830	16.9	ug/Kg
		3-Nitroaniline	830	15.2	ug/Kg
		4-Nitroaniline	830	13.6	ug/Kg
		Nitrobenzene	330	20.0	ug/Kg
		2-Nitrophenol	330	13.3	ug/Kg
		4-Nitrophenol	830	11.0	ug/Kg
		N-Nitroso-di-n-propylamine	330	7.6	ug/Kg
		N-Nitrosodiphenylamine	330	7.2	ug/Kg
		Pentachlorophenol	330	7.4	ug/Kg
		Phenanthrene	330	6.3	ug/Kg
		Phenol	330	6.8	ug/Kg
		Pyrene	330	6.9	ug/Kg
		2,4,5-Trichlorophenol	330	6.1	ug/Kg
		2,4,6-Trichlorophenol	330	6.2	ug/Kg
TCL PCB - soil	Polychlorinated Biphenyls (PCBs) by Gas Chromatography	Aroclor-1016	330	0.7	ug/Kg
		Aroclor-1221	330	0.5	ug/Kg
		Aroclor-1232	330	0.7	ug/Kg
		Aroclor-1242	330	1.3	ug/Kg
		Aroclor-1248	330	1.4	ug/Kg
		Aroclor-1254	330	0.6	ug/Kg
		Aroclor-1260	330	0.5	ug/Kg

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TAL Metals - soil	Metals (ICP)	Aluminum	100	101.4	ug/Kg
	Mercury (CVAA)	Antimony	300	1.8	ug/Kg
		Arsenic	100	14.0	ug/Kg
		Barium	1000	9.6	ug/Kg
		Beryllium	500	5.4	ug/Kg
		Cadmium	200	5.0	ug/Kg
		Calcium	1000	720.0	ug/Kg
		Chromium	2000	3.6	ug/Kg
		Cobalt	500	2.6	ug/Kg
		Copper	1000	2.8	ug/Kg
		Iron	1000	48.6	ug/Kg
		Lead-Total	1000	3.8	ug/Kg
		Magnesium	5000	42.4	ug/Kg
		Manganese	1000	2.0	ug/Kg
		Mercury	50	0.7	ug/Kg
		Nickel	1000	5.2	ug/Kg
		Potassium	1000	480.0	ug/Kg
		Selenium	200	49.0	ug/Kg
		Silver	100	9.8	ug/Kg
		Sodium	5000	218.0	ug/Kg
		Thallium	5.0	8.8	ug/Kg
		Vanadium	1000	1.4	ug/Kg
		Zinc	1000	27.6	ug/Kg
TCL PCB - wipes	Polychlorinated Biphenyls (PCBs) by Gas Chromatography	Aroclor-1016	0.500	0.240	ug/Wipe
		Aroclor-1221	0.500	0.230	ug/Wipe
		Aroclor-1232	0.500	0.160	ug/Wipe
		Aroclor-1242	0.500	0.200	ug/Wipe
		Aroclor-1248	0.500	0.170	ug/Wipe
		Aroclor-1254	0.500	0.140	ug/Wipe
		Aroclor-1260	0.500	0.180	ug/Wipe

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCLP VOC -waste	Volatile Organic Compounds (GC/MS)	Benzene	100	0.160	ug/L
		Carbon Tetrachloride	100	0.259	ug/L
		Chlorobenzene	100	0.229	ug/L
		Chloroform	100	0.200	ug/L
		1,4-Dichlorobenzene	100	0.165	ug/L
		1,1-Dichloroethene	100	0.242	ug/L
		1,2-Dichloroethane	100	0.262	ug/L
		2-Butanone	1000	3.972	ug/L
		Tetrachloroethene	100	0.213	ug/L
		Trichloroethene	100	0.352	ug/L
		Vinyl Chloride	100	0.332	ug/L
TCLP SVOC -waste	Semivolatile Organic Compounds (GC/MS)	2-Methylphenol	1000	0.199	ug/L
		3-, 4-Methylphenol	1000	0.404	ug/L
		2,4-Dinitrotoluene	90	0.183	ug/L
		Hexachlorobenzene	90	0.204	ug/L
		Hexachlorobutadiene	100	0.200	ug/L
		Hexachloroethane	100	0.245	ug/L
		Nitrobenzene	100	0.219	ug/L
		Pentachlorophenol	1000	0.208	ug/L
		Pyridine	100	0.235	ug/L
		2,4,5-Trichlorophenol	1000	0.224	ug/L
		2,4,6-Trichlorophenol	1000	0.188	ug/L

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	Method Description	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCLP Metals - waste	Metals (ICP)	Arsenic	1.0	0.085	ug/L
	Mercury (CVAA)	Barium	5.0	0.156	ug/L
		Cadmium	0.5	0.030	ug/L
		Chromium	5.0	0.041	ug/L
		Lead	3.0	0.019	ug/L
		Mercury	0.2	0.009	ug/L
		Selenium	5.0	0.480	ug/L
		Silver	0.2	0.014	ug/L

Notes:

[1] - Please note that these are estimated quantitation limits and are presented for guidance only.
Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target

[2] - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic effect when the samples are analyzed will be used for reporting purposes.

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Table 5.1

Container, Preservation, Shipping and Packaging Requirements
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Analyses	Sample Containers[1]	Preservation	Maximum Holding Time from Sample Collection[2]	Volume of Sample	Shipping	Normal Packaging
Water						
VOC	Three 40 mL teflon-lined septum vials per analysis	HCl to pH < 2 Iced, 4 ± 2° C	14 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
SVOC, PCB	Two 1 liter (100 ml -EPA 608) amber glass bottles per analysis	Iced, 4 ± 2° C	7 days for SVOC extraction (1 year-PCB) 40 days after extraction for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals	One 500 ml plastic bottle	HNO_3 to pH < 2 Iced, 4 ± 2° C	180 days (mercury-28 days) for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
pH	One 250 ml plastic bottle	Iced, 4 ± 2° C	Analyze Immediately	Fill to neck of bottle	Overnight or Hand Deliver	Bubble-wrap
Conductivity	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble-wrap
Chloride	One 250 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble-wrap
HEM	Two 1 liter amber glass bottle	H2SO4 to pH<2 Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble-wrap
TSS	One 250 ml plastic bottle	Iced, 4 ± 2° C	7 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble-wrap
Solid (Soil/Sediment)						
VOC[3]	One 40 ml Teflon-lined septum vial, Two 40 ml Teflon-lined septum vial	10 ml methanol Iced, 4 ± 2° C 5 ml H20 Iced, 4 ± 2° C	14 days for analysis 48 hrs frozen preservation 14 days for analysis	10 g soil 5 g soil	Overnight or Hand Deliver Overnight or Hand Deliver	Foam Liner or Bubble-wrap Bubble-wrap
SVOC, PCB	One 4-ounce glass jar per analysis	Iced, 4 ± 2° C	14 days for SVOC extraction (1 year - PCB) 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble-wrap

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Table 5.1

Container, Preservation, Shipping and Packaging Requirements
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Analyses	Sample Containers[1]	Preservation	Maximum Holding Time from Sample Collection[2]	Volume of Sample	Shipping	Normal Packaging
Solid (Soil/Sediment) continued						
Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble-wrap
TCLP VOC	One 8-ounce glass jar	Iced, 4 ± 2° C	14 days for extraction 14 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble-wrap
TCLP SVOC	One 16-ounce glass jar	Iced, 4 ± 2° C	14 days for TCLP extraction;7 days for prep extraction; 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble-wrap
TCLP Metals	One 16-ounce glass jar	Iced, 4 ± 2° C	180 days (28-Hg) for TCLP extraction; analysis	Fill to shoulder of jar	Deliver	Bubble-wrap
pH	One 4-ounce glass jar	Iced, 4 ± 2° C	Analyze Immediately	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble-wrap
Reactivity as total Cn & S/Ignitability	One 8-ounce glass jar	Iced, 4 ± 2° C	Not applicable	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble-wrap
Paint Filter	One 8-ounce glass jar	Iced, 4 ± 2° C	Not applicable	Fill to shoulder of jar	Overnight or Hand Deliver	Bubble-wrap
Wipe						
PCB	One 2-ounce glass jar plus gauze and hexane	Iced, 4 ± 2° C	14 days for extraction 40 days after extraction for analysis	wipe 100 square cm area	Overnight or Hand Deliver	Bubble-wrap

Notes:

[1] - Multiple parameters on a single sample may be combined into one single 16 ounce glass jar.

[2] - These are technical holding times, i.e., are based on time elapsed from time of sample collection.

[3] - Soil VOC samples will require in addition to the methanol preserved sample an additional container of sample for dry weight determination if no other analyses are required. Sediment samples if non-cohesive, may require standard bulk sampling techniques using a 4 ounce glass jar with no head space.

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Table 8.1

Summary of Analytical Methods - Eurofins Testamerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Parameter[1]	Preparation Method[2]	Laboratory Preparation SOP	Analytical Method[2]	Laboratory Analytical SOP
Eurofins TestAmerica North Canton				
Water Samples				
VOC	--	--	SW-846 8260B	NC-MS-006 (624), NC-MS-019 (8260)
SVOC	SW-846 3510/3520	NC-OP-037,-038	SW-846 8270C	NC-MS-003 (625),NC-MS-018 (8270)
PCB	SW-846 3510/3520	NC-OP-037,-038	SW-846 8082, EPA 608	NC-GC-007, NC-GC-045
Metals[3]				
ICP & ICP/MS Metals	SW-846 3010/3020	NC-IP-011, NC-IP-010	SW-846 6010/6020	NC-MT-002, NC-MT-012
Mercury	SW-846 7470A	NC-MT-014	SW-846 7470A	NC-MT-014
Chloride	--	--	EPA300.0	NC-WC-084
Conductivity	--	--	EPA 120.1	NC-WC-079
pH	--	--	SM 4500	NC-WC-010
TSS	--	--	SM 2540	NC-WC-004
HEM	--	--	EPA 1664	NC-WC-091
Wipe Samples				
PCB	--	NC-OP-025	SW 8082	NC-OP-021
Soil, Solid, Waste Samples				
TCL VOC	SW-846 5035	NC-MS-019	SW-846 8260B	NC-MS-019
TCL SVOC	SW-846 3540/3550	NC-OP-039,NC-OP-040	SW-846 8270C	NC-MS-018
PCB	SW-846 3510/3520	NC-OP-037,-038	SW-846 8082	NC-GC-045
Metals[3]	SW-846 3540/3550	NC-OP-039,NC-OP-040	SW-846 8082	NC-GC-045
ICP & ICP/MS Metals	SW-846 3050A	NC-IP-010	SW-846 6010B/6020	NC-MT-012, NC-MT-002
Mercury	SW-846 7471A	NC-MT-014	SW-846 7471A	NC-MT-014
TCLP VOC	SW-846 1311	NC-OP-033	SW-846 8260B	NC-MS-019
TCLP SVOC	SW-846 1311	NC-OP-033	SW-846 8270C	NC-MS-018
TCLP Metals	SW-846 1311	NC-OP-033	SW-846 6010/7470A	NC-MT-012, NC-MT-001
pH	--	--	SW-846 9045	NC-WC-010
Reactivity-as Cyanide & Sulfide	--	NC-WC-032	SW-846 9012	NC-WC-031, NC, WC-060
Ignitablilty	--	--	SW-846 1010	NC-WC-034
Paint filter	--	--	SW-846 9095	NC-WC-046

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Table 8.1

Summary of Analytical Methods - Eurofins Testamerica
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Parameter[1]	Preparation Method[2]	Laboratory Preparation SOP	Analytical Method[2]	Laboratory Analytical SOP
Eurofins TestAmerica - Pittsburgh				
Water Samples				
PCB	SW-846 3500C	PT-OP-001/PT-OP-28	SW-846 8082	PT-GC-002, PT-GC-005
TSS	--	--	EPA 160.4	PT-WC-043
HEM	--	--	EPA 1664	PT-WC-028
Soil, Waste Samples				
PCB	SW-846 3500C	PT-OP-026/PT-OP-28	SW-846 8082	PT-GC-005

Notes:

[1] Refer to Table 1.2 for the compounds/elements of each parameter group.

[2] Preparation and Analytical Method References:
- SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986.

[3] Metals by Method

Soil ICP:	Arsenic, Antimony, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Nickel, Silver, Vanadium.
Soil ICP/MS:	Selenium, Thallium, Zinc.

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Table 8.2

Summary of Analytical Methods - Pace
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Parameter[1]	Preparation Method[2]	Laboratory Preparation SOP	Analytical Method[2]	Laboratory Analytical SOP
Pace - Indianapolis				
Water/ Soil				
PCB	SW-846 3510/3546	SOP IND1-0500,S-IN-O-130	SW-846 8082A, EPA 608	S-IN-O-050,S-IN-O-168

Notes:

[1] Refer to Table 1.3 for the compounds/elements of each parameter group.

[2] Preparation and Analytical Method References:
- SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986.

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Table 8.3

Summary of Analytical Methods - Merit
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Parameter[1]	Preparation Method[2]	Laboratory Preparation SOP	Analytical Method[2]	Laboratory Analytical SOP
Merit				
Water Samples				
VOC	SW-846 5030C	ORL-005	SW-846 8260C	ORL-007
SVOC	SW-846 3510/3520	EXL-006	SW-846 8270D	ORL-004
PCB	SW-846 3510/3520	EXL-003	SW-846 8082A, EPA 608	ORL-002
Metals				
ICP & ICP/MS Metals	SW-846 3050/3015A	MET-001/MET-003	SW-846 6020A	MET-005
Mercury	SW-846 7471B	MET-008	SW-846 7470A	MET-008
Chloride	--	--	EPA300.0	IRL-023
Conductivity	--	--	EPA 120.1	IRL-032
pH	--	--	SM 4500	IRL-027
TSS	--	--	SM 2540	IRL-029
HEM	--	--	EPA 1664	EXL-012
Wipe Samples				
PCB	SW-846 3550C	EXL-004	SW 8082A	ORL-002
Soil, Solid, Waste Samples				
TCL VOC	SW-846 5035	ORL-005	SW-846 8260C	ORL-007
TCL SVOC	SW-846 3546	EXL-018	SW-846 8270D	ORL-004
PCB	SW-846 3510/3520	EXL-017	SW-846 8082A	ORL-002
Metals[3]				
ICP & ICP/MS Metals	SW-846 3050b	MET-001	SW-846 6020a	MET-005
Mercury	SW-846 7471B		SW-846 7471B	MET-008

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Table 8.3

Summary of Analytical Methods - Merit
GM Global Propulsion Systems-Bedford Facility
Bedford, Indiana

Parameter[1]	Preparation Method[2]	Laboratory Preparation SOP	Analytical Method[2]	Laboratory Analytical SOP
Merit				
Soil, Solid, Waste Samples				
TCLP VOC	SW-846 1311	EXL-015	SW-846 8260C	ORL-007
TCLP SVOC	SW-846 1311	EXL-015	SW-846 8270D	ORL-004
TCLP Metals	SW-846 1311	EXL-015	SW-846 6020A/7471B	MET-005/MET-008
pH	--	--	SW-846 9045D	IRL-027
Reactivity-as Cyanide & Sulfide	--	IRL-013	SW 9010B/9030B	IRL-012
Ignitablilty	--	--	SW-846 1030	EXL-007/EXL-008
Paint filter	--	--	SW-846 9095	EXL-014

Notes:

1 Refer to Table 1.4 for the compounds/elements of each parameter group.

2 Preparation and Analytical Method References:

- SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986.

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Appendix A
Analytical Laboratory List

Appendix A Analytical Laboratory List

Eurofins TestAmerica Laboratory	
Denise Heckler	Project Manager
Aaron Martin	Laboratory Operations Manager
Mark Loeb	Laboratory QA Officer
Heather Migoni	Laboratory Sample Custodian
Laboratory Address 1	4101 Shuffel Street NW, North Canton, Ohio
Phone	330-966-9477
Laboratory Address 2	301 Alpha Drive, Pittsburgh, Pennsylvania 15238
Phone	330-966-9477
Pace Analytical Services	
Tina Sayer	Project Manager
Steve Sayer	Laboratory Operations Managers
Beth Schrage	Laboratory QA Officer
Erik Boice	Laboratory Sample Custodian
Laboratory Address	7726 Moller Road, Indianapolis, Indiana 46268
Phone	317 228-3100
Merit Labs	
Barbara Ball	Project Manager
Maya Murshak	Laboratory Operations Manager
Barbara Ball	Laboratory QA Officer
John Laverty	Laboratory Sample Custodian
Laboratory Address	2680 East Lansing Drive, East Lansing, Michigan 48823
Phone	517 827-2747

Appendix B
Laboratory Analytical Standard Operating Procedures

Appendix B

Table of Contents

Pace Analytical – Indianapolis - Lab SOPs

Title	SOP Number
PCBs by EPA SW-846 METHOD 8082A	S-IN-O-050
PCBs by EPA 608	S-IN-O-168
Separatory Funnel Extraction	S-IN-D1-050
Microwave Extraction	S-IN-O-130

TestAmerica – North Canton - Lab SOPs

Title	SOP Number
Analysis of Pesticides and PCBs, EPA Method 608	NC-GC-007-608
Gas Chromatographic Analysis of PCB Based on Methods 8082 and 8082A	NC-GC-045-8082
Acid Digestion for Solid Samples Based on Method 3050B	NC-IP-010
Acid Digestion for Aqueous Samples Based on Methods SW846 3005A and MCAWW 200 Series	NC-IP-011
GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on Methods 625 and 625.1	NC-MS-003
GC/MS Volatile Organic Compounds Based on Method 624	NC-MS-006-624
GC/MS Analysis Based on Methods 8270C AND 8270D	NC-MS-018
Determination of Volatile Organics by GC/MS Based on Methods 8260C, 8260B, and 8260A	NC-MS-019
Preparation and Analysis Of Mercury In Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence Based on Method 1631E	NC-MT-001
Inductively Coupled Plasma – Mass Spectrometry Based on EPA Method 200.8, SW846 Methods 6020, 6020A, and 6020B	NC-MT-002

TestAmerica – North Canton - Lab SOPs (cont'd)

Title	SOP Number
Inductively Coupled Plasma – Atomic Emission Spectroscopy, Spectrometric Method for Element Analyses Based on Methods: SW846 Methods 6010B, 6010C, 6010D, and EPA Method 200.7	NC-MT-012
Preparation and Analysis Of Mercury In Aqueous and Solid Samples by Cold Vapor Atomic Absorption Spectroscopy Based on Method: MCAWW Method 245.1, SW846 Method 7470A, SW846 7471A, and 7471B	NC-MT-014
Cleanup Procedures for Organic Extractable Samples Based on Method: SW846 Method 3660B, 3665A, 3630C, 3610B and 3620C	NC-OP-025
Toxicity Characteristic Leaching Procedure and Synthetic Precipitation Leaching Procedure Based on Method: SW846 Methods 1311 and 1312	NC-OP-033
Continuous Liquid/Liquid Extraction Of Organic Compounds From Waters Based On Method SW846 3520C and 600 Series	NC-OP-037
Separatory Funnel Extraction Of Organic Compounds From Waters Based On Method SW846 3510C and 600 Series	NC-OP-038
Sonication Extraction Of Organic Compounds From Soils Based On Method SW846 3550C	NC-OP-039
Soxhlet (Traditional) Extraction Of Organic Compounds From Soils Based On Method SW846 3540C	NC-OP-040
Waste Dilution Based on Method SW846 Method 3580A	NC-OP-043
Total Solids, Percent Moisture, and Total Settleable Solids Based on Method: Standard Method 2540F and ASTM D2216-80	NC-WC-004
pH Electrometric Method Based on Methods: SW846 Methods 9040B, 9040C, 9041A, 9045C and 9045D, and SM4500 H+B	NC-WC-010
Cyanide Automated, Pyridine-Barbituric Acid Method Based on Method: SW846 Method 9012A, 9012B, EPA Method 335.4, and Standard Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G	NC-WC-031
Flashpoint Closed Cup Based on Method SW846 Method 1010, 1010A, and ASTM D93-80	NC-WC-034
Paint Filter Based on Method SW846 Method 9095A and 9095B	NC-WC-04
Sulfide Based on Methods: SW846 Methods 9030B and 9034, and SM4500 S2-F	NC-WC-060

TestAmerica – North Canton - Lab SOPs (cont'd)

Title	SOP Number
Specific Conductance Based on Method: EPA Method 120.1, SW846 9050A and Standard Method 2510B	NC-WC-079
Determination Of Inorganic Anions by Ion Chromatography Based on EPA Method 300.0A and SW846 Method 9056A	NC-WC-084
HEM/SGT-HEM by Solid Phase Extraction (SPE) Based on Method 1664A	NC-WC-091
Determination Of Solids In Waters and Wastes Base on Standard Methods 2540B, 2540C, 2540D	NC-WC-092

TestAmerica – Pittsburgh - Lab SOPs

Title	SOP Number
Analysis of Organochlorine Pesticides and PCBs, EPA Method 608	PT-GC-002
Polychlorinated Biphenyls (PCBs) and PCBs as Congeners by GC/ECD Method SW-846 8082 and 8082A	PT-GC-005
Extraction of Organic Compounds from Waters, Methods SW-846 3500 Series and EPA 600 Series	PT-OP-001
Extraction of Organic Compounds from Solids, Sediments, Tissue and Wipes, Method SW-846 3500 Series	PT-OP-026
Cleanup of Organic Compounds from Waters, Solids, Sediments, Tissue and Wipes, Methods SW-846 3600 Series and CarboPrep 90	PT-OP-028
Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated Hexane Extractable Material (SGT-HEM; TPH) Method 1664A/1664B and SW-846 Method 9070A	PT-WC-028
Determination of Total and Volatile Suspended Solids in Waters and Wastes, Methods EPA 160.4 and Standard Methods 2540D and 2540E	PT-WC-043

Merit – East Lansing - Lab SOPs

Title	SOP Number
Separatory Funnel Liquid-Liquid Extraction for PCB/Pesticides USEPA Method 3510C	M-EXL-003
Ultrasonic Extraction for PCBS/Pesticides USEPA Method 3550C	M-EXL-004

Merit – East Lansing - Lab SOPs (cont'd)

Title	SOP Number
Ultrasonic Extraction for BNAS/PNAS/DRO EPA Method 3550C	M-EXL-005
Separatory Funnel Extraction for BNAS/PNAS/TCLP/DRO EPA Method 3510C	M-EXL-006
Flash Point for Solids SW-846 Method 1030	M-EXL-007
Flash Point for Liquids ASTM D3278	M-EXL-008
Oil and Grease Extraction Using Hexane (Gravimetric) EPA Method 1664A	M-EXL-012
Paint Filter SW846 Method 9095	M-EXL-014
Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) SW-846 Method 1311 and Method 1312	M-EXL-015
Microwave Extraction For PCBs/Pesticides USEPA Method 3546	M-EXL-017-Rev 1
Microwave Extraction For BNAs/PNAs/DRO USEPA Method 3546	M-EXL-018-Rev 1
Pyridine-Pyrazalone Colorimetric Method for Analyzing Cyanide Using the DR/4000 Hach Spectrophotometer Method EPA 335.4 and Standard Method 4500-CN-E	M-IRL-012
Lachatcn SOP for Total Cyanide Distillation (LACHAT MICRO-DIST) Method EPA 335.4 and Standard Method 4500-CN-E	M- IRL-013
Ion Chromatography for Analyzing Anions (Chloride, Fluoride, Nitrate, Nitrite, Bromide and Sulfate) Using the DX-100 Dionex Ion Chromatograph EPA Method 300.0	M- IRL-023
pH On Water Matrix Standard Method 4500-H+ B, pH On Solid Matrix EPA SW-846 Method 9045D	M- IRL-027
Total Suspended Solids (TSS) and Total Volatile Suspended Solids (TVSS) Standard Method 2540D (TSS), EPA 160.4 (TVSS)	M- IRL-029
Specific Conductance by EPA 120.1/Salinity by Standard Method 2520B	M-IRL-032
Microwave Assisted Acid Digestion of Solid Samples USEPA Method 3050B	M-MET-001
Microwave Assisted Acid Digestion of Liquid Samples and Extracts USEPA Method 3015A	M-MET-003
Metals by Inductively Couple Plasma-Mass Spectrometry Methods 6020, 6020A, 200.8	M-MET-005
Mercury In Waters, Solids, and Wastes (Cold-Vapor Technique) USEPA Method 245.1 and SW-846 Methods 7470A/7471B	M-MET-008

Merit – East Lansing - Lab SOPs (cont'd)

Title	SOP Number
Polychlorinated Biphenyls (PCBS) by GC Method 8082A	M-ORL-002
Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry Method SW-846 8270D	M-ORL-004
Purge and Trap for Aqueous and High and Low Concentration Soil Samples Method 5030C/5035A	M-ORL-005
Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry Method SW-846 8260C	M-ORL-007

Document Information

Document Number: ENV-SOP-IND1-0050 **Revision:** 01

Document Title: Separatory Funnel Extraction

Department(s): Organic Prep

Previous Document Number: S-IN-O-054-rev.17

Date Information

Effective Date: 18 Nov 2018

Next Review Date: 18 Nov 2020 **Last Review Date:**

Notes

Document Notes:

All Dates and Times are listed in: Central Time Zone

Signature Manifest

Document Number: ENV-SOP-IND1-0050 **Revision:** 01

Title: Separatory Funnel Extraction

All dates and times are in Central Time Zone.

ENV-SOP-IND1-0050

QM Approval

Name/Signature	Title	Date	Meaning/Reason
Elizabeth Schrage (008534)	Quality Manager	15 Nov 2018, 08:01:43 PM	Approved

Management Approval

Name/Signature	Title	Date	Meaning/Reason
Steven Sayer (004775)	General Manager	16 Nov 2018, 07:14:44 AM	Approved

1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for extracting non-volatile and semi-volatile organic compounds from groundwater and surface water samples in a separatory funnel while meeting the requirements specified in SW-846 Method 3510C.

2. Summary of Method

2.1. A measured volume of sample, normally about 1 liter, is serially extracted with solvent in a separatory funnel. Reduced sample volumes may be used providing that the ratio of sample to solvent remains consistent with the ratio indicated in Method 3510C. Reduced sample volume extraction may also be referred to as Reduced Volume Extraction (RVE). Some extractions also require the monitoring and adjusting of the pH of the sample. The extract is separated from the sample and is concentrated, followed by cleanup, if necessary, or analysis.

3. Scope and Application

3.1. Applicable compounds, volumes/weights utilized, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.2. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of separatory funnel equipment and reagents. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is for extracting water insoluble or slightly water soluble organic compounds from groundwater, surface water and other aqueous samples using methylene chloride as the extraction solvent.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Solvents, reagents and glassware can all contribute to compound artifacts or raised baselines; both conditions that can affect chromatography. Analyzing method blanks is therefore crucial in determining the presence of contaminants.

6.2. Phthalate esters are common contaminant products in many products in the lab. All plastic products should be avoided when performing this method.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Amber Glass container with Teflon-lined lid, preferably 1L, 125mL widemouth, or equivalent.	None	Cool to ≤6°C	Samples must be extracted within 7 days of collection date and extracts must be analyzed within 40 days of extraction date. Samples for **PCB** analysis must be extracted within 6 months of collection date and extract must be analyzed within 40 days of extraction date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Description / Comments
N-EVAP concentrator	Organomation	Or equivalent equipment
Zymark concentrator (2) and glassware	Zymark	Or equivalent equipment
Shaker Tables	Glass-Col	Or equivalent equipment

9.2. General Supplies

Item	Description
Separatory Funnels	2L or 125mL, Teflon, with PTFE stopcocks and Teflon lids or equivalent
Glass beakers	400mL Pyrex or equivalent
Autosampler vials	~2mL, clear glass with aluminum crimp-top seals
Micro-syringes	Various sizes
Glass funnels	
Glass wool	
Graduated cylinders	Glass, Class A
Kuderna-Danish Concentrator Sets	250mL or 500mL flask with 10mL concentrator tube and 3-ball Snyder column
Heated water bath	Temperature controlled
Boiling Chips	Teflon or equivalent
Pasteur pipettes	For testing sample pH
pH paper	pH range 1-12
Glass stirring rods	For breaking up emulsions
Glass tubes	Disposable, 20x150mm or equivalent
Filter paper	For filtration of extract
Pipettes	Volumetric, Class A, various sizes

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sodium Sulfate	Anhydrous, granular 10-60 mesh, meets ACS specs or equivalent. Rinse thoroughly with methylene chloride and allow it to dry prior to use.
Methylene Chloride	Extraction solvent, pesticide grade or equivalent
Acetone	Extraction solvent, pesticide grade or equivalent
Hexane	Exchange solvent, pesticide grade or equivalent
Sulfuric acid solution (1:1)	Reagent grade
Sodium Hydroxide solution (10N)	Dissolve 400g sodium hydroxide pellets into 1L of reagent water or purchase premade

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for preparing LCS, MS, and MSD samples and for spiking surrogate into all samples.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Surrogate standard	Surrogates are added to each sample and QC sample to monitor extraction efficiency.	
Spiking Standard	This solution contains all target analytes.	Same solution can be used for the LCS and MS/MSD

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock BNA RVE spike standard	1. Restek; catalog # 31004, B/N spike; 1000ug/mL, or equivalent 2. Restek; catalog # 31014, Acid spike; 2000ug/mL, or equivalent 3. Restek; catalog # 561763, Custom PAH spike; 5000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working BNA RVE spike standards	Refer to Section 10.2.3.1	Good for 6 months from preparation date	Refrigerate
Stock/Working BNA RVE surrogate standard	O2si; catalog # 110004-83-1L; 100ug/mL, or equivalent. Use 100uL for each BNA RVE.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock Full-list BNA RVE spike standard	1. SVOA Mega Mix; Restek; cat#31850; 1000ug/mL, or equivalent 2. 8270 Mix 1; Restek; cat#572178, 2000ug/mL, or equivalent 3. 8270 Mix 2: Restek; cat#572448, 2000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working Full-list BNA RVE spike standard	Refer to Section 10.2.3.2	Good for 6 months from preparation date	Refrigerate

Standard Type	Description	Expiration	Storage
Stock PCB RVE spike standard	Restek; catalog #32039, Aroclors 1016/1260; 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB RVE spike standard	Refer to Section 10.2.3.3	Good for 6 months from preparation date	Refrigerate
Stock PCB/8081 RVE surrogate standard	Restek; catalog#32457, TCMX/DCB mix; 200ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB/8081 RVE surrogate standard	Refer to Section 10.2.3.4	Good for 6 months from preparation date	Refrigerate
Stock 8081 RVE spike standard	Restek; catalog #32292, 8-80ug/mL of each compound, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8081 RVE spike standard	Refer to Section 10.2.3.5	Good for 6 months from preparation date	Refrigerate
Stock DRO spike standard	Restek; catalog # 31258, Diesel #2 standard; 50,000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working DRO spike standard	Refer to Section 10.2.3.7	Good for 6 months from preparation date	Refrigerate
Stock DRO surrogate standard	Restek; catalog # 31487, Pentacosane; 10,000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working DRO surrogate standard	Refer to Section 10.2.3.8	Good for 6 months from preparation date	Refrigerate
Stock PAH-SIM RVE spike standard	Restek; catalog # 31622, Cal. Mix 5; 2000ug/mL of each compound, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PAH-SIM RVE spike standard	Refer to Section 10.2.3.9	Good for 6 months from preparation date	Refrigerate
Stock PAH-SIM RVE surrogate standard	Restek; catalog # 31062, B/N surrogate; 5000ug/mL of each compound, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PAH-SIM RVE surrogate standard	Refer to Section 10.2.3.10	Good for 6 months from preparation date	Refrigerate
Stock/Working Scan/SIM Combo RVE spike standard	O2si, catalog #114072-06, 10-100ug/mL or equivalent. Use 100uL for the RVE LCS, MS, and MSD.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Freeze after opening.
Stock/Working Scan/SIM Combo RVE surrogate spike standard	O2si, catalog #114071-06; 10-100ug/mL or equivalent. Use 100uL for the RVE LCS, MS, and MSD.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Freeze after opening.
Stock TCLP BNA RVE spike standard	1. Restek; catalog # 31028, TCLP B/N spike; 2000ug/mL of each compound, or equivalent 2. Restek; catalog # 31027, TCLP Acid spike; 2000ug/mL of each compound, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working TCLP BNA RVE spike standard	Refer to Section 10.2.3.11	Good for 6 months from preparation date	Refrigerate

Standard Type	Description	Expiration	Storage
Stock 8141 spike standard	Ultra; catalog #CUS-12835, 100ug/mL of each compound or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock Dichlorvos spike standard	Ultra; catalog #PST-380H1000, 1000ug/mL or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8141 spike standard	Refer to Section 10.2.3.12	Good for 2 months from preparation date	Refrigerate
Stock 8141 surrogate standard	AccuStandard; catalog #M-507-1S-10X, Triphenylphosphate 5000ug/mL or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8141 surrogate standard	Refer to Section 10.2.3.13	Good for 2 months from preparation date	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1. Working BNA RVE Spike Standard Preparation

Dilute 2.5mL of the stock Acid spike standard (2000ug/mL), 5mL of the stock B/N spike standard (1000ug/mL) and 1mL of the stock Custom PAH spike (5000ug/mL) to 50mL with acetone for a final concentration of 100ug/mL. Add 100uL of this working standard to each BNA RVE LCS, MS and MSD.

10.2.3.2. Working Full-list BNA RVE Spike Standard Preparation

Dilute 5mL of Stock Mega Mix(1000ug/mL), 2.5mL of Stock Mix #1 (2000ug/mL) and 2.5mL of Stock Mix #2 (2000ug/mL) to 50mL in acetone for a final concentration of 100ug/mL. Add 100uL of this working full-list spike standard to each BNA RVE LCS, MS, and MSD.

10.2.3.3. Working PCB RVE Spike Standard Preparation

Dilute 100uL of the Stock PCB standard (1000ug/mL) to 1000mL with acetone for a final concentration of 1ug/mL. Add 500uL of this working spike to each PCB RVE LCS, MS and MSD.

10.2.3.4. Working PCB/8081 RVE Surrogate Standard Preparation

Dilute 5mL of Stock 8081/PCB Surrogate Standard (200ug/mL) to 400mL in acetone for a final concentration of 2.5ug/mL. Add 100uL of this working standard to each PCB/8081 RVE sample, Method Blank, LCS, MS and MSD.

10.2.3.5. Working 8081 RVE Spike Standard Preparation

Dilute 5mL of 8081 Stock Spike Standard (8-80ug/mL) to 20mL in acetone for a final concentration of 2-20ug/mL. Add 50uL of this working spike standard to each 8081 RVE LCS, MS and MSD.

10.2.3.6. Working DRO Spike Standard Preparation

Dilute 10mL of the stock DRO surrogate standard (50,000ug/mL) to 200mL with acetone for a final concentration of 2500ug/mL. Add 1mL of this working spike to each DRO/ERO/OHIO MOD LCS, MS and MSD.

10.2.3.7. Working DRO Surrogate Standard Preparation

Dilute 7.5mL of the stock DRO surrogate standard (10,000ug/mL) to 500mL with acetone for a final concentration of 150ug/mL. Add 1ML of this working surrogate to each DRO/ERO/Ohio mod sample, Method Blank, LCS, MS and MSD.

10.2.3.8. Working PAH-SIM RVE Spike Standard Preparation

Dilute 5mL of the stock PAH-SIM RVE spike standard (2000ug/mL) to 200mL with acetone for a final concentration of 50ug/mL. Add 20uL of this working spike to each PAH-SIM RVE LCS, MS and MSD.

10.2.3.9. Working PAH-SIM RVE Surrogate Standard Preparation

Dilute 5.0mL of the stock PAH-SIM RVE surrogate standard (5000ug/mL) to 500mL with acetone for a final concentration of 50ug/mL. Add 20uL of this working surrogate to each PAH-SIM RVE sample, Method Blank, LCS, MS and MSD.

10.2.3.10. Working TCLP BNA RVE Spike Standard Preparation

Dilute 5mL of the stock TCLP acid spike standard (2000ug/mL) and 5mL of the stock TCLP B/N spike standard (2000ug/mL) to 100mL with acetone for a final concentration of 100ug/mL. Add 100uL of this working spike to each TCLP BNA RVE LCS, MS and MSD.

10.2.3.11. Working 8141 Spike Standard Preparation

Dilute 1mL of the Stock 8141 spike standard (100ug/mL) and 100uL of Stock Dichlorvos standard (1000ug/mL) to 5mL in acetone for a final concentration of 20000ug/L. Add 100uL of this working spike to each 8141 LCS, MS and MSD.

10.2.3.12. Working 8141 Surrogate Standard Preparation

Dilute 1mL of the Stock 8141 Surrogate Standard (5000ug/mL) to 50mL in acetone for a final concentration of 100ug/mL. Add 25uL of this working surrogate standard to each 8141 sample, Method Blank, LCS, MS and MSD.

11. Calibration

11.1. Not applicable to this SOP.

12. Procedures

12.1. Make sure that all glassware and Teflon separatory funnels used for this procedure have been properly washed. All washed glassware must be rinsed prior to use with acetone to remove residual water and rinsed with methylene chloride to remove any residual contaminants.

12.2. Measure the initial pH of each sample using wide range pH paper by dipping a clean disposable Pasteur pipette into each sample and touching the pipette to a piece of pH paper. Record the initial pH in the extraction log.

12.3. A nominal sample volume of 100mL of aqueous sample is routinely extracted for Reduced Volume Extractions (RVE); otherwise, a nominal sample volume of 1L is used. Refer to Table 1 – Extraction Conditions for more information. For samples expected to contain high concentrations of analytes, use

a smaller aliquot of sample diluted to 1L or 100mL with reagent water.

12.4. For each extraction batch of 20 or fewer samples, prepare a method blank by placing 1L or 100mL of reagent water in to a labeled separatory funnel on the black separatory funnel racks, or on the trellis. The method blank will be used to check for contamination in the system.

12.5. For each extraction batch of 20 or fewer samples, prepare an LCS by placing 1L or 100mL of reagent water in to a labeled separatory funnel on the black separatory funnel rack, or on the trellis. Spike the reagent water with the appropriate amount of spike solution. The LCS will be used to determine the efficiency of the extraction method.

12.6. If the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle for later volume determination. If only an aliquot of the sample is needed, measure the desired volume using a Class A graduated cylinder and record the volume in mLs. Transfer the sample from the sample bottle or graduated cylinder into a clean separatory funnel on the rack or the trellis.

12.7. For each extraction batch of 20 or fewer samples, prepare a matrix spike (MS) and matrix spike duplicate (MSD) in separate, labeled separatory funnels whenever available sample volume allows.

12.8. Add the appropriate **surrogate** solution to each method blank, sample, LCS, MS and MSD. Add the appropriate **spiking** solution to the LCS, MS and MSD. Refer to the standard preparation log and the sample preparation log for details regarding the appropriate surrogate and spiking solutions and volumes to be used for each method.

12.9. Adjust the sample pH, if necessary, to the pH indicated in Table 1 using 1:1 Sulfuric Acid or 10N Sodium Hydroxide. The pH is checked by dipping the tip of a disposable glass pipet into each well-mixed sample and placing the tip onto the pH paper to obtain a pH measurement.

12.10. Rinse the sample bottle (or graduated cylinder) with the first 60mL portion of extraction solvent for a 1L sample or the first 6mL portion of extraction solvent for a 100mL sample and transfer the rinsate to the separatory funnel. If the sample was transferred to the separatory funnel directly from the sample bottle, refill the bottle to the mark made in Section 12.6 with water and then measure the volume of sample that was in the bottle using a Class A graduated cylinder and record the volume in mLs as the initial sample volume.

12.11. Seal the separatory funnels with Teflon lids and shake for two minutes with periodic venting. This can be done manually or on an automatic shaker. When using the automatic shaker that holds separatory funnels in an inverted position, the stopcocks of the separatory funnels can be left open as an alternative to periodic venting. **NOTE**: Methylene chloride may cause excessive pressure in the separatory funnel. It is recommended to shake slightly and vent before placing funnels on an automatic shaker.

12.12. Return the 2L separatory funnels to the trellis and allow the solvent layer to separate from the aqueous phase. The 125mL separatory funnels remain in the automatic shaker for draining. If an excessive emulsion is present in the solvent layer, it can be broken up manually by using a clean glass stirring rod. If this is not successful, the sample can be drained into a clean secondary container (i.e. VOA vial) and transferred to a centrifuge tube. The extract can be centrifuged and then decanted into the drying funnel.

12.13. Drain the solvent layer through a drying funnel consisting of a clean funnel containing a plug of clean glass wool topped with a portion of clean sodium sulfate. The solvent should be collected in labeled beakers, labeled KD glassware, or labeled glass tubes.

12.14. Repeat the extraction two additional times with 60mL or 6mL aliquots of solvent added for each extraction. Drain the solvent through the drying funnel after each extraction. After the final solvent extraction has been collected, rinse the funnel with methylene chloride and remove the drying funnel.

12.15. If extraction at a secondary pH is required, add acid or base as necessary and serially extract the sample, as described in Sections 12.11-12.14, at the adjusted pH. Collect all sample extract fractions together for concentration. Refer to Table 1 for extraction conditions.

12.16. **Concentration procedure for 8270 BNA, 8270 Scan/SIM Combo, and TCLP samples:** Pour the extract into a labeled Kuderna-Danish concentrator with a concentrator tube securely attached. Add one or two clean boiling chips to the KD flask and attach a 3-ball Snyder column. Place the KD apparatus on a hot water bath so that the flask is partially immersed in the water. At the proper rate of distillation, the balls of the Snyder column should actively chatter but the chambers should not flood with solvent. Adjustment of the angle of the apparatus and the water temperature may be necessary to make the boiling more efficient. When the apparent volume of the extract reaches 4-6mL, remove the apparatus from the water bath and allow it to cool. Once cooled, carefully disassemble the KD apparatus rinsing each joint into the concentrator tube with a small amount of extraction solvent. Place the concentrator tube into the N-Evap and further concentrate the extract until the apparent volume is slightly below 1mL. Continue to Section 12.20.

12.17. **Concentration of PAH-SIM LVE samples:** Pour the extract into a labeled 20x150mm glass tube and place the tube on the N-Evap concentrator in a warm water bath (about 40°C) and evaporate the solvent volume using a gentle stream of nitrogen. The tube should be positioned so that water will not condense into the sample and the sample should not be allowed to go below 0.5mL, this could lead to losses of semi-volatile compounds.

12.18. **Concentration procedure for all other samples:** Pour the entire sample extract into a labeled Zymark extractor tube and place in the Zymark concentrator apparatus. Adjust the settings per manufacturer's instructions. When the apparent volume is slightly below the intended final volume, remove the concentrator from the apparatus and allow it to cool.

12.19. If a solvent exchange is required, see Table 1, add 50mL of the exchange solvent to the Zymark tube. Concentrate the extract to slightly below the intended final volume, remove from the water bath and allow it to cool.

12.20. If further concentration is necessary for any sample extract, nitrogen blowdown can be performed. For this procedure, place the concentrator tube on the N-Evap concentrator in a warm water bath (about 40°C) and evaporate the solvent volume using a gentle stream of nitrogen. The tube should be positioned so that water will not condense into the sample and the sample should not be allowed to go below 0.5mL, this could lead to the loss of semi-volatile compounds.

12.21. Prepare a calibrated vial by volumetrically dispensing the required volume of the solvent being used into a vial and securely capping the vial to eliminate evaporation. The calibrated vial must be prepared daily using a Class A pipet. Quantitatively transfer the sample extract from the Zymark tube or concentrator tube to a vial. Bring the sample extract in the vial to the required final volume listed in Table 1 by visually comparing the sample extract vial volume to the calibrated vial volume. Securely cap the sample extract vial. Store all extracts in the appropriate storage cooler. For extracts that will not concentrate to the usual final volume, use the procedure described above to bring the extract to the next higher practical volume for which a calibrated vial can be prepared.

12.22. Refer to appropriate cleanup SOPs if extract cleanup is required.

13. Quality Control

13.1. Refer to the SOP for the determinative method for batch quality control acceptance criteria and corrective actions.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. Analysts performing this method must document acceptable accuracy and precision by passing a demonstration of capability study (DOC) on an annual basis.

19. Method Modifications

19.1. Spikes not added to graduated cylinder or sample bottle but instead added to the separatory funnel.

20. Instrument/Equipment Maintenance

20.1. Refer to manufacturer's instructions.

21. Troubleshooting

21.1. Refer to manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, latest revision. Method 3510 "Separatory Funnel Extraction".

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Extraction Conditions

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-054-rev.13	1. Effective date added to cover page and body header. 2. Table 9.1: added preparation of sodium sulfate for use by solvent rinsing. 3. Section 11: revised to add new process of determining sample volume prior to extraction using Class A graduated cylinder. Removed language referring to the previous method of sample volume determination. Reordered sections to reflect the addition of surrogates and spike prior to the addition of solvent. Added a reference to extract cleanup SOPs. 4. Section 13.1: added optional LOD/LOQ verification. 5. Section 14: removed previous method modification of determining sample volume post extraction.	03Nov2013
S-IN-O-054-rev.14	1. Section 3.2: added Pesticides. 2. Section 9.2.2: added detail for 8081 and 8141 standards 3. Section 9.2.3: added detail for 8081 and 8141 standards 4. Table 1: added detail for 8081 and 8141 extractions.	28Feb2015
S-IN-O-054-rev.15	1. Table 7.1: revised holding time for extraction of samples for PCB analysis. 2. Table 9.3: updated storage conditions for standards and added Combo LVE spike. 3. Section 12: removed equations for LCS, RSD, MS. 4. Section 13: removed MDL study requirement.	02Sep2015
S-IN-O-054-rev.16	1. Converted to 27 section format. 2. Table 7.1: updated storage temperature format. 3. Table 10.3: updated standard descriptions. 4. Section 10.2.3: updated standard preparation where needed. 5. Section 12: separated instructions for method blank, LCS and MS/MSD. Specified "first portion" of solvent used to rinse cylinder or bottle. 6. Section 19: removed modification for some samples getting two extractions at each pH. 7. Section 25.3: added years 2003 and 2009 to TNI reference. 8. Table 1: removed columns for # of extractions.	05Sep2017

S-IN-O-054-rev.17	1. Section 2.1: changed LVE reference to RVE for reduced volume extraction. 2. Section 10.2.1: removed reference to calibration standards. 3. Table 10.3: added Dichlorvos stock standard, changed LVE to RVE in all instances, and removed references to full-volume analysis where needed. 4. Section 10.2.3: updated standard preparation procedures where needed. 5. Section 12: changed LVE to RVE in all instances. Changed ring stand language to separatory funnel rack or trellis. Added language to require a method blank, LCS and MS/MSD for each extraction batch of 20 or fewer samples. Added an alternative to periodic venting for inverted separatory funnels on certain automatic shakers. 6. Section 13: removed table 13.1 and referred to SOP for the determinative method. 7. Section 25.3: added years 2003 and 2009 to TNI reference. 8. Table 1: added nominal sample volume column and changed LVE to RVE in all instances.	26Apr2018
S-IN-O-054-rev.18	1. Section 9.2: added 250mL KD as an option. 2. Table 10.3: updated DRO standards. 3. Section 12.6: added procedure for marking bottle for later initial sample volume determination. 4. Section 12.10: added procedure for initial sample volume determination when entire bottle content is used. 5. Section 25.3: added NELAC to reference. 6. Table 1: updated DRO information.	8Jul2018

Table 1 – Extraction Conditions

Determinative Method	Nominal Sample Volume Extracted	Initial Extraction pH	Secondary Extraction pH	Extraction Solvent	Exchange Solvent	Final Extract Volume (mL)
8015 DRO (includes ERO and Ohio mod)	1000mL	<2	N/A	Methylene Chloride	N/A	1
8081 OC PEST RVE	100mL	5-9	N/A	Methylene Chloride	Hexane	10
8082 PCB RVE	100mL	5-9	N/A	Methylene Chloride	Hexane	10
8141 OP PEST	1000mL	As received	N/A	Methylene Chloride	Hexane	10
8270 PAH-SIM RVE	100mL	>11	N/A	Methylene Chloride	N/A	1
8270 BNA RVE	100mL	<2	>11	Methylene Chloride	N/A	1
8270 BNA Scan/SIM Combo RVE	100mL	<2	>11	Methylene Chloride	N/A	1
8270 TCLP BNA RVE	10mL	<2	>11	Methylene Chloride	N/A	1

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STANDARD OPERATING PROCEDURE

THE DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBS)

REFERENCE METHOD: EPA SW-846 METHOD 8082A

SOP NUMBER:	S-IN-O-050-rev.16
EFFECTIVE DATE:	May 1, 2018
SUPERSEDES:	S-IN-O-050-rev.15

APPROVAL

General Manager — April 27, 2018 Date

Quality Manager — April 27, 2018 Date

Department Manager — April 26, 2018 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

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1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of polychlorinated biphenyls (PCBs) in aqueous and solid samples, including oils and wipes, while meeting the requirements specified in EPA method 8082A.

2. Summary of Method

2.1. Samples are extracted using a technique and solvent system appropriate for the given matrix.

2.2. Cleanup steps may be applied to the extract, if necessary, depending on the nature of the matrix interferences and the target analytes.

2.3. The extract is analyzed by a gas chromatograph fitted with an electron capture detector (ECD). Aroclor identification is confirmed by a secondary column.

3. Scope and Application

3.1. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

3.2. Reporting limits, control limits, volumes/weights used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC systems and interpretation of GC PCB data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is used to determine the concentrations of PCBs as Aroclors in extracts from solid, aqueous, oil and wipe matrices.

5. Limits of Detection and Quantitation

5.1. The list of reporting limits can be found in Table 1. Reporting limits may vary as a function of volume or weight of sample extracted and extract final volume. Refer to LIMS for method detection limits

6. Interferences

6.1. Matrix interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. These interferences lead to discrete artifacts or elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a major problem in pesticide analysis. Common flexible plastics contain varying amounts of phthalates, which are easily extracted during lab operations. Avoiding the use of plastics in the lab can best minimize interferences from phthalates.

6.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. Cleanup procedures may be used to remove such interferences. Refer to the appropriate cleanup SOPs if extract cleanup to remove interferences is required.

6.3. Equipment

Portions of the preparation and analytical equipment operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage, and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	100mL widemouth amber glass bottle	None required	Cool to $\leq 6^{o}$C	Extract within 6 months of collection and analyze within 40 days of extraction
Solid	>100 grams in 4 or 8oz glass jar	None required	Cool to $\leq 6^{o}$C	Extract within 6 months of collection and analyze within 40 days of extraction
Oils	>10 grams in a glass container	None required	Cool to $\leq 6^{o}$C	Extract within 6 months of collection and analyze within 40 days of extraction
Wipes	One wipe per glass container	None required	Cool to $\leq 6^{o}$C	Extract within 6 months of collection and analyze within 40 days of extraction

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Description / Comments
GC	Agilent, 7890A LTM module optional or equivalent	Equipped with dual ECD Detectors; dual columns, and dual injectors, or equivalent system.
Autosampler	Agilent, 7693 or equivalent	150 position
Data System	Chemstation acquisition; Target integrations	Or equivalent software

Equipment	Vendor	Description / Comments
GC Columns	Restek, DB5-MS or DB35-MS or equivalent RTX-CLP1 and RTX-CLP2 or equivalent	Fused silica; 30 meters, 0.32mm ID, 0.25um film thickness, or equivalent column Fused silica: 30m x0.32mm ID x 0.32um and 30m x 0.32mm x 0.25um, or equivalent
LTM GC Columns	Restek, DB-35-MS LTM or equivalent Restek, DB5-MS LTM or equivalent	Fused silica; 15 meters, 0.32mm ID, 0.25um film thickness, or equivalent column Fused silica; 15 meters, 0.32mm ID, 0.25um film thickness, or equivalent column

9.2. General Supplies

Item	Vendor	Description
Glass syringes	Hamilton or equivalent	Various sizes
Glass vials	Fisher or equivalent	20mL volume with Teflon lined caps
Autosampler vials	Fisher or equivalent	2mL volume with Teflon lined crimp tops
Micro-inserts	Hewlett Packard or equivalent	Various sizes

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Hexane	Pesticide or reagent grade or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, initial calibration verification and continuing calibration verification.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for required target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	CCV
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the calibration curve.	ICV

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock PCB Calibration standards	Ultra Scientific 1016 cat#EPA-1282, 1260 cat#EPA-1362, each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate PCB Calibration standards	Refer to Section 10.2.3.1	Solution good for 6 months from preparation.	Refrigerate
Working PCB Calibration standards	Refer to Section 10.2.3.2	Solution good for 6 months from preparation.	Refrigerate
Stock PCB ICV standard	Restek 1016/1260 cat#32039, each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate PCB ICV standard	Refer to Section 10.2.3.3	Solution good for 6 months from preparation.	Refrigerate
Working PCB ICV standard	Refer to Section 10.2.3.4	Solution good for 6 months from preparation.	Refrigerate
Stock PCB Surrogate standard	Ultra; catalog #ISM-320; TCMX; 200ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock Single Point PCB Calibration Standards	Ultra Scientific 1221 cat #EPA-1292, 1232 cat #EPA-1302, 1242 cat #EPA-1312, 1248 cat #EPA-1342, 1254 cat #EPA-1352, 1262 cat #EPA-1372 and 1268 cat #EPA-1382, each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate Single Point PCB Calibration Standards	Refer to Section 10.2.3.5	Solution good for 6 months from preparation.	Refrigerate
Working Single Point PCB Calibration Standards	Refer to Section 10.2.3.6	Solution good for 6 months from preparation.	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1. Intermediate PCB Calibration Standard Preparation

Dilute 100uL of the Stock Aroclor 1016 Calibration standard (1000ug/mL), 100uL of the Stock Aroclor 1260 Calibration standard (1000ug/mL) and 50uL of the Stock PCB Surrogate standard (200ug/mL) to 50mL with Hexane for a final Aroclor 1016/1260 concentration of 2ug/mL and a final surrogate concentration of 0.2ug/mL. This recipe can also be used to prepare an intermediate calibration standard for other Aroclors.

10.2.3.2. Working PCB Calibration Standard Preparation

The following are examples of calibration standard concentrations and could vary based on requirements:

Standard	Intermediate PCB Cal. Std. amount	Final Volume in Hexane	Final PCB Conc, ug/L	Final Surr Conc, ug/L
CAL1	2.5uL	1mL	5	0.5
CAL2	5uL	1mL	10	1
CAL3	25uL	1mL	50	5
CAL4	50uL	1mL	100	10
CAL5 (CCV)	250uL	1mL	500	50
CAL6	300uL	800uL	750	75
CAL7	500uL	1mL	1000	100

10.2.3.3. Intermediate PCB ICV Standard Preparation

Dilute 20uL of the Stock PCB ICV standard (1000ug/mL) and 10uL of the Stock PCB Surrogate standard (200ug/mL) to 20mL with hexane for a final Aroclor 1016/1260 concentration of 1ug/mL and a final surrogate concentration of 0.1ug/mL. This recipe can also be used to prepare an intermediate ICV standard for other Aroclors.

10.2.3.4. Working PCB ICV Standard Preparation

Dilute 500uL of the Intermediate PCB ICV standard (1/0.1ug/mL) to 1mL with hexane for a final Aroclor 1016/1260 concentration of 500ug/L and a final surrogate concentration of 50ug/L.

10.2.3.5. Intermediate Single Point PCB Calibration Standard Preparation

The following are examples of intermediate single point calibration standards and could vary based on requirements:

Standard	Stock Single Point PCB Calibration Standard amount	Stock PCB Surr. amount	Final Volume in Hexane	Final PCB Concentration, ug/mL	Final Surr Concentration, ug/mL
Working 1221/1254	10uL each	5uL	20mL	0.5 each	0.05
Working 1232/1262	10uL each	5uL	20mL	0.5 each	0.05
Working 1242/1268	10uL each	5uL	20mL	0.5 each	0.05
Working 1248	10uL	5uL	20mL	0.5	0.05

10.2.3.6. Working Single Point PCB Calibration Standard Preparation

The following are examples of working single point calibration standards and could vary based on requirements:

Standard	Intermediate Single Point PCB Calibration Standard amount	Final Volume in Hexane	Final PCB Concentration, ug/L	Final Surr Concentration, ug/L
Working 1221/1254	200uL	1mL	100 each	10
Working 1232/1262	200uL	1mL	100 each	10
Working 1242/1268	200uL	1mL	100 each	10
Working 1248	200uL	1mL	100	10

11. Calibration

11.1. Before the initial calibration standards are injected, it is advisable to perform routine injection port and column maintenance due to the sensitivity of the ECD detector.

11.2. **Initial Calibration**: Initial calibration standards are introduced into the GC from the lowest to highest concentration by direct injection. Five calibration points, at a minimum, are analyzed to evaluate linearity. The lowest calibration standard must be at or below the required reporting limit. Refer to the Quality Manual for more information regarding calibration curves.

11.2.1. A mixture of Aroclor 1016 and 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. An initial 5-point calibration is performed using the mixture of Aroclors 1016 and 1260.

11.2.2. Standards of the other Aroclors are necessary for pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining Aroclor may be used to determine a single-point calibration factor for each Aroclor. The standards for these other Aroclors should be analyzed before the analysis of any samples, and before the analysis of the Aroclor 1016/1260 initial calibration curve.

11.2.3. In situations where only one or a few Aroclors are of interest for a specific project, the analyst may employ a five-point initial calibration of each of the Aroclors of interest and not use the 1016/1260 mixture or the pattern recognition standards.

11.3. Record the peak area (or height) for each Aroclor peak to be used for quantitation. A minimum of 3 peaks must be chosen for each Aroclor, preferably 5 peaks are used. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. A book of reference chromatograms for each Aroclor has been created for each instrument. Refer to these books for the preferred peaks used for calibration of each Aroclor.

11.4. Calculate the Calibration Factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the calculation below:

$$CF = \frac{\text{Peak Area or Height in the Standard}}{\text{Mass of the Standard Injected, ng}}$$

Five sets of calibration factors will be generated for the Aroclor 1016/1260 mixture, each set consisting of the calibration factors for each of the 5 peaks chosen for this mixture. The single standard for each of the other Aroclors will generate at least 3 calibration factors, one for each selected peak.

11.5. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = \frac{(SD)}{CF_{avg}} \times 100$$

where: SD = Standard deviation of average RF for a compound
CF_{avg} = Mean of CFs for a peak

11.6. If the %RSD of the CFs is $\leq$ 20% over the calibration range, then the slopes of the lines for each standard are sufficiently close to one another and the average CF may be used to determine sample concentrations.

11.7. If any %RSD is >20%, the analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be $\geq$ 0.99. Refer to Method 8000C for additional information regarding calibration.

11.8. When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model chosen for this mixture must be applied to the other 5 Aroclors for which only single standards are analyzed. If multi-point calibration is performed for individual Aroclors, use the calibration factors from those standards to evaluate linearity.

11.9. **Initial Calibration Corrective Action:** If the initial calibration curve does not meet the required criteria to be used for quantitative purposes, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.10. Each day that analysis is performed, the calibration standard(s) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Are the retention times consistent over the range of calibration for each compound? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably. Additionally, examination of signal-to-noise ratio of analytes in low-level standards may be a useful diagnostic tool to monitor instrument performance. Signal-to-noise ratio is defined as the ratio of the analyte signal to the noise measured on a blank. It is recommended but not required that the signal-to-noise ratio be at least three to confirm detection.

11.11. **Initial Calibration Verification (ICV):** In addition to meeting the response and linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known true value. This step is referred to as the Initial Calibration Verification. The ICV must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent recovery (%Rec) of the observed

ICV according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Observed concentration}}{\text{Theoretical concentration}} \times 100$$

The ICV is analyzed immediately following the initial calibration curve. The ICV recoveries are evaluated against a default acceptance range of 70-130% recovery.

11.12. ICV Corrective Action: If the ICV exceeds the acceptance range, another ICV may be analyzed. If the second ICV also exceeds the acceptance range, a new initial calibration should be prepared. Alternatively, the allowance for use of the ICV when the criterion is not met is documented and is at the discretion of the Department Manager, Quality Manager, General Manager or designee.

11.13. Daily and Continuing Calibration: Verify the initial calibration each 12-hour shift by injecting a Continuing Calibration Verification (CCV) standard prior to conducting any sample analyses.

The CCV must also be analyzed at intervals of once every 20 client samples and at the end of the analysis sequence. For Aroclor analyses, the CCV standard should be a mixture of Aroclors 1016 and 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition.

11.14. For initial calibrations that employed average calibration factor, the calibration factor (CF_v) for each analyte calculated from the CCV must not exceed a %Difference (%D) of more than +/-20% when compared to the CF_{avg} from the initial calibration curve. For initial calibrations that employed a linear calibration, the % Drift for each analyte calculated from the CCV must be within +/-20% in order to use the calibration model to quantitate sample results.

$$\% \text{ Drift} = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

11.15. CCV Corrective Action: If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

12. Procedures

12.1. All sample extracts must be analyzed at room temperature and the system must be tuned and calibrated as per Section 11, and free of contamination before samples are analyzed.

12.2. Gas Chromatography conditions: Configure the GC per manufacturer's instructions.

12.3. Inject aliquots of all sample extracts and quality control into the GC under the same operating conditions as used for the calibration standards. The sample vials are loaded onto the autosampler that is programmed via the data system to inject the necessary volume.

12.4. Qualitative Analysis: Compounds are identified as present when the following criteria are met:

12.4.1. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established on both the primary and the confirmation column to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize

the occurrence of both false positive and false negative results. To establish retention time windows, make three or more injections of a standard over the course of a 72-hour period, at a minimum. Record the retention time in minutes for the major peaks and surrogate to three decimal places. Calculate the mean and standard deviation of the absolute retention times of the standard. The retention time window is defined as +/-3 times the standard deviation of the mean absolute retention time established during the 72-hour period or 0.03 minutes, whichever is greater.

12.4.2. Establish the center of the retention time window for each major peak and surrogate by using the absolute retention time for each major peak and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

12.4.3. It may also be useful to establish the center of the retention time window for single point standards by using the absolute retention time for each major peak and surrogate from the single point standards analyzed at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the single point standards analyzed with the initial calibration.

12.4.4. Tentative identification of a PCB compound is made when peaks from the sample extract fall within the established retention time windows for Aroclor peaks. The results of a single column/single injection analysis may be confirmed, if necessary, on a second, dissimilar, GC column. In order to be used for confirmation, retention time windows must have been established for the second GC column. In addition the analyst must demonstrate the sensitivity of the second column analysis. This demonstration must include the analysis of a standard of the target analyte at a concentration at least as low as the concentration estimated from the primary analysis. When the dual-column approach is employed, the target Aroclors are identified and confirmed when they meet the identification criteria on both columns. When confirmation is made on a second column, that analysis should meet all of the QC criteria described above for calibration, retention times, etc.

12.4.5. A book of reference chromatograms for each Aroclor has been created for each instrument. Refer to these books for the preferred peaks and ratios between peaks that are characteristic of each Aroclor. When interferences are present, degradation has occurred, or multiple Aroclors are suspected, the following tools are helpful for proper identification:

- Overlays of the sample chromatogram with chromatograms of Aroclor standards
- Comparison of characteristic peak retention times with Aroclor standards
- Comparison of the ratio between characteristic peaks with ratios of Aroclor standards
- Comparison with historical results, if available
- Analyst judgment and consultation with other experienced analysts
- Consistent application of evaluation tools

12.5. Quantitative Analysis

12.5.1. The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

12.5.2. Once the Aroclor pattern has been identified, compare the responses of 3 to 5 major peaks in the calibration standard for that Aroclor with the peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen and the calibration model established from the multi-point calibration of 1016/1260. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor. Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard or calibration standards interspersed within the samples. The results from these bracketing standards must meet the calibration verification criteria in Sections 11.13 through 11.15.

12.5.3. A book of reference chromatograms for each Aroclor has been created for each instrument. Refer to these books for the preferred peaks used for quantitation of each Aroclor. When interferences are present or degradation has occurred, peaks yielding concentrations or areas that are dissimilar to the others may be excluded. When multiple co-eluting Aroclors are suspected, quantitation of Aroclor(s) should be based on the best match with established Aroclor patterns as determined using the tools outlined in Section 12.4.5.

12.5.4. When PCB concentrations exceed the calibration range, the sample extract should be rerun at a dilution or the result must be qualified as estimated.

12.5.5. Refer to the Manual Integrations SOP for guidance on performing and documenting manual integrations.

13. Quality Control

13.1. Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water or sodium sulfate	One per preparation batch of up to 20 samples, per matrix.	Target analytes must be less than reporting limits	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits.	Re-extract and re-analyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS/MSD set per preparation batch of up to 20 samples, per matrix.	Lab-generated limits Refer to the LIMS for acceptance limits.	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogate	Applicable surrogate compound	Added to each sample, standard and method blank	Lab-generated limits Refer to the LIMS for acceptance limits.	Samples with surrogate failures must be re-extracted and reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample results are non-detect, the sample results may be reported without qualifiers. The surrogate must be qualified. 3) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

Aqueous Sample (ug/L) = $\frac{(X_s)(V_f)(D)}{(V_i)} * 1000$ **Solid Sample (ug/kg)** = $\frac{(X_s)(V_f)(D)}{(W_s)} * 1000$

Where: X_s = On-column concentration of the analyte in ug/mL
V_f = Final volume of extract in Liters
D = Dilution factor of concentrated extract
V_i = Volume of aqueous sample extracted in Liters
W_s = Weight of solid sample extracted in kilograms

Moisture corrected concentration = $\frac{\text{(Final concentration as received)}}{\text{(100 - \%Moisture)}} \times 100$

Oil Sample (mg/kg) = $\frac{(X_s)(V_f)(D)}{(W_s)}$ **Wipe Sample (Total ug)** = $(X_s)(V_f)(D)$

Where: X_s = On-column concentration of the analyte in ug/mL
V_f = Final volume of extract in milliliters
D = Dilution factor of concentrated extract
W_s = Weight of solid sample extracted in kilograms

14.2. LCS equation

$$\mathbf{R = (C/S) * 100}$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation

$$\mathbf{R = \frac{(Cs - C)}{S} * 100}$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD calculations:

$$\mathbf{RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100}$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. MDLs must be conducted per EPA *Definition and Procedure for the Determination of the Method Detection Limit, Revision 2*; December 2016.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability (DOC) study.

19. Method Modifications

19.1. Extracts are not stored in the dark. Sample extracts are analyzed within a few days of extraction and are not exposed to light for an extended period of time.

19.2. A standard of the DDT analogs is not analyzed and evaluated because interference from DDT and its breakdown components is more applicable to congener analysis than Aroclor analysis. Analysis of the DDT analogs is not considered a method requirement.

19.3. Single point Aroclor standards may be combined in the same way that Aroclors 1016 and 1260 are combined.

20. Instrument/Equipment Maintenance

20.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

21. Troubleshooting

21.1. Refer to instrument maintenance logs and/or manufacturer's instructions.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. **Equipment:** Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment.

Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in the Waste Handling or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Wastes", EPA SW-846, methods 8082A, 8000C.

25.2. Pace Analytical Quality Manual; latest revision.

25.3. NELAC/TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Analytes and reporting limits for the analysis of PCBs by 8082A.

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-050-rev.13	1. Section 2.1: removed specific method references for extraction procedures. 2. Section 3.1: created a table for reporting limits of each matrix and added 1262, 1268 and Total PCBs. 3. Table 7.1: revised hold time to extraction to 6 months. 4. Table 8.1: updated equipment and columns information. 5. Table 9.3: updated standards in use and storage conditions. 6. Section 9.2.3: updated standards used and preparation. 7. Section 10.2.2: clarified that single points should be analyzed before ICAL. 8. Section 10: removed quadratic curve fit criteria. 9. Section 11: removed calculations for average and linear curve fits. 10. Section 14: clarified method modifications.	10Aug2015
S-IN-O-050-rev.14	1. Converted to 27-section format. 2. Section 5: moved table of reporting limits to Table 1 attachment. 3. Table 7.1: revised storage temperature format. 4. Section 9.1: updated LTM column information. 5. Section 10.2.3: updated standard preparation to reflect current procedures. Added intermediate combined single point standards. 6. Section 14: corrected equations for aqueous and solid samples to put them in like terms with instrument output. Added equations for oil and wipe samples. 7. Section 19: added modification for combination of single point Aroclors. 8. Section 25.3: added years 2003 and 2009 to TNI reference. 9. Section 26: added reference to Table 1. 10. Table 1: added table for reporting limits.	27Jul2017
S-IN-O-050-rev.15	1. Section 8.1: removed reference to Glossary section of QAM. 2. Section 10.2.1: removed reference to LCS and MS/MSD standards. 3. Section 11.3: added language for example chromatograms and preferred Aroclor peaks used to calibration. 4. Section 12.4.5: added language and a list of tools to help in the identification of Aroclors in a complex matrix. 5. Section 12.5.3: added language to help in the quantitation of Aroclors in a complex matrix. 6. Section 18.1: updated MDL language to new EPA procedure.	7Mar2018
S-IN-O-050-rev.16	1. Table 7.1: updated collection per sample for aqueous samples to reflect RVE. 2. Section 9.1: updated GC columns. 3. Section 10.2.3.2: added lower CAL1 to example ICAL. 4. Section 25.3: added NELAC to reference.	26Apr2018

Table 1: Analytes and Reporting limits for PCBs analyzed by 8082A

Analyte	CAS Number	Water Reporting Limit	Soil Reporting Limit	Oil Reporting Limit	Wipes Reporting Limit
PCB-1016 (Aroclor 1016)	12674-11-2	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1221 (Aroclor 1221)	11104-28-2	0.2 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1232 (Aroclor 1232)	11141-16-5	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1242 (Aroclor 1242)	53469-21-9	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1248 (Aroclor 1248)	12672-29-6	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1254 (Aroclor 1254)	11097-69-1	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1260 (Aroclor 1260)	11096-82-5	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1262 (Aroclor 1262)	37324-23-5	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB-1268 (Aroclor 1268)	11100-14-4	0.1 ug/L	100 ug/kg	1 mg/kg	0.5 total ug
PCB, Total (Aroclor)	1336-36-3	0.2 ug/L	100 ug/kg	1 mg/kg	0.5 total ug

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STANDARD OPERATING PROCEDURE

MICROWAVE EXTRACTION
REFERENCE METHOD: EPA SW-846 METHOD 3546

SOP NUMBER:	S-IN-O-130-rev.06
EFFECTIVE DATE:	September 18, 2017
SUPERSEDES:	S-IN-O-130-rev.05

APPROVAL

General Manager — September 5, 2017 Date

Quality Manager — September 5, 2017 Date

Department Manager — September 5, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

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1. Purpose

1.1 The purpose of this SOP is to provide a laboratory specific procedure for extracting non-volatile and semi-volatile organic compounds from solid samples, such as soil and sediment, using a microwave extraction system while meeting the requirements specified in EPA method 3546.

2. Summary of Method

2.1. An aliquot of sample is weighed and loaded into an extraction vessel and the appropriate solvent mixture is added and the vessel is sealed. The vessel is heated to the extraction temperature and extracted for a pre-determined length of time. The mixture is allowed to cool. The vessel is opened and the contents are filtered. The solid material is rinsed and the various solvent fractions are combined. The extract is concentrated and exchanged as necessary.

3. Scope and Application

3.1. Methylene chloride or a mixture of methylene chloride and acetone are routinely used as extraction solvents. Other solvent systems may be used provided adequate performance can be demonstrated for the target analytes.

3.2. Applicable compounds, volumes/weights, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of microwave extraction equipment and reagents. Each analyst work cell must demonstrate their capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is for extracting water insoluble or slightly water soluble organic compounds from soils, sediments or other solid waste materials.

5. Limits of Detection and Quantitation

5.1. Not applicable to this SOP.

6. Interferences

6.1. Solvents, reagents and glassware can all contribute to compound artifacts or elevated baselines; both conditions that can affect chromatography. Method blanks must be analyzed to determine the presence of contaminants.

6.2. Phthalate esters are common contaminant products in many products in the lab. All plastic products should be avoided when performing this method.

6.3. Extracts that exhibit interferences can be run through a cleanup procedure-see EPA method 3600. Before using a cleanup method, the analyst must run a series of calibration standards through the procedure to ensure that the elution order of compounds remains the same and that no new interferent has been introduced by the cleanup method.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Solid	Glass container with Teflon-lined lid (4oz jar).	None	Cool to ≤6°C	Samples must be extracted within 14 days of the collection date and extract must be analyzed within 40 days of extraction date. Samples for **PCB** analysis must be extracted within 6 months of collection date and extract must be analyzed within 40 days of extraction date.

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment

Equipment	Vendor	Description / Comments
Microwave Extractor	CEM MARS Express	or equivalent microwave extractor
Mechanical Capper	CEM	or equivalent
Analytical Balance	AND or equivalent	Capable of measuring to 0.1g
Concentrator apparatus	Zymark Turbo VAP II	or equivalent concentrator

9.2. Supplies

Item	Description
Weigh boats/Aluminum pans	For weighing soil samples
Teflon tubes	For use in the microwave extraction system
Concentrator tubes	Graduated for concentration of sample to 1 mL
Autosampler vials	~2mL, clear glass with aluminum crimp-top seals
Micro-syringes	Various sizes
Glass funnels	
Glass wool	
Filter paper	For filtering extracts
Spatulas	
Pipettes	Volumetric, Class A, various sizes

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sodium Sulfate	Anhydrous, granular 10-60 mesh, meets ACS specs or equivalent. Rinse thoroughly with methylene chloride and allow it to dry prior to use.
Methylene Chloride	Extraction solvent, pesticide grade or equivalent
Acetone	Extraction solvent, pesticide grade or equivalent
Hexane	Exchange solvent, pesticide grade or equivalent
Solvent Mixture	3:1 Methylene Chloride:Acetone
Ottawa sand	Mesh size 20-30 or other equivalent simulated soil matrix.

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, initial calibration verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Surrogate standard	Surrogate compounds must be added to each sample and QC sample to monitor extraction efficiency.	
Spiking Standard	This solution contains method-specific spike compounds.	Same solution can be used for LCS and MS/MSD

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock BNA spike standard	1. Restek; catalog # 31004, B/N spike; 1000ug/mL, or equivalent 2. Restek; catalog # 31014, Acid spike; 2000ug/mL, or equivalent 3. Restek; catalog # 561763, Custom PAH spike; 5000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working BNA spike standards	Refer to Section 10.2.3.1	Good for 6 months from preparation date	Refrigerate
Stock/Working BNA surrogate standard	O2si; catalog # 11004-83-1L; 100mg/L, or equivalent. Use 1mL for each BNA.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Stock Full-list BNA spike standard	1. SVOA MegaMix; Restek; cat#31850; 1000ug/mL 2. 8270 Mix 1; Restek; cat#572178, 2000ug/mL 3. 8270 Mix 2: Restek; cat#572448, 2000ug/mL or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.

Standard Type	Description	Expiration	Storage
Working Full-list BNA spike standard	Refer to Section 10.2.3.2	Good for 6 months from preparation date	Refrigerate
Stock PCB spike standard	Restek; catalog # 32039, Aroclor 1016/1260; 1000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB spike standard	Refer to Section 10.2.3.3	Good for 6 months from preparation date	Refrigerate
Stock PCB/8081 surrogate standards	Restek; catalog#32457, TCMX/DCB mix; 200ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB/8081 surrogate standard	Refer to Section 10.2.3.4	Good for 6 months from preparation date	Refrigerate
Stock 8081 spike standard	Restek; catalog #32292, 8-80ug/mL of each compound, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8081 spike standard	Refer to Section 10.2.3.5	Good for 6 months from preparation date	Refrigerate
Stock DRO spike standard	Restek; catalog # 31258, Diesel #2 standard; 50,000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working DRO spike standard	Refer to Section 10.2.3.6	Good for 6 months from preparation date	Refrigerate
Stock DRO surrogate standard	Restek; catalog # 31487, Pentacosane; 10,000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working DRO surrogate standard	Refer to Section 10.2.3.7	Good for 6 months from preparation date	Refrigerate
Stock PAH-SIM spike standard	Restek; catalog # 31622, Cal. Mix 5; 2000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PAH-SIM spike standard	Refer to Section 10.2.3.8	Good for 6 months from preparation date	Refrigerate
Stock PAH-SIM surrogate standard	Restek; catalog # 31062, B/N surrogate; 5000ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PAH-SIM surrogate standard	Refer to Section 10.2.3.9	Good for 6 months from preparation date	Refrigerate
Stock/Working Scan/SIM Combo spike standard	O2si; catalog#114072-06, 10-100ug/mL or equivalent. Use 1mL each for each Scan/SIM Combo LCS, MS, and MSD.	Manufacturer's recommended expiration date	Manufacturer's recommended expiration date. Freeze after opening.
Stock/Working Scan/SIM Combo surrogate standard	O2si; catalog#114071-06, 10-100ug/mL or equivalent. Use 1mL each for each Scan/SIM Combo	Manufacturer's recommended expiration date	Manufacturer's recommended expiration date. Freeze after opening.
Stock 8141 spike standard	Ultra; catalog #CUS-12835, 100ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8141 spike standard	Refer to Section 10.2.3.10	Good for 2 months from preparation date	Refrigerate

Standard Type	Description	Expiration	Storage
Stock 8141 surrogate standard	Accustandard; catalog #M-507-1S-10X, Triphenylphosphate 5000ug/mL or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working 8141 surrogate standard	Refer to Section 10.2.3.11	Good for 2 months from preparation date	Refrigerate

10.2.3. Standard Preparation Procedures

10.2.3.1. Working BNA Spike Standard Preparation

Dilute 2.5mL of the stock Acid spike standard (2000ug/mL), 5mL of the stock B/N spike standard (1000ug/mL) and 1mL of the stock Custom PAH spike (5000ug/mL) to 50mL with acetone for a final concentration of 100ug/mL. Add 1mL of this working standard to each BNA LCS, MS and MSD.

10.2.3.2. Working Full-list BNA Spike Standard Preparation

Dilute 5mL of SVOA MegaMix (1000ug/mL), 2.5mL of Stock 8270 Mix 1 (2000ug/mL), and 2.5 mL of Stock 8270 Mix 2 (2000ug/mL) to 50mL with acetone for a final concentration of 100ug/mL. Add 1mL of this working standard to each Full-list BNA LCS, MS, and MSD.

10.2.3.3. Working PCB Spike Standard Preparation

Dilute 1mL of the stock PCB spike standard, Aroclors 1016/1260, (1000ug/mL each) to 200mL with acetone for a final concentration of 5ug/mL. Add 1mL of this working spike to each PCB LCS, MS and MSD.

10.2.3.4. Working PCB/8081 Surrogate Standard Preparation

Dilute 5mL of the Stock 8081/PCB surrogate standard (200ug/mL) to 400mL with acetone for a final concentration of 2.5ug/mL of each surrogate. Add 200uL of this working standard to each PCB and 8081sample, Method Blank, LCS, MS and MSD.

10.2.3.5. Working 8081 Spike Standard Preparation

Dilute 5mL of the Stock 8081 spike standard (8-80ug/mL) to 20mL with acetone for a final concentration of 2-20 ug/mL. Add 100uL of this working spike standard to each 8081 LCS, MS and MSD.

10.2.3.6. Working DRO Spike Standard Preparation

Dilute 10mL of the stock DRO spike standard (50,000ug/mL) to 200mL with acetone for a final concentration of 2500ug/mL. Add 1mL of this working standard to each DRO/ERO/Ohio mod LCS, MS and MSD.

10.2.3.7. Working DRO Surrogate Standard Preparation

Dilute 7.5mL of the stock DRO surrogate standard (10,000ug/mL) to 500mL with acetone for a final concentration of 150ug/mL. Add 1mL of this working surrogate to each DRO/ERO/Ohio mod sample, Method Blank, LCS, MS and MSD.

10.2.3.8. Working PAH-SIM Spike Standard Preparation

Dilute 5mL of the stock PAH-SIM spike standard (2000ug/mL) to 200mL with acetone for a final concentration of 50ug/mL. Add 200uL of this working spike to each PAH-SIM LCS, MS and MSD.

10.2.3.9. Working PAH-SIM Surrogate Standard Preparation

Dilute 5.0mL of the stock PAH-SIM surrogate standard (5000ug/mL) to 500mL with acetone for a final concentration of 50ug/mL. Add 200uL of this working surrogate to each PAH-SIM sample, Method Blank, LCS, MS and MSD.

10.2.3.10. Working 8141 Spike Standard Preparation

Dilute 1mL of the Stock 8141 Spike standard (100ug/mL) to 5mL with acetone for a final concentration of 20ug/mL. Add 100uL of this working spike to each 8141 LCS, MS and MSD.

10.2.3.11. Working 8141 Surrogate Standard Preparation

Dilute 200uL of the Stock 8141 Surrogate Standard (5000ug/mL) to 10mL with acetone for a final concentration of 100ug/mL. Add 25uL of this working surrogate standard to each 8141 sample, Method Blank, LCS, MS and MSD.

11. Calibration

11.1. Not applicable to this SOP.

12. Procedures

12.1. Configure the microwave extraction unit per the manufacturer's instructions.

12.2. Make sure that all glassware and Teflon tubes used for this procedure have been properly cleaned. All washed glassware and Teflon tubes must be rinsed prior to use with acetone to remove residual water and with methylene chloride to remove any residual contaminants.

12.3. Water and/or foreign objects should be excluded from sample portion weighed for analysis. If the soil sample contains a water layer or foreign objects such as sticks, leaves, rocks, etc., decant water or remove objects and place into an aluminum pan. Sample must be homogenized as much as possible prior to weighing for analysis. Once sample portion is weighed for analysis, add water or foreign objects back into the original sample container.

12.4. Weigh either 30g or 20g sample into a weigh boat or aluminum pan – see Table 1. Quantitatively transfer the sample into a labeled Teflon tube.

12.5. Prepare a method blank by weighing 30g or 20g of simulated soil matrix and transferring it to a labeled Teflon tube – see Table 1. The method blank will be used to detect potential laboratory contamination.

12.6. Prepare an LCS by weighing 30g or 20g of simulated soil matrix and transferring it to a labeled Teflon tube. Spike the matrix in the tube with the appropriate amount of spike solution. The LCS will be used to determine the efficiency of the extraction method in recovering target compounds

12.7. Choose one sample in the batch to use as a matrix spike (MS) and matrix spike duplicate (MSD). Weigh two additional 30g or 20g portions of the sample for the MS and MSD and transfer each portion to labeled Teflon tubes. Spike the soil in each tube with the appropriate amount of spike solution.

12.8. Spike each tube with the appropriate amount of surrogate solution.

12.9. Add 25mL of the appropriate solvent (see Table 1) to each Teflon tube and seal the vessels tightly using a mechanical capper.

12.10. Place all Teflon tubes into the extraction unit and proceed with microwave extraction per manufacturer's instructions. Once established, the same extraction conditions must be used for all method blanks, client samples, and QC samples in the same extraction batch.

12.11. Once the microwave cycle is complete, allow the extracts to cool to room temperature. After cooling, carefully open the Teflon tubes using the mechanical capper and filter each extract through a funnel fitted with filter paper or a glass wool plug and containing sodium sulfate. Collect the filtered extract in a clean, labeled concentrator tube. Rinse extraction vessel with methylene chloride and pour into funnel. Once the extract and rinse is filtered, rinse the sodium sulfate with methylene chloride and collect in the concentrator tube.

12.12. Concentration procedure: Refer to Table 1 for routine final volumes. Place each concentrator tube into the Zymark concentrator apparatus. Adjust the settings per manufacturer's instructions. When the volume of the extract reaches a level slightly below the required final volume, remove the concentrator tube from the apparatus and allow extract to cool.

12.13. If a solvent exchange is required, see Table 1, add 50mL of the exchange solvent to the Zymark tube. Concentrate the extract to slightly below the intended final volume, remove from the water bath and allow it to cool.

12.14. Prepare a calibrated vial by volumetrically dispensing the required volume of the solvent being used into a vial and securely capping the vial to eliminate evaporation. The calibrated vial must be prepared daily. Quantitatively transfer the extract from the Zymark tube or concentrator tube to a vial. Bring the sample extract in the vial to the required final volume listed in Table 1 by visually comparing the sample extract vial volume to the calibrated vial volume. Securely cap the sample extract vial. Store all extracts in the appropriate storage cooler. For extracts that will not concentrate to the usual final volume, use the procedure described above to bring the extract to the next higher practical volume for which a calibrated vial can be prepared.

12.15. Refer to appropriate cleanup SOPs if extract cleanup is required.

13. Quality Control

13.1. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Simulated soil matrix	One per preparation batch of up to 20 samples.	Target analytes must be less than reporting limits	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If the method blank concentration is less than 1/10 of the amount measured in the sample, corrective action is not required, affected data must be qualified. 2) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, affected data must be qualified. 3) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples.	Lab-generated limits Refer to LIMS for control limits.	Re-extract and re-analyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS/MSD set per preparation batch of up to 20 samples.	Lab-generated limits Refer to LIMS for control limits.	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogate	Applicable surrogate compound	Added to each sample, standard and method blank	Lab-generated limits Refer to LIMS for control limits.	Samples with surrogate failures must be re-extracted and reanalyzed. QC samples with surrogate failures require the re-extraction and reanalysis of the QC samples and the associated client samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample or method blank results are non-detect, the sample or method blank results may be reported without qualifiers. The surrogate must be qualified. 3) If only one surrogate for BNA or Combo fails and it is >10% recovery, re-extraction is not required but data must be qualified. 4) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.

14. Data Analysis and Calculations

14.1. Not applicable to this SOP.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Not applicable to this SOP.

16. Corrective Actions for Out-of-Control Data

16.1. Not applicable to this SOP.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Not applicable to this SOP.

18. Method Performance

18.1. Demonstration of Capability (DOC): Analysts performing this method must document acceptable accuracy and precision by passing a demonstration of capability study (DOC).

18.2. Microwave Power Test: The microwave should be power tested per manufacturer's instructions monthly, at a minimum.

19. Method Modifications

19.1. Samples not air dried and ground nor are they mixed with sodium sulfate prior to extraction.

19.2. Balance weighs to 0.1g instead of 0.01g because dry weight is not determined by this procedure.

19.3. Samples are not particle sized or sieved prior to extraction but are homogenized.

19.4. Soil samples for 8081 and 8141 are weighed at 20g, not 30g.

20. Instrument/Equipment Maintenance

20.1. Refer to manufacturer's instructions and/or maintenance log.

21. Troubleshooting

21.1. Refer to manufacturer's instructions and/or maintenance log.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All digestions must be conducted under a fume hood.

22.3. Equipment: Portions of the preparation and analytical equipment may operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other applicable SOP. All wastes are accumulated, managed and disposed of in accordance with all federal and state laws and regulations.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention and Waste Management

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods"; EPA SW-846, latest revision. Method 3546 "Microwave Extraction".

25.2. Pace Analytical Quality Manual; latest revision.

25.3. TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Table 1: Extraction Conditions

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-130-rev.04	1. Table of Contents: new Section 14, Method Modifications added. 2. Table 8.1: updated balance details 3. Table 8.2: added volumetric pipettes 4. Table 9.1: updated solvent manufacturers 5. Table 9.3: updated for current standards, vendors and concentrations 6. Section 9.2.3: updated for current standards and volumes 7. Section 11.2: added Teflon tubes require washing and rinsing 8. Section 11.8: changed specific solvent to "appropriate solvent" 9. Section 11.11: updated final volumes for methods where needed 10. Section 11.13: added instructions for determination of non-standard final volumes 11. Section 11.14: added reference to cleanup SOPs. 12. Table 12.1: updated corrective action for Method Blank. 13. New Section 14, Method Modifications added. 14. Section 15.1: revised SOP reference. 15. Section 16: added reference to cleanup SOPs.	16May2013
S-IN-O-130-rev.05	1. Cover page: updated phone number 2. Section 3.2: added pesticides. 3. Section 3.3: updated solvents used. 4. Table 7.1: updated holding time for extraction of samples for PCBs to 6 months. 5. Table 9.1: updated reagents and added sodium sulfate rinsing procedure. 6. Table 9.3: updated standards and storage conditions and added standards for pesticides analysis. 7. Section 9.2.3: updated Full-list BNA standard prep and added preparation of pesticide standards. 8. Section 11: added references to the newly created Table 1 showing extraction conditions. 9. Section 12: removed equations for LCS, RSD, and MS. 10. Section 13: removed reference to MDL because it is covered in each determinative procedure SOP. 11. Section 16: removed the specific reference to cleanup SOPs. 12. Section 17: added Table 1 for extraction conditions.	02Sep2015
S-IN-O-130-rev.06	1. Converted to 27 section format. 2. Table 7.1: updated storage temperature format. 3. Section 9.2: added weigh boats/aluminum pans. 4. Table 10.3: updated standard descriptions. 5. Section 10.2.3: updated standard preparation where needed. 6. Section 12: clarified sample amounts and weighing procedure. Separated instructions for method blank and LCS. 7. Section 19: added method modification for reduced 8081 and 8141 weights. 8. Section 25.3: added years 2003 and 2009 to TNI reference. 9. Table 1: added column for routine sample weight by method and added BNA Scan/SIM Combo details.	05Sep2017

Table 1 – Extraction Conditions

Determinative Method	Initial Sample Weight (g)	Clean Soil Matrix Used for QC	Extraction Solvent	Exchange Solvent	Final Extract Volume (mL)
8015 DRO (includes ERO and Ohio mod)	30	Ottawa Sand	Methylene Chloride	N/A	1
8081 OC PEST	20	Sodium Sulfate	3:1 Methylene Chloride to Acetone	Hexane	10
8082 PCB	30	Sodium Sulfate	3:1 Methylene Chloride to Acetone	Hexane	10
8141 OP PEST	20	Sodium Sulfate	3:1 Methylene Chloride to Acetone	Hexane	10
8270 PAH-SIM	30	Ottawa Sand	3:1 Methylene Chloride to Acetone	N/A	1
8270 BNA	30	Ottawa Sand	3:1 Methylene Chloride to Acetone	N/A	1
8270 BNA Scan/SIM Combo	30	Ottawa Sand	3:1 Methylene Chloride to Acetone	N/A	1

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STANDARD OPERATING PROCEDURE

THE DETERMINATION OF POLYCHLORINATED BIPHENYLS (PCBS)

REFERENCE METHOD: EPA METHOD 608

SOP NUMBER:	S-IN-O-168-rev.02
EFFECTIVE DATE:	July 31, 2017
SUPERSEDES:	S-IN-O-168-rev.01

APPROVAL

General Manager — July 18, 2017 Date

Quality Manager — July 18, 2017 Date

Department Manager — July 18, 2017 Date

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

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1. Purpose

1.1. The purpose of this SOP is to provide a laboratory specific procedure for determining the concentration of polychlorinated biphenyls (PCBs) in municipal and industrial discharges while meeting the requirements specified in EPA method 608.

2. Summary of Method

2.1. A measured volume of sample is extracted with methylene chloride using a separatory funnel. The extract is dried and exchanged to hexane during concentration.

2.2. Cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes.

2.3. After cleanup, the extract is analyzed by a gas chromatograph fitted with an electron capture detector (ECD). Aroclor identification is confirmed by a secondary column.

3. Scope and Application

3.1. Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

3.2. Reporting limits, control limits, volumes used, standard concentrations, vendors, instrumentation, equipment and supplies are subject to change.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of GC systems and interpretation of GC PCB data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

4. Applicable Matrices

4.1. This procedure is applicable to aqueous samples and municipal and industrial wastewater samples.

5. Limits of Detection and Quantitation

5.1. The target Aroclors and default reporting limits associated with this procedure are listed below:

Analyte	CAS Number	Reporting Limit
PCB-1016 (Aroclor 1016)	12674-11-2	0.1 ug/L
PCB-1221 (Aroclor 1221)	11104-28-2	0.2 ug/L
PCB-1232 (Aroclor 1232)	11141-16-5	0.1 ug/L
PCB-1242 (Aroclor 1242)	53469-21-9	0.1 ug/L
PCB-1248 (Aroclor 1248)	12672-29-6	0.1 ug/L
PCB-1254 (Aroclor 1254)	11097-69-1	0.1 ug/L
PCB-1260 (Aroclor 1260)	11096-82-5	0.1 ug/L
PCB-1262 (Aroclor 1262)	37324-23-5	0.1 ug/L
PCB-1268 (Aroclor 1268)	11100-14-4	0.1 ug/L
PCB, Total (Aroclor)	1336-36-3	0.2 ug/L

5.2. Reporting limits may vary as a function of the volume of sample extracted and extract final volume. Refer to LIMS for method detection limits.

6. Interferences

6.1. Matrix interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware. These interferences lead to discrete artifacts or elevated baselines in gas chromatograms. Routinely, all of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running reagent blanks. Interferences caused by phthalate esters can pose a problem in the analysis. Common flexible plastics contain varying amounts of phthalates, which are easily extracted during lab operations. Avoiding the use of plastics in the lab can best minimize interferences from phthalates.

6.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the site being sampled. Cleanup procedures may be used to remove such interferences.

7. Sample Collection, Preservation, and Handling

Table 7.1 – Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	1 liter in amber glass bottle	None required	Cool to $\leq 6^{o}C$	Extract within 7 days of collection and analyze within 40 days of extraction

Samples must be stored separately from all standards, reagents, and highly contaminated samples. To avoid contamination, no food or drink products can be located near samples.

8. Definitions

8.1. Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions.

9. Equipment and Supplies

9.1. Equipment/Instrumentation

Equipment	Vendor	Description / Comments
N-EVAP concentrator	Organomation	Or equivalent equipment
Extraction glassware	Zymark	Or equivalent equipment
Shaker Tables	Glas-Col	Or equivalent equipment
GC	Agilent, 7890A with LTM module or equivalent	Equipped with dual ECD Detectors; dual columns, and dual injectors, or equivalent system.
Autosampler	Agilent, 7693 or equivalent	150 position
Data System	Chemstation acquisition; Target integrations	Or equivalent software

Equipment	Vendor	Description / Comments
GC Columns	Restek, DB5-MS or equivalent	Fused silica; 30 meters, 0.32mm ID, 0.25um film thickness, or equivalent column
	Restek, DB35-MS or equivalent	Fused silica; 30 meters, 0.32mm ID, 0.25um film thickness, or equivalent column
LTM GC Columns	Restek, DB-35 LTM or equivalent	Fused silica; 15 meters, 0.32mm ID, 0.50um film thickness, or equivalent column
	Restek, DB5-MS LTM or equivalent	Fused silica; 15 meters, 0.32mm ID, 0.50um film thickness, or equivalent column

9.2. General Supplies

Item	Description
Separatory Funnels	2L or 125mL, Teflon, with PTFE stopcocks and Teflon lids or equivalent
Glass beakers	400mL Pyrex or equivalent
Glass funnels	
Glass wool	
Graduated cylinders	Glass, Class A
Heated water bath	Temperature controlled
Boiling Chips	Teflon or equivalent
Pasteur pipettes	For determining sample pH
pH paper	pH range 1-12
Glass stirring rods	For breaking up emulsions
Glass tubes	Disposable, 20x150mm or equivalent
Filter paper	Filter paper
Pipettes	Volumetric, Class A, various sizes
Glass syringes	Various sizes
Glass vials	20mL volume with Teflon lined caps or equivalent
Autosampler vials	2mL volume with Teflon lined crimp tops or equivalent
Micro-inserts	Various sizes

10. Reagents and Standards

10.1. Reagents

Reagent	Concentration/ Description
Reagent water	ASTM Type II water
Sodium Sulfate	Anhydrous, granular 10-60 mesh, meets ACS specs or equivalent. Thoroughly rinse with methylene chloride and dry prior to use.
Methylene Chloride	Extraction solvent, pesticide grade or better
Sulfuric acid solution (1:1)	Reagent grade
Sodium Hydroxide solution (10N)	Dissolve 400g sodium hydroxide pellets into 1L of reagent water or purchase premade.
Hexane	Pesticide or reagent grade or equivalent

10.2. Analytical Standards

10.2.1. Definitions

Standards are required for initial calibration, calibration verification standards, second source verification, and for preparing LCS, MS, and MSD samples.

Table 10.2 Standard Definitions and vendors

Standard	Description	Comments
Initial Calibration Standards	Standards prepared at varying levels to determine calibration range of the instrument.	ICAL
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	CCV
Initial Calibration Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the calibration curve.	ICV
Spiking Standard	This solution contains method specified analytes and is used to spike LCS, MS and MSD.	Same solution can be used for the LCS and MS/MSD
Surrogate standard	Surrogates are added to each sample and QC sample to monitor extraction efficiency.	

10.2.2. Storage Conditions

Table 10.3 – Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Standards for Sample Extraction			
Stock PCB Spike standard	Restek; catalog #32039, Aroclor 1016/1260; 1000 ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB Spike standard	Refer to Section 10.2.3.1	Good for 6 months from preparation date	Refrigerate
Stock PCB Surrogate Spike standard	Restek; catalog # 32457, TCMX; 200ug/mL, or equivalent	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Working PCB Surrogate Spike standard	Refer to Section 10.2.3.2	Good for 6 months from preparation date	Refrigerate
Standards for Sample Analysis			
Stock PCB Calibration standards	Ultra Scientific 1016 cat#EPA-1282, 1221 cat #EPA-1292, 1232 cat #EPA-1302, 1242 cat #EPA-1312, 1248 cat #EPA-1342, 1254 cat #EPA-1352, 1260 cat#EPA-1362, 1262 cat #EPA-1372 and 1268 cat #EPA-1382, each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.

Standard Type	Description	Expiration	Storage
Intermediate PCB Calibration standards	Refer to Section 10.2.3.3	Solution good for 6 months from preparation.	Refrigerate
Working PCB Calibration standards	Refer to Section 10.2.3.4	Solution good for 6 months from preparation.	Refrigerate
Stock PCB ICV standard	Restek 1016/1260 cat#32039, 1221 cat#32007, 1232 cat#32008, 1242 cat#32009, 1248 cat#32010, 1254 cat#32011, 1262 cat#32409, and 1268 cat#32410 each at 1000ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.
Intermediate PCB ICV standard	Refer to Section 10.2.3.5	Solution good for 6 months from preparation.	Refrigerate
Working PCB ICV standard	Refer to Section 10.2.3.6	Solution good for 6 months from preparation.	Refrigerate
Stock PCB Surrogate Calibration standard	Ultra; catalog #ISM-320; TCMX; 200ug/mL, or equivalent.	Manufacturer's recommended expiration date	Manufacturer's recommended storage conditions. Refrigerate after opening.

10.2.3. Standard Preparation Procedures

10.2.3.1. Working PCB Spike Standard Preparation (For Extraction Procedure)

Dilute 0.1mL the stock PCB spike standard, Aroclors 1016/1260 (1000ug/mL each) to 100mL with Acetone for a final concentration of 1ug/mL. Add 1mL of this working spike to each PCB LCS, MS and MSD for a final concentration of 1ug/L.

10.2.3.2. Working PCB Surrogate Spike Standard Preparation (For Extraction Procedure)

Dilute 5mL of the Stock PCB Surrogate standard (200ug/mL) to 400mL with acetone for a final concentration of 2.5ug/mL. Add 200uL of this working surrogate to each PCB sample, Method Blank, LCS, MS and MSD for a final concentration of 0.5ug/L.

10.2.3.3. Intermediate PCB Calibration Standard Preparation

To prepare an Aroclor 1016/1260 intermediate calibration standard, dilute 100uL of the Stock Aroclor 1016 Calibration standard (1000ug/mL), 100uL of the Stock Aroclor 1260 Calibration standard (1000ug/mL) and 50uL of the Stock PCB Surrogate standard (200ug/mL) to 50mL with Hexane for a final Aroclor 1016/1260 concentration of 2ug/mL and a final surrogate concentration of 0.2ug/mL. This recipe can also be used to prepare an intermediate calibration standard for other Aroclors.

10.2.3.4. Working PCB Calibration Standard Preparation

The following are examples of calibration standard concentrations and could vary based on requirements:

Standard	Intermediate PCB Cal. Std. amount	Final Volume in Hexane	Final PCB Conc, ug/L	Final Surr Conc, ug/L
Standard 1	5uL	1mL	10	1
Standard 2 (CCV)	50uL	1mL	100	10
Standard 3	250uL	1mL	500	50

10.2.3.5. Intermediate PCB ICV Standard Preparation

To prepare an Aroclor 1016/1260 intermediate ICV standard, dilute 20uL of the Stock PCB 1016/1260 ICV standard (1000ug/mL) and 10uL of the Stock PCB Surrogate Calibration standard (200ug/mL) to 20mL with Hexane for a final PCB concentration of 1ug/mL and a final surrogate concentration of 0.1ug/mL. This recipe can also be used to prepare an intermediate ICV standard for other Aroclors.

10.2.3.6. Working PCB ICV Standard Preparation

Dilute 100uL of the Intermediate PCB ICV standard (1ug/mL/0.1ug/mL) to 1mL with hexane for a final PCB concentration of 100ug/L and a final surrogate concentration of 10ug/L.

11. Calibration

11.1. Before the initial calibration standards are injected, it is advisable to perform routine injection port and column maintenance due to the sensitivity of the ECD detector.

11.2. **Initial Calibration**: Initial calibration standards are introduced into the GC from the lowest to highest concentration by direct injection. Three calibration points, at a minimum, are analyzed to evaluate linearity for the purpose of quantitation. The lowest calibration standard must be at or below the required reporting limit. Refer to the Quality Manual for more information regarding calibration curves.

11.2.1. A mixture of Aroclor 1016 and 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. An initial 3-point calibration is performed using the mixture of Aroclors 1016 and 1260.

11.2.2. Single point standards of the other Aroclors are necessary for pattern recognition and Aroclor identification. If a sample is found to contain an Aroclor other than 1016 or 1260, a calibration curve for the identified Aroclor with a minimum of three concentration points is required for quantitation.

11.2.3. In situations where only one or a few Aroclors are of interest for a specific project, the analyst may employ a three-point initial calibration of each of the Aroclors of interest and not use the 1016/1260 mixture or the pattern recognition standards.

11.3. Record the peak height or area responses against mass injected for each Aroclor peak to be used for quantitation. A minimum of 3 peaks must be chosen for each Aroclor, preferably 5 peaks are used. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor.

11.4. Calculate the Calibration Factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the calculation below:

$$CF = \frac{\text{Peak Area or Height in the Standard}}{\text{Mass of the Standard Injected, ng}}$$

Three to five sets of calibration factors will be generated for each calibration standard, each set consisting of the calibration factors for each of the peaks chosen for the standards.

The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = \frac{(SD)}{CF_{avg}} \times 100$$

where: SD = Standard deviation of average CF for a compound
CF_{avg} = Mean of CFs for a peak

11.5. If the calibration factor is constant, <10% RSD over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

11.6. If any %RSD is >10%, the analyst may employ a regression equation that does not pass through the origin. The regression calculation will generate a correlation coefficient (r) that is the measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, the correlation coefficient must be ≥ 0.99.

11.7. Initial Calibration Corrective Action: If the initial calibration curve does not meet the required criteria to be used for quantitative purposes, a new initial calibration curve must be analyzed. Instrument maintenance and/or preparation of new calibration standards must also be considered. Samples associated with a failed initial calibration must be reanalyzed.

11.8. Each day that analysis is performed, the calibration standard(s) should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Are the retention times consistent over the range of calibration for each peak? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably. Additionally, examination of signal-to-noise ratio of analytes in low-level standards may be a useful diagnostic tool to monitor instrument performance. Signal-to-noise ratio is defined as the ratio of the analyte signal to the noise measured on a blank. It is recommended but not required that the signal-to-noise ratio be at least three to confirm detection.

11.9. Initial Calibration Verification (ICV): In addition to meeting the response and linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. To assess the accuracy, a single standard from a secondary source must be analyzed and the results obtained must be compared to the known true value. This step is referred to as the Initial Calibration Verification. The ICV must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent recovery (%Rec) of the observed ICV according to the following equation:

$$\%\text{ Recovery} = \frac{\text{Observed concentration}}{\text{Theoretical concentration}} \times 100$$

The ICV is analyzed immediately following the initial calibration curve. The ICV recoveries are evaluated against a default acceptance range of 70-130% recovery.

11.10. ICV Corrective Action: If the ICV exceeds the acceptance range, another ICV may be analyzed. If the second ICV also exceeds the acceptance range, a new initial calibration should be prepared. Alternatively, the allowance for use of the ICV when the criterion is not met is documented and is at the discretion of the Department Manager, Quality Manager, General Manager or designee.

11.11. Daily and Continuing Calibration: Verify the initial calibration each 12-hour shift by injecting a Continuing Calibration Verification (CCV) standard prior to conducting any sample analysis. The CCV must also be analyzed at intervals of not less than once every 10 samples and at the end of the analysis sequence. The CCV standard should be composed of the same Aroclor(s) used for the initial calibration.

11.12. The percent recovery for each analyte calculated from the CCV must not exceed +/-15% when compared to the CF_{avg} from the initial calibration curve.

11.13. CCV Corrective Action: If a CCV fails the acceptance criteria, check the instrument operating conditions, and if necessary, restore them to the original settings, and analyze another CCV. If the response still fails the acceptance criteria, then a new initial calibration must be prepared. Samples associated with a failed CCV must be reanalyzed. **Exception:** If the CCV is outside of the upper control limit, indicating high bias, associated samples determined to be <RL may be reported.

12. Procedures

12.1. Separatory Funnel Extraction

12.1.1. Make sure that all glassware and Teflon separatory funnels used for this procedure have been properly washed. All washed glassware must be rinsed prior to use with acetone to remove residual water and with methylene chloride to remove any residual contaminants.

12.1.2. For each batch of 20 or fewer samples, prepare a Method Blank and an LCS using 1L aliquots of reagent water. The Method Blank will be used to demonstrate that the process is free of contamination. The LCS will be used to determine the efficiency of the extraction process. The laboratory must on an ongoing basis spike at least 10% of samples to assess accuracy, assuming adequate sample volume is available.

12.1.3. Using a Class A graduated cylinder, measure the desired volume of sample to be used for the extraction and record the volume in mLs. Transfer the sample into a clean separatory funnel in a ring stand on a secured rack.

12.1.4. Add the surrogate standard to each sample, Method Blank, LCS, MS and MSD. Add the spiking standard to each LCS, MS and MSD.

12.1.5. Measure the initial pH of each sample using wide range pH paper. Dip a clean disposable Pasteur pipette into each sample and touch the pipette tip to a piece of pH paper. Record the initial pH. If sample pH is <5 or >9, adjust each sample to pH 5-9 using 1:1 sulfuric acid or 10N sodium hydroxide.

12.1.6. Rinse the graduated cylinder or sample bottle with a 60mL portion of methylene chloride and transfer the rinsate to the separatory funnel.

12.1.7. Cap the separatory funnels with Teflon lids and shake for 2 minutes with periodic venting. This can be done manually or with an automatic shaker. **NOTE:** Methylene chloride may cause excessive pressure in the separatory funnel. It is recommended to shake slightly and vent prior to placing separatory funnels on an automatic shaker.

12.1.8. Return the separatory funnels to their ring stands and allow the solvent layer to separate from the aqueous phase. If an excessive emulsion is present in the solvent layer, it can be broken up manually using a clean glass stirring rod. It this is not successful, the emulsion can be drained into a clean secondary container such as a VOA vial and centrifuged then decanted into the drying funnel.

12.1.9. Drain the methylene chloride layer through a drying funnel consisting of a clean funnel containing a plug of clean glass wool or filter paper topped with 1-2 inches of clean sodium sulfate. The solvent should be collected in a labeled beaker or flask.

12.1.10. Repeat steps 12.1.7 through 12.1.9 two more times with additional 60mL aliquots of methylene chloride. With each extraction, drain the solvent through the drying funnel and collect the extracts. After the last extraction has been collected, rinse the drying funnel with methylene chloride.

12.1.11. Pour the entire sample extract into a labeled Zymark concentrator tube and place in the Zymark concentrator apparatus. Adjust the settings per manufacturer's instructions.

12.1.12. After concentrating the sample to 1-2mL, a solvent exchange is required. Add 50mL of hexane to the Zymark tube. Concentrate the extract to slightly below 10mL and then remove from the water bath and allow it to cool.

12.1.13. Prepare a calibrated vial by volumetrically dispensing 10mL of hexane into a vial and securely capping the vial to eliminate evaporation. The calibrated vial must be prepared daily. Quantitatively transfer the sample extract from the Zymark tube to a labeled vial. Bring the extract in the vial to 10mL by visually comparing the sample extract volume to the calibrated vial volume. Securely cap the sample extract vial. Store all extracts in the appropriate storage cooler.

12.1.14. Refer to appropriate cleanup SOPs if extract cleanup is required.

12.2. GC Analysis

12.2.1. All sample extracts must be analyzed at room temperature and the system must be calibrated as per Section 11, and free of contamination before samples are analyzed.

12.2.2. **Gas Chromatography conditions**: Configure the GC per manufacturer's instructions.

12.2.3. Inject all samples and quality control samples into the GC under the same operating conditions as used for the calibration standards. The sample vials are loaded onto the autosampler programmed via the data system to inject the necessary volume.

12.3. Qualitative Analysis: Compounds are identified as present when the following criteria are met:

12.3.1. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established on both the primary and the confirmation column to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. To establish retention time windows, make three or more injections of a standard over the course of a 72-hour period, at a minimum. Record the retention time in minutes for the major peaks and surrogate to three decimal places. Calculate the mean and standard deviation of the absolute retention times of the standard. The retention time window is defined as +/-3 times the standard deviation of the mean absolute retention time established during the 72-hour period or 0.03 minutes, whichever is greater

12.3.2. Establish the center of the retention time window for each major peak and surrogate by using the absolute retention time for each major peak and surrogate from the calibration verification standard at the

beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

12.3.3. Tentative identification of a PCB compound is made when peaks from the sample extract fall within the established retention time windows for Aroclor peaks in calibration standards. Tentative Aroclor identification must be confirmed using a second GC column of dissimilar stationary phase, based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS. Qualitative confirmation of Aroclors through separate injection onto a dissimilar column does not require the confirmation column to meet the calibration criteria outlined in Section 11.

12.4. Quantitative Analysis

12.4.1. The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

12.4.2. Once the Aroclor pattern has been identified, a 3-point calibration curve of the identified Aroclor must be used for quantitation. When PCB concentrations are above the calibration range, the sample extract should be diluted and reanalyzed or reported as an estimated concentration.

12.4.3. Refer to the Manual Integrations SOP for guidance on performing and documenting manual integrations.

13. Quality Control

13.1. Batch Quality Control Criteria

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per preparation batch of up to 20 samples, per matrix.	Target analytes must be less than reporting limits.	Re-extract and re-analyze if target compound is >RL in method blank and associated samples. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, the reported method blank and samples must be qualified. 2) If a contaminant is present only in the method blank and not the samples, no action is required.
Laboratory Control Sample (LCS)	Applicable target analytes	One per preparation batch of up to 20 samples, per matrix.	Attachment 1, Method 608 Table 3, Range for Ps. Lab-generated limits used for compounds not listed.	Re-extract and re-analyze associated samples if original LCS is outside acceptance limits. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported data must be qualified. 2) If LCS recovery is >QC limits and sample results are non-detect, the sample data may be reported without qualifiers. The LCS data must be qualified.
Matrix Spike (MS)/Matrix Spike Duplicate (MSD)	Applicable target analytes	One MS per batch plus an additional MS if >10 samples in the batch. At least one MS per month is required.	Attachment 1, Method 608 Table 3, Range for Ps. Lab-generated limits used for compounds not listed.	No corrective actions necessary. If LCS recovery is in range, the system is considered in-control and the out-of-control MS/MSD must be qualified appropriately.
Surrogate	Applicable surrogate compound	Added to each sample, standard and method blank	Lab-generated limits Refer to the LIMS for acceptance limits.	Samples with surrogate failures must be re-extracted and reanalyzed. *Exceptions:* 1) If no additional sample remains for reanalysis or if reanalysis cannot take place within holding time, reported surrogate data must be qualified. 2) If surrogate result is >QC limits, and sample results are non-detect, the sample results may be reported without qualifiers. The surrogate must be qualified. 3) MS/MSD surrogate recovery failures do not constitute the re-extraction or reanalysis of samples but the surrogate data must be qualified.

14. Data Analysis and Calculations

14.1. Calculate the final concentration in the sample as follows:

$$\textbf{Aqueous Sample (ug/L)} = \frac{(X_s)(V_f)(D)}{(V_i)} * 1000$$

Where: X_s = On-column concentration of the analyte, ug/mL
V_f = Final volume of sample extract, L
D = Dilution factor of extract
V_i = Initial volume of sample extracted, L

14.2. LCS equation

$$R = (C/S) * 100$$

Where R = percent recovery
C = spiked LCS concentration
S = concentration of analyte added to the clean matrix

14.3. MS/MSD equation

$$R = \frac{(Cs - C)}{S} * 100$$

Where R = percent recovery
Cs = spiked sample concentration
C = sample concentration
S = concentration of analyte added to the sample

14.4. RPD calculations:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} * 100$$

Where RPD = relative percent difference
D_1 = first sample result
D_2 = second sample result

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Sections 11 and 13.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Sections 11 and 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Sections 11 and 13.

18. Method Performance

18.1. An MDL study and/or LOD/LOQ verification must be conducted every 12 months for each matrix per instrument.

18.2. Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability (DOC) study. Compare standard deviation to Attachment 1 (Table 3) for "s" and compare recovery to "Range for X."

19. Method Modifications

19.1. Sample pH is adjusted to between pH 5 and 9 at the time of extraction.

19.2. Sample volume for extraction is measured using a graduated cylinder prior to pouring it into the separatory funnel. The graduated cylinder or the sample bottles are rinsed with the first portion of solvent.

19.3. Zymark concentration tubes are used instead of the Kuderna-Danish apparatus.

20. Instrument/Equipment Maintenance

20.1. Refer to maintenance log and/or instrument manufacturer's instructions.

21. Troubleshooting

21.1. Refer to maintenance log and/or instrument manufacturer's instructions.

22. Safety

22.1. Standards and Reagents

The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible. The stock PCB standards are toxic and should be handled with extreme care.

22.2. Samples

Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves**,** lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible. All distillations should be conducted under a fume hood. **NOTE: All sample waste and waste products from PCB extraction and analysis must be stored in a separate satellite waste container, which shall remain closed unless waste is being actively added.**

22.3. Equipment

Portions of the preparation and analytical equipment operate at high temperatures. Care must be taken to minimize accidents and injuries when working on or with this equipment. Equipment should be turned off or the temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on equipment.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in Waste Handling or other applicable SOP.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. 40CFR, Part 136, Appendix A, EPA Method 608.

25.2. "Test Methods for Evaluating Solid Wastes", EPA SW-846, Method 8082A.

25.3. Pace Analytical Quality Manual; latest revision.

25.4. TNI Standard; Quality Systems section; 2003 and 2009.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Attachment 1: Method 608 Table 3

27. Revisions

Document Number	Reason for Change	Date
S-IN-O-168-rev.00	1. First issue.	01Nov2013
S-IN-O-168-rev.01	1. Section 3.1: default reporting limits added to table. 2. Table 9.3: stock calibration and ICV details updated and storage conditions for intermediate and working standards updated. 3. Section 9.2.3: updated standard preparation. 4. Section 10: removed option for quadratic curve fit. 5. Section 10.2: reworded to clarify that quantitation must employ a 3-point curve of the identified Aroclor. 6. Section 10.13: changed CCV frequency from every 20 samples to every 10 samples and clarified that CCVs should be composed of same Aroclor used in calibration. 7. Section 11.1.2: added pH adjustment of samples to pH 5-9. 8. Section 11.4: removed calculations for curve fits and for soils. 9. Section 14: added pH adjustment at extraction as a modification. 10. Section 16: added reference to Method 8082A for calibration scheme.	28Jul2015
S-IN-O-168-rev.02	1. Converted to 27-section format. 2. Table 7.1: revised storage temperature format. 3. Section 9.1: updated column information. 4. Section 10.1: updated reagent information. 5. Table 10.3: updated standard information and storage requirements. 6. Section 10.2.3: updated standard preparation to current procedures. 7. Section 11.3: removed sentence about using at least 5 peaks for the 1016/1260 mixture. 8. Section 12.1: moved pH adjustment procedure to take place after addition of spikes and surrogates. 9. Table 13.1: added that statistical limits will be used for spiked compounds not listed in Table 3 and revised language for frequency of matrix spikes. Changed batch size to 20 samples while maintaining 10% frequency of spikes. 10. Section 14.1: revised equation to be compatible with units of instrument output. 11. Section 25: added years 2003 and 2009 to TNI reference.	18Jul2017

Attachment 1: Method 608 Table 3

Table 3—QC Acceptance Criteria—Method 608

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P_s %)
Aldrin	2.0	0.42	1.08 - 2.24	42 - 122
α-BHC	2.0	0.48	0.98 - 2.44	37 - 134
β-BHC	2.0	0.64	0.78 - 2.60	17- 147
δ-BHC	2.0	0.72	1.01 - 2.37	19 - 140
γ-BHC	2.0	0.46	0.86 - 2.32	32 - 127
Chlordane	50	10.0	27.6 - 54.3	45 - 119
4,4'-DDD	10	2.8	4.8 - 12.6	31 - 141
4,4'-DDE	2.0	0.55	1.08 - 2.60	30 - 145
4,4'-DDT	10	3.6	4.6 - 13.7	25 - 160
Dieldrin	2.0	0.76	1.15 - 2.49	36 - 146
Endosulfan I	2.0	0.49	1.14 - 2.82	45 - 153
Endosulfan II	10	6.1	2.2 - 17.1	D - 202
Endosulfan Sulfate	10	2.7	3.8 - 13.2	26 - 144
Endrin	10	3.7	5.1 - 12.6	30 - 147
Heptachlor	2.0	0.40	0.86 - 2.00	34 - 111
Heptachlor epoxide	2.0	0.41	1.13 - 2.63	37 - 142
Toxaphene	50.0	12.7	27.8 - 55.6	41 - 126
PCB-1016	50	10.0	30.5 - 51.5	50 - 114
PCB-1221	50	24.4	22.1 - 75.2	15 - 178
PCB-1232	50	17.9	14.0 - 98.5	10 - 215
PCB-1242	50	12.2	24.8 - 69.6	39 - 150
PCB-1248	50	15.9	29.0 - 70.2	38 - 158
PCB-1254	50	13.8	22.2 - 57.9	29 - 131
PCB-1260	50	10.4	18.7 - 54.9	8 - 127

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.

NOTE: These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

Title: ANALYSIS OF PESTICIDES AND PCBs

[Method: EPA Method 608]

Approvals (Signature/Date):

Technology Specialist	04/27/17 Date	Health & Safety Coordinator	05/01/17 Date
Quality Assurance Manager	05/30/17 Date	Technical Director	06/29/17 Date

This SOP was previously identified as SOP No. NC-GC-007, Rev 7, dated 2/19/16

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of concentrations of pesticides and PCBs (Table 4) in wastewater. It is based on EPA Method 608. The working linear range is highly instrument, column, and compound dependent. Working linear ranges are listed in Table 1. Reporting limits are listed in Table 4.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. This method provides gas chromatographic conditions for detection and identification of pesticides and PCBs in wastewater. After the initial preparation step, the sample is introduced into the GC and the concentration of each target analyte is measured by the detector response within a defined retention time (RT) window, relative to the response of the reference standards.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Contamination by carryover may occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a hexane blank to check for cross-contamination.

4.3. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including, but not limited to, Sulfuric Acid Cleanup (Method 3665A) and TBA cleanup (Method 3660B). These cleanup procedures are included in SOP NC-OP-025.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and

this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table.** A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded. Other gloves will be cleaned immediately.

5.4. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds should be prepared in a hood.

5.5. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.6. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.

5.7. Exposure to chemicals must be maintained **as low as reasonably achievable;** therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.8. The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.10. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.11. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Gas chromatographic system

6.1.1. Gas chromatograph: equipped with Electron Capture Detectors (ECDs)

6.1.2. Software: Chem Station data system or equivalent

6.1.3. Gas chromatographic columns are shown in Table 2.

6.1.4. Autosampler: capable of reproducible injections

6.1.5. Autosampler vials, inserts, and caps

6.1.6. Class A volumetric flasks: various sizes,

6.1.7. Microsyringes and syringes: various sizes, for standards preparation, sample injection, and extract dilution

6.1.8. Transferring pipettes: disposable

6.1.9. VOA vials

6.1.10. Carrier gas: Hydrogen

6.1.11. Make-up gas: Nitrogen

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Hexane: pesticide residue grade

7.2. Standards

7.2.1. The pesticides and PCB stock standards are purchased from chemical suppliers. Certificates of analysis are supplied with each standard.

7.2.2. Stock Standard Solution

7.2.2.1. All individual pesticides and PCBs are prepared in hexane. The solutions are stored per manufacturer's instruction. Stocks may be stored for one year, after which time they must be replaced.

7.2.3. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If vendor-supplied standard has an earlier expiration date then the vendor's expiration date is used. Refer to SOP NC-QA-017, Standards and Reagents, for additional information. The standard preparation information is detailed in the LIMS standards and reagents module.

7.2.4. Working Standards

7.2.4.1. A series of at least three working standards is prepared in hexane at concentrations that cover the linear range of the instrument. The lowest level must be at, or near, the method reporting limit. These solutions are stored at 4°C ± 2°C for up to six months. They are replaced sooner if comparisons with laboratory control samples indicate a problem.

7.2.5. A system evaluation mix PEM (performance evaluation mix) is prepared in hexane and contains the components shown in Table 3. This mix must be replaced after six months or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates.

7.3. Surrogate Standards

7.3.1. Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are the surrogate standards.

7.4. Internal Standard

7.4.1. The internal standard used for PCB analysis is 1-Bromo-2-nitrobenzene (BNB)

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Water samples are stored in glass containers with Teflon®-lined caps at 4°C ± 2° C until the time of extraction.

8.2. Sample extracts and dilutions are stored in test tubes and vials at 4°C ± 2°C until the time of analysis.

8.3. The holding time for pesticide samples is seven days from sampling to extraction. The holding time for PCB samples is one year from sampling to extraction (See MUR 2013 Table 2, Footnote 11). .

8.4. The holding time for sample extracts is 40 days.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, and MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest at or above the reporting limit.

9.2.2. Corrective Action for MBs

9.2.2.1. If the analyte level in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, or the sample result is greater than 10 times the MB result, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical

procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Corrective Action for LCS

9.3.2.1. If an analyte of interest is outside established control limits the system is out of control and corrective action must occur.

9.3.2.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the analyte(s) of interest, the batch is acceptable. **This must be addressed in the project narrative**

9.3.2.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike (MS)

9.4.1. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. Some client specific data quality objectives (DQO's) may require the use of an un-spiked sample duplicate in place of or in addition to an MS. The MS results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS analysis.

9.4.2. An MS sample will be extracted for every ten samples.

9.4.3. Corrective Action for MS

9.4.3.1. If the analyte recovery falls outside of the acceptance range, the results should be evaluated to determine the cause of the error.

9.4.3.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability. Re-preparation and / or re-analysis may be necessary.

9.4.3.3. If matrix interference is suspected, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.4.3.4. If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data is reported and flagged with a "4" in the LIMS.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Each sample, blank, and QC Sample (LCS, MS, and MSD) is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.5.3. -. The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination.

9.5.4. The LCS must have acceptable surrogate recoveries. If the surrogate recoveries are not acceptable, the data must be evaluated to determine if the LCS has served the purpose of demonstrating the effectiveness of the extraction process.

9.5.5. Corrective action for surrogate recoveries that are not acceptable in the samples (except for dilutions greater than 5X):

9.5.5.1. Check all calculations to ensure that no errors were made; check internal standard (if applicable) and surrogate spiking solution for degradation, contamination, etc.; also check instrument performance.

9.5.5.2. If the above step fails to reveal a problem, re-analyze samples. If re-analysis does not confirm original results and is within QC acceptance criteria, then the problem was within the analyst's control and only the re-analyzed data should be reported.

9.5.5.3. If the surrogates are out of control for the sample and MS/MSD, then matrix effect has been demonstrated for that sample and no further corrective action is necessary.

9.5.5.3.1. Corrective action, which may include re-extraction and re-analysis is necessary if DCB and TCMX are both outside of acceptance limits or if recovery is less than 10% for either surrogate.

9.6. Internal Standard (IS)

9.6.1. This procedure is an IS procedure. 1-Bromo-2-nitrobenzene (BNB) is the internal standard used.

9.6.2. Prior to analysis, IS must be added to all standards, field samples, and QC samples. The concentration of the IS must be the same in all calibration samples, field samples and QC samples. A concentration of 0.05 ug/mL is used.

9.6.3. The response of the IS in the CCV must be within 50-200% of the response of the IS in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the IS response will require recalibration.

9.6.4. The response of the IS in the samples and batch QC items must be within 50-200% of the response of the previous CCV. If the response is outside of the range, corrective action must be taken which can include re-analysis of the extract, re-spiking the extract with IS and re-analysis, or re-calibration of the analytical system. Obvious matrix interferences are qualified and noted in an NCM.

9.7. Control Limits

9.7.1. Laboratory control limits are method specified. Control limits are easily accessible via the LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006

9.8.2. MDLs are easily accessible via the LIMs.

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. If the injection port or front of the column is dirty, 4,4'-DDT and endrin are easily degraded in the injection port. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting an appropriate volume of the PEM. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 15% replace the glass injection insert with a cleaned and deactivated insert. If this procedure fails to eliminate degradation problem, clip off up to one foot of the injection port side of the column. Calculate the percent breakdown as follows:

$$\%Breakdown\ from\ 4,4'\text{-}DDT = \frac{Total\ DDT\ Degradation\ Peak\ Area\ (DDE + DDD)}{Total\ DDT\ Peak\ Area\ (DDT + DDE + DDD)} \times 100$$

$$\%Breakdown\ (Endrin) = \frac{Total\ Endrin\ Degradation\ Peak\ Area\ (Endrin\ Aldehyde + Endrin\ Ketone)}{Total\ Endrin\ Peak\ Area\ (Endrin + Endrin\ Aldehyde + Endrin\ Ketone)} \times 100$$

10.1.2. The initial calibration block for PCB must include at least one level with 1016 analyzed separately for pattern recognition purposes. This run does not have to be part of the calibration.

10.1.3. Analyze calibration standards at a minimum of three concentration levels utilizing the GC conditions in Section 11.5. One of the standards is analyzed at, or near, the concentration which corresponds to the detection limit.

10.1.4. Each calibration standard is injected into the GC with the same technique used to inject the samples (i.e., autosampler injection, manual injection).

10.1.5. Calculations for the different calibration fits can be found in section 12.

10.1.6. If the %RSD is less than 10% over the working range linearity through the origin can be assumed and the average calibration factor may be used in place of a calibration curve.

10.1.7. Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted. Removal of points for individual analytes from levels other than the highest and lowest is not permitted.

10.1.8. Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

10.1.9. Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method

10.2. Continuing Calibration

10.2.1. Mid-level standards are used for the calibration verifications.

10.2.2. Evaluate the resolution requirements. For PCB the minimum resolution requirement for the triplet towards the end of the 1260 chromatogram is 25% on

one of the two columns used. For Pesticide all single component analytes must be 80% resolved.

10.2.3. For external calibration models, the calibration mid-point working standard solution is analyzed at the beginning of the run. Samples quantitated by external standard should be bracketed by calibration verification standards that meet the criteria listed in section 10.2.6.1. Bracketing CCVs are not required for internal standard calibrations.

10.2.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.2.5. If highly contaminated samples are expected, it is acceptable to analyze solvent blanks or primers at any point in the run.

10.2.6. The continuing calibration CF (calibration factor) or RF (response factor) for each pesticide and PCB is calculated using the equation in Section 12.

10.2.6.1. CFs and RFs for all analytes in the continuing calibration on the primary or quantitation column can vary by no more than ± 15%. If these conditions are not met corrective action must be taken. This may include clipping the column, changing the liner, or other minor instrument adjustments, followed by re-analyzing the standard. If the overall average percent drift still varies by more than ± 15% a new calibration curve may be prepared.

10.2.7. Corrective Action for Samples

10.2.7.1. Any samples injected after the standard exceeding the continuing calibration criteria (for external calibration, samples before and after) must be re-injected unless the CCV fails high and the samples are non-detect. The ND samples may be reported with proper narration.

10.2.7.2. The only exception is that if the CCV recoveries are biased high and the associated sample is ND for the compound(s) of interest, the batch is acceptable. This must be addressed in the project narrative.

10.3. Retention Time Windows

10.3.1. Retention time (RT) windows must be determined for all analytes.

10.3.2. Initial determination of Retention time windows

10.3.2.1. The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV in the daily analytical sequence, whichever is more recent.

10.3.2.2. Evaluate the deviation from expected retention time for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours.

10.3.2.3. If three days of analytical data are not available, use a default RT window of 0.01 minutes. At the end of the batch evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.

10.3.2.4. Multiply the standard deviation by 3. This is the retention time window, unless the result is less than 0.01 min, in which case the window is set at 0.01 min.

10.3.2.5. An alternative method to determine the retention time window is to multiply the maximum deviation of all points by 1.5. The minimum retention time window is 0.01 minutes. For example, if the maximum RT deviation for a specific analyte is 0.008 min, then the RT window is set at +/- 0.012 min.

Note: For the multi-component analytes, for example Aroclors, Toxaphene and Technical Chlordane, the maximum deviation must be evaluated for each of the 3 to 6 major peaks used for sample calculations.

10.3.2.6. If the retention time windows for analytes of interest overlap, the analyte must be confirmed on a dissimilar column.

10.3.3. Ongoing evaluation of retention time windows

10.3.3.1. Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV of the day and verified every 12 hours. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the retention time window (except as discussed below).

10.3.3.2. Matrix spike analytes may fall outside the retention time window if there is a large non-target peak coeluting with the analyte in the matrix spike.

10.3.3.3. If any analytes fall outside the retention time window in CCVs, LCS or matrix spikes (except as discussed above for matrix spikes) then the RT windows for those analytes shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

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10.3.3.4. Retention time windows should be reliably narrower than +/- 0.03 min. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Refer to the Organic Preparation SOPs NC-OP-037 and NC-OP-038.

11.4. Sample Analysis

11.4.1. The sample extract may be screened to determine if the level of the pesticides or PCBs exceed the working range of the calibration curve, an appropriate dilution is performed to maintain a level within the initial calibration curve.

11.5. Recommended Instrument Conditions (may vary by instrument and column used)

11.5.1. Hydrogen carrier gas flow rate: 5 - 6 mL/minute

11.5.2. Nitrogen make-up gas flow rate: 30 - 35 mL/minute

11.5.3. GC Conditions – refer to Table 2 for Recommended Instrument Conditions

11.5.4. Two columns of dissimilar phase are required (see Section 6.1.3 for column selection).

11.5.5. Injection volume: 1μL or 2μL

11.5.6. For samples analyzed by IS calibration models, transfer 100 uL of the extract to an autosampler vial and add 5 uL of the IS solution or equivalent volumes to give an IS concentration of 0.05 ug/mL. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples.

11.5.7. For samples analyzed by external calibration models, transfer an adequate amount of extract into an autosampler vial and load the vials onto the instrument.

11.5.8. The sample extract must be injected using the same injection volume used for the calibration standards.

11.6. Identification

11.6.1. Compare the samples chromatographic peak retention times to the retention time windows established for the analyte of interest. For multi-response analytes, rely primarily on pattern recognition.

11.6.2. If the retention time for an unknown peak yields a positive match on the primary column, then the secondary or confirmation column must also yield a positive match.

11.6.3. If a positive match is not established on both columns, then no pesticides or PCBs of interest are confirmed in the sample.

11.7. Dual Column Quantitation of Pesticides and PCBs

11.7.1. Reference the current version of Corporate Policy CA=Q-P-004 Reporting Results for Methods that Require Dual-Column confirmation when performing Pesticide and PCB analysis.

11.7.2. The primary column approach is utilized for Pesticides and PCB analysis unless the RPD between columns is greater than 40%. When the RPD between columns is greater than 40%, this may be evidence of chromatographic interference on the higher value. The lower result may be most appropriate in this case. Analyst professional judgment must weigh heavily in the decision of which column to report.

11.7.3. For PCBs, use 3-10 major peaks or total area for quantitation

11.7.4. If the analyst believes that a combination of Aroclors is present due to weathering or other environmental processes, then only the predominant Aroclor is quantitated and reported; but the suspicion of multiple Aroclors is discussed in the narrative. If well-separated Aroclor patterns are present, then multiple Aroclors may be quantitated and reported.

11.7.5. Every sample undergoes dual column analysis, however, reporting the second column results will only be performed when requested by the client or regulatory program. The appearance of the multiple characteristic peaks in the sample usually serves as a confirmation of Aroclor presence.

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11.8. Multi-response Analytes

11.8.1. Retention time windows are also used for identification of multi-component analytes, but the “fingerprint” produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time RT windows of the standard, if in the analyst’s judgment the fingerprint (retention time RT and peak ratios) resembles the standard chromatogram.

11.9. Quantitation of Multi-Response Analytes

11.9.1. Select 3-10 major peaks from the analyte pattern. Calculate the response of each of the 3-10 peaks per multi-response analyte, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result.It is appropriate to remove peaks that appear to be co-eluting with contaminant peaks from the quantitation. (i.e., peaks which are significantly larger than would be expected from the rest of the pattern.).

11.9.2. If there are no interfereing peaks within the RT window of the multi-response analyte, the total area of the standards and samples may be used for quantitation. Any surrogate of extraneous peaks within the RT window must be subtracted from the total area.

11.10. Identification of Aroclors

11.10.1. Retention time windows are used for identification of Aroclors, but the “fingerprint” produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

11.10.2. A clearly identifiable Aroclor pattern serves as confirmation of single column GC analysis. Dual column confirmation may be used for specific program requirements or by client request.

11.11. Analytical Documentation

11.11.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.11.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.11.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.11.4. Record all sample results and associated QC directly into the LIMS during analysis. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calibration Factor (CF) for external calibration and Response Factor (RF) internal standard calibration

$$CF = \frac{A_s}{M_s}$$

Where A_s = Peak area (or height) in standard

M_s = Total mass of standard injected

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where: A_x = Peak Area (or height) of the analyte or surrogate

A_{is} = Peak Area (or height) of the internal standard

C_x = Concentration of the analyte or surrogate (µg/L)
C_{is} = Concentration of the internal standard (µg/L)

12.1.2. Evaluating the linearity of the initial calibration using an Average Calibration fit:

Mean CF = $\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$ (external calibration)

Mean RF = $\overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$ (internal standard calibration)

Where n = the number of calibration standards

Standard Deviation (SD) = $\sqrt{\frac{\sum_{i=1}^{n} (CF_i - \overline{CF})^2}{n-1}}$ (external calibration)

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}}$$ (internal standard calibration)

Where n = the number of calibration standards

$$\%RSD = \frac{SD}{\overline{CF}} \times 100$$ (external)

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$ (internal standard)

Note: If the RSD of the calibration or response factors is less than or equal to 20%, the average calibration or response factor may be used to determine sample concentrations.

12.1.3. Percent Difference (%D)

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where CF_c = The calibration factor from the CCV or ICV

$\overline{CF}$ = The average calibration factors from the initial calibration

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

Where RF_c = The response factor from the CCV or ICV

$\overline{RF}$ = The average response factors from the initial calibration

12.2. Linear and weighted linear regressions

y = ax + b

or for weighted linear:

$$y = \frac{1}{SD^2} \times (ax + b)$$

Where y = Instrument response

a = Slope of the line

x = Concentration of the calibration standard

b = The intercept

SD = Standard deviation from 12.1.2

12.2.1. For internal standard the equation for weighted or non-weighted linear regression is:

$$C_s = \frac{\left(\frac{A_s C_{is}}{A_{is}} - b\right)}{a}$$

Where A_s = Area (or height) of the peak for the target analyte in the sample

A_{is} = Area (or height) of the peak for the internal standard

C_s = Concentration of the target analyte in the calibration standard

C_{is} = Concentration of the internal standard

a = Slope of the line

b = The intercept

12.2.2. Correlation Coefficient

$$r = \frac{\sum d_x d_y}{\sqrt{\sum d_x^2 \sum d_y^2}}$$

Where:

d_x = deviation of x from the mean

d_y = deviation of y from the mean

12.2.3. Relative Standard Error (%RSE)

$$\%\,RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where: N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_I = True concentration for level i
PC_i = Predicted concentration for level i

12.2.4. Percent Drift for CCV and ICV

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3. Quadratic calibration fit (only to be used if applicable)

$y = ax^2 + bx + c$

Where: y = Response

x = Concentration

a = Slope

b = Intercept

c = Curvature

12.3.1. Coefficient of Determination (COD)

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2}$$

Where: y_{obs} = Observed response (area) for each concentration from each initial calibration standard

$\bar{y}$ = Mean observed response from the initial calibration

y_i = Calculated response at each concentration from the initial calibration

n = Total number of calibration points

p = Number of adjustable parameters in the polynomial equation (2 for second order polynomial)

12.4. Concentration

12.4.1. Aqueous

$$\text{Concentration, ug/L} = \frac{C_{ex} V_t}{V_o}$$

Where C_{ex} = Concentration in ng on column

V_t = Volume of total extract in uL

V_o = Volume of water extracted in mL

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Vials containing sample extracts: These vials are placed in waste containers located in the GC/MS laboratory and identified as "PCB Vial Waste".

15.2.1.2. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste. Solid PCB waste is placed in containers labeled "PCB Solids Waste". Liquid PCB waste is placed in containers labeled "PCB Liquids Waste". PCB vials are place in containers labeled "PCB Vial Waste". PCB containing samples are located through a LIMS query and disposed of as PCB containing.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

16.1.2. Method Update Rule 40CFR136 Table 2, 2013

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Revision History

Historical File:		Revision 0: 09/18/95		Revision 5: 05/25/11
		Revision 1: 06/12/03		Revision 6: 08/06/14
		Revision 2: 11/15/04		Revision 7: 02/19/16
		Revision 3: 02/27/07		
		Revision 4: 03/27/09		

16.2. Associated SOPs and Policies, current version

16.2.1. Continuous Liquid/Liquid Extraction of Organic Compounds from Waters Based on Method SW846 3520C and 600 Series and Waste Dilution Based on Method 3580A, NC-OP-037

16.2.2. Separatory Funnel Extraction of Organic Compounds from Waters Based on Method SW846 3510C and 600 Series and Waste Dilution Based on Method 3580A, NC-OP-038

16.2.3. QA Policy, QA-003

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. Cleanup Procedure for Organic Extractable Samples, NC-OP-025

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. See Table 4

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method deviations

17.2.1. Method 608 calls for the standards to be made in Iso-octane. The laboratory makes their standards in Hexane.

17.2.2. Method 608 specifies that stock standards should be kept for 6 months or less. The laboratory keeps the stock standards for one year.

17.2.3. Vials with Teflon® lined caps are not used. The laboratory uses vials that are clear and the caps are not Teflon® lined.

17.2.4. Method 608 does not include wording for performing Sulfuric Acid and TBA cleanups prior to sample analysis. In order to minimize interferences from various matrices, the laboratory will utilize sulfuric acid and/or TBA cleanups as needed.

17.2.5. A rinse/equipment blank is analyzed at the beginning of the analytical sequence to demonstrate cleanliness of the analytical system.

17.2.6. The calculated concentration of each peak of a multi-response analyte is averaged to determine the final concentration instead of calculating the concentration based upon the sum of the areas of all the peaks.

17.2.7. Method 608 only refers to the use of Average calibration models. The laboratory also utilizes Linear and Quadratic as needed.

17.3. Tables

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Table 1: Calibration Levels ng/mL

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB						
Aldrin	5	10	25	50	100	200
ɣ-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Heptachlor Epoxide ***	5	10	25	50	100	200
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
Multi-Component Standards						
Chlordane (Technical)	20	50	100	200	500	
Toxaphene	200	500	1000	2000	5000	
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200
Aroclor 1016/1260	50	100	200	500	1000	2000
Aroclor 1242	50	100	200	500	1000	2000
Aroclor 1221/1254	50	100	200	500	1000	2000
Aroclor 1232	50	100	200	500	1000	2000
Aroclor 1248	50	100	200	500	1000	2000

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Table 2: Suggested Instrument Conditions

Parameter	Recommended Conditions
Injection port temp	225°C
Detector temp	300°C
Temperature program	110°C for 1 min, 12°C/min to 220 °C to 290 °C, 2 min hold
Column 1	RTX-CLPesticides 30m x 0.53mm id, 0.5µm
Column 2	RTX-CLPesticides II 30m x 0.53mm id, 0.25µm
Injection	1 or 2 µL
Carrier gas	Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table 3: Performance Evaluation Mix

Compound
4,4'DDT
Endrin
TCMX (Surrogate)*
DCB (Surrogate)*

**Both surrogates are in the PEM, but only 4,4'DDT and Endrin are evaluated for breakdown.*

Table 4: Reporting Limits

Common Name	Reporting Limits, µg/L
Aldrin	0.05
α-BHC	0.05
β-BHC	0.05
δ-BHC	0.05
γ-BHC (Lindane)	0.05
Chlordane (technical)	0.5
4,4'-DDD	0.05
4,4'-DDE	0.05
4,4'-DDT	0.05
Dieldrin	0.05
Endosulfan I	0.05
Endosulfan II	0.05
Endosulfan Sulfate	0.05
Endrin	0.05
Endrin Aldehyde	0.05
Heptachlor	0.05
Heptachlor Epoxide	0.05
Toxaphene	2.0
Aroclor-1016	0.1
Aroclor-1221	0.1
Aroclor-1232	0.1
Aroclor 1242	0.1
Aroclor-1248	0.1
Aroclor-1254	0.1
Aroclor-1260	0.1

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Title: GAS CHROMATOGRAPHIC ANALYSIS of PCBs BASED ON METHODS 8082 and 8082A

Approvals (Signature/Date):

Technology Specialist	04/17/18 Date	Health & Safety Coordinator	04/06/18 Date
Quality Assurance Manager	04/17/18 Date	Technical Director	04/06/18 Date

This SOP was formerly known as NC-GC-045 Rev. 1, dated 1/14/16

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1. SCOPE AND APPLICATION

1.1. This SOP describes procedures to be used when SW-846 Method 8082 or 8082A are applied to the analysis of polychlorinated biphenyls (PCB) as Aroclors by GC/ECD. This SOP is applicable to extracts derived from any matrices which are prepared according to the appropriate sample extraction SOPs. PCBs are determined and quantitated as Aroclor mixes.

1.2. Table 1 lists compounds routinely determined by this method and the CAS Number. RLs are easily accessible via the Laboratory Information Management System (LIMS). Matrix interferences and/or high concentrations of PCB compounds may result in higher RLs.

2. SUMMARY OF METHOD

2.1. PCBs in aqueous samples are prepared for analysis using continuous liquid/liquid or separatory funnel extraction (SOP NC-OP-037 and NC-OP-038). Solid samples are prepared using sonication or soxhlet extraction (SOP NC-OP-039 and NC-OP-040). After the initial preparation step, the sample is introduced into the GC and the concentration of each target analyte is measured by the detector response within a defined retention time (RT) window, relative to the response of the reference standards.

3. DEFINITIONS

3.1. Refer to the Test America Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

4.1. Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. All glassware is cleaned per SOP NC-QA-014.

4.2. Interferences in the GC analysis can arise from many compounds which are amenable to gas chromatography and give a measurable response on the electron capture detector (ECD). Phthalate esters, which are common contaminants found in plastics, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.

4.3. Compounds extracted from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD) will cause interference. A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

4.4. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-025.

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4.5. Interferences co-extracted from samples will vary considerably. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts. These cleanup procedures are included in SOP NC-OP-025.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document. Eye protection that prevents splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Refer to the TestAmerica Canton Corporate Environmental Health and Safety Manual for a complete description of personal protection equipment.

5.2. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately. Nitrile gloves provide adequate protection against the solvents used in this method.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Note: Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.5. All ^{63}Ni sources (ECD) must be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.6. All ^{63}Ni sources must be inventoried every six months. If a detector is missing, the EH&S Director must be immediately notified and a letter sent to the NRC or local state agency.

5.7. Exposure to chemicals must be limited as much as reasonably achievable. All samples with stickers that read "Caution/Use Hood!" must be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.8. Opened containers of neat standards must be handled in a fume hood.

5.9. Sample extracts and standards, which are in a flammable solvent, must be stored in an explosion-proof refrigerator.

5.10. When using hydrogen gas as a carrier, all precautions listed in the CSM must be observed.

5.11. Standard preparation and dilution must be performed inside an operating fume hood.

5.12. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.13. There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.14. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph (GC) equipped with Electron Capture Detectors (ECDs)

6.2. Software: ChemStation or equivalent

6.3. Refer to Table 2 for analytical columns and run conditions

6.4. Microsyringes and syringes: various sizes, for standards preparation, sample injection, and extract dilution

6.5. Autosampler vials, inserts, and caps

6.6. Class A volumetric flasks: various sizes

6.7. Transfer pipettes: disposable

6.8. VOA vials

6.9. Carrier gas: Hydrogen

6.10. Makeup gas: Nitrogen

7. REAGENTS AND STANDARDS

7.1. Stock Standards: Stock standards are purchased as certified solutions or prepared from pure solutions.

7.1.1. Other stock standard solutions are stored as recommended by the manufacturer. All stock standards must be protected from light. Stock standard solutions must be brought to room temperature before using.

7.1.2. Stock standard solutions must be replaced after one year.

7.1.3. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If vendor-supplied standard has an earlier expiration date then the vendor's expiration date is used. Refer to SOP NC-QA-017, Standards and Reagents, for additional information. The standard preparation information is detailed in the LIMS standards and reagents module.

7.2. Calibration Standards

7.2.1. PCB Calibration Standards

7.2.1.1. PCB calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method. PCB calibration solutions must be refrigerated at 4° C ± 2° C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.2.1.2. See the LIMS Reagent module for details on standard concentration and preparation.

7.3. Surrogate Standards

7.3.1. Tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) are the surrogate standards. Refer to the LIMS for details of surrogate standards.

7.4. Internal Standard

7.4.1. The internal standard used for PCB analysis is 1-Bromo-2-nitrobenzene (BNB)

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Unless otherwise specified by regulatory or client programs, holding time for PCB samples (regardless of matrix) is 1 year.

8.2. Sample extracts are stored at 4 ± 2°C. The holding time for PCB sample extracts is 40

days.

9. QUALITY CONTROL

9.1. Batch definition

9.1.1. The batch is a set of up to 20 samples of the same matrix processed at the same time using the same procedures and reagents. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). Laboratory generated QC samples (Method Blank, LCS and MS/MSD do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with an MS and an un-spiked sample duplicate (DU).

9.2. Method Blank (MB)

9.2.1. For each batch of samples, analyze an MB. The MB consists of reagent water for aqueous PCB samples and sodium sulfate for PCB soils tests and all surrogates required for the analysis. Refer to SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040 for details.

9.2.2. The MB must not contain any analyte of interest at, or above, the reporting limit or at, or above, 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

Note: Some programs require that the MB be clean to ½ the RL. Method notes should inform the analyst if the samples are part of a special program. Analysts are responsible for checking the program requirements.

9.2.3. Corrective action

9.2.3.1. Corrective action may include re-analysis of the MB. If the re-analysis fails to meet criteria, re-extraction and re-analysis of samples associated with an unacceptable MB is required when concentrations greater than the RL are detected in the samples.

9.2.3.2. If there is no target analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers.

Note: For Ohio VAP projects, the MB result must be below the reporting limit or samples must be re-extracted, unless the samples have no detections above the RL.

9.3. Laboratory Control Samples (LCS)

9.3.1. For each batch of samples, analyze an LCS. The LCS contains a representative subset of the analytes of interest and all surrogates required for the analysis. The LCS standard contains the same analytes as the matrix

spike. If any LCS analyte is outside the laboratory established historical control limits, corrective action must occur.

9.3.2. Corrective Action

9.3.2.1. Corrective action may include re-analysis of the LCS. If the re-analysis fails to meet criteria, re-extraction and re-analysis of the batch may be needed. If the LCS is biased high, samples that have no analytes detectable above the RL may be reported with proper narration.

Note: For Ohio VAP samples, re-analyze an aliquot of the LCS to verify the outlier; if the LCS exhibits the same anomaly upon re-analysis, the sample batch must be re-extracted and re-analyzed. The exceptions are as follows: (a) insufficient sample for re-extraction, (b) expired holding times, or (c) the LCS is biased high and the samples have no detections above the RL for those analytes. Under the above circumstances, results may be reported with proper narration.

9.3.3. LCS compound lists and surrogates are included in the reagent module of the LIMS.

9.4. Matrix Spikes/Spike Duplicates (MS/MSD)

9.4.1. For each QC batch, analyze an MS/MSD. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory-specific historically generated limits.

9.4.2. If any individual recovery or RPD falls outside the acceptable range, corrective action must occur unless samples for this compound are ND. The initial corrective action must be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, adverse matrix effect is indicated, the laboratory operation is in control and analysis may proceed.

9.4.3. If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the laboratory process is out of control and corrective action must be taken.

9.4.4. The MS/MSD must be analyzed at the same dilution as the un-spiked sample, unless the matrix spike components would then be above the calibration range.

9.5. Surrogates

9.5.1. Surrogates are added to all samples, and batch QC during the preparation procedure. Surrogates are added to instrument QC for the 1016/1260 Aroclor mix, which includes the calibration standards, and the CCVs. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits.

9.5.2. Method Blank

9.5.2.1. Surrogates are added to the MB and the MB is carried through the entire analytical procedure. The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the MB and affected samples will normally be required. If surrogate recoveries are high, and the samples are non-detect, the data may be reported with proper narration.

Note: For Ohio VAP samples, all MB surrogates must meet criteria or the samples must be re-extracted if sufficient volume of sample remains. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the surrogates are biased high and the samples have no detections above the RL.

9.5.3. LCS

9.5.3.1. The LCS must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the LCS has served the purpose of demonstrating effectiveness of the extraction process. If surrogate recoveries are low, re-extraction of the LCS and affected samples will normally be required. None of the surrogate recoveries can fall below 10% in the LCS. If surrogate recoveries are high, and the samples have no detections above the RL, the data may be reported with proper narration.

Note: For Ohio VAP samples, all LCS surrogates must meet criteria or the samples must be re-extracted if sufficient volume of sample remains. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the surrogates are biased high and the samples have no detections above the RL.

9.5.4. Instrument QC

9.5.4.1. Surrogates in the 1016/1260 calibration standards must meet the same criteria as the ICAL. See section 10 for ICAL criteria.

9.5.4.2. Surrogates in the CCVs must have a %D of <15% for Method 8082, and <20% for Method 8082A.

9.5.4.3. Corrective actions for failing surrogates in the instrument QC are discussed in section 10.

9.5.5. Samples

9.5.5.1. If either surrogate is outside limits, the following corrective actions must take place (except for dilutions greater than 5X):

9.5.5.1.1. Check all calculations for error.

9.5.5.1.2. Ensure instrument performance is acceptable.

9.5.5.1.3. Recalculate the data and/or re-analyze the extract if either of the above checks reveals a problem.

9.5.5.2. It is only necessary to re-prepare / re-analyze a sample once to demonstrate poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

Note: For Ohio VAP Projects, all surrogates must meet criteria unless the surrogates are out high and the samples have no detections above the RL. Otherwise, the analyst should re-analyze the sample, re-prep and re-analyze the sample, or a dilution may be performed if the analyst believes it will solve the issue. When there is an obvious interference causing the surrogate outlier that the analyst knows a corrective action would not resolve, it is permissible to flag the data with a qualifier indicating matrix interference.

9.5.5.3. If the surrogates are out of control for the sample and MS/MSD, then matrix effect has been demonstrated for that sample and re-preparation is not necessary. If the sample is out of control and the MS/MSD is in control, then re-preparation or flagging of the data is required. Re-preparation includes the parent sample and the MS/MSD.

9.5.6. Refer to TestAmerica Canton QC Program document (Policy QA-003) for further details of the corrective actions.

9.6. Internal Standard (IS)

9.6.1. This procedure is an IS procedure. 1-Bromo-2-nitrobenzene (BNB) is the internal standard used.

9.6.2. Prior to analysis, the IS must be added to all standards, field sample extracts, and QC sample extracts. The concentration of the IS must be the same in all calibration standards, field sample extracts, and QC sample extracts. A concentration of 0.05 ug/mL is used.

9.6.3. The response of the IS in the ICV/CCV must be within 50-200% of the response of the IS in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the ICV/CCV must be repeated and any samples associated with the ICV/CCV must also be re-analyzed. Repeated failure of the IS response will require recalibration.

9.6.4. The response of the IS in the samples and batch QC items must be within 50-200% of the response of the previous CCV. If the response is outside of the range, corrective action must be taken which may include re-analysis of the extract, re-spiking the extract with IS and re-analysis, or re-calibration of the analytical system. Obvious matrix interferences are qualified and noted in an NCM.

Note: OVAP samples with failing internal standards must be re-analyzed unless matrix interference is apparent. In cases where matrix interference is not obvious, spike a fresh aliquot of sample with IS solution and re-analyze. If the IS fails to meet criteria again, and the IS meets criteria in batch and instrument QC, the re-analysis serves to confirm matrix interference and the sample will be re-analyzed at a dilution as described below. If matrix interference is apparent, dilute the sample with hexane for re-analysis. When, in the analyst's professional judgment, there is obvious interference causing the IS failure that corrective action will not remedy, data must be flagged with a qualifier to indicate the effect of matrix interference. If the batch QC (MB and/or LCS) has failing internal standards, re-spike a fresh aliquot of the applicable QC sample with internal standard solution and re-analyze. If there is continuing failure, the batch may require re-preparation of the IS solution, and/or recalibration. If the ICV and/or CCV have failing internal standards, the batch must be re-analyzed. Continued failure may necessitate re-preparation of the IS solution and/or recalibration.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

10. CALIBRATION AND STANDARDIZATION

10.1. Internal or external calibration may be used. Prepare standards containing each analyte of interest at a minimum of five concentration levels. The low-level standard must be at, or below, the reporting limit. The other standards define the working range of the detector.

10.2. The initial PCB calibration must include at least one level with 1016 analyzed separately for pattern recognition purposes. This run does not have to be part of the calibration.

10.3. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance, unless CCV criteria cannot be met.

10.4. With the exception of section 10.5 below, it is not acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or

lowest on the curve and the reporting limit and/or linear range is adjusted accordingly. In any event, at least five points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points.

Note: Quadratic calibrations are not acceptable for PCB analysis for OVAP projects.

10.5. A level may be removed from the calibration if the reason can be clearly documented (for example, a broken vial or no purge run). A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be re-analyzed and the re-analysis used for the calibration. All initial calibration points in a single calibration curve must be analyzed without any changes to instrument conditions, and all points in a single calibration curve must be analyzed within 24 hours.

10.6. Internal Standard Calibration

10.6.1. Internal standard calibration involves the comparison of instrument responses from the target compounds in the sample extract to the response of a specific standard added to the r sample extract prior to injection. This specific standard is referred to as the internal standard (IS) because it is contained within the aliquot of the sample extract and is actually injected into the instrumentation. The ratio of the peak area (or height) of the target compound in the sample extract to peak area (or height) of the IS in the sample extract is compared to a similar ratio derived for each calibration standard. The ratio is termed the response factor (RF), or relative response factor (RRF).

10.6.2. When preparing calibration standards for use with internal standard calibration, add the same amount of internal standard solution to each calibration standard, such that the concentration of each internal standard is constant across all of the calibration standards, whereas the concentrations of the target analytes will vary. The mass of the internal standard added to each sample extract immediately prior to injection into the instrument must be the same as the mass of the internal standard in each calibration standard. The volume of the solution spiked into sample extracts should be such that minimal dilution of the extract occurs.

10.6.3. Prepare calibration standards at a minimum of five concentration levels for each parameter of interest and each surrogate. Six standards must be used for a quadratic least squares calibration. Add the appropriate amount of the IS mixture to result in a 0.05 ug/mL concentration. The low standard must be at or below the reporting limit

10.6.4. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound and surrogate using the equations in Section 12.

10.7. External standard calibration

10.7.1. Quantitation by the external standard method assumes a proportional relationship between the analyte or surrogate response and the concentration

that is the same in all of the calibration standards and the samples. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected is used to prepare a calibration curve.

10.8. Calibration Curve Fits

10.8.1. The calculations for all calibration curve fits are found in section 12.

10.8.2. Weighted linear regression, average calibration factor, non-weighted linear regression, or quadratic curves may be used to fit the data. - Average calibration factor is the preferred calibration model used for PCB.

10.9. Average calibration factor (CF) / response factor (RF)

10.9.1. The average CF (external calibration) or RF (internal standard) may be used if the average percent relative standard deviation (% RSD) of all the CFs / RFs taken together is $\leq$ 20%. The average % RSD is calculated by summing the %RSD value for each peak and dividing by the total number of peaks.

10.10. Linear Regression / Weighted Linear Regression

10.10.1. Linear / weighted linear regressions must have a minimum of 5 calibration levels with the lowest being at or below the reporting limit. The correlation coefficient (r) must be >0.990. The ICV %D must be <20%, and the CCV %D must be <15% for Method 8082. For Method 8082A, the criteria for both ICV and CCV are < 20% % D.

10.11. Quadratic Curve

10.11.1. A quadratic calibration curve must only be used if the analyst has reason to believe that a linear or average model does not fit the normal concentration-to-response behavior of the detector. A quadratic curve fit may be used only if the compounds have historically exhibited a non-linear response and cannot be used to extend the calibration range for compounds that normally exhibit a linear response, but within a narrower calibration range.

10.11.2. A quadratic calibration curve must have a minimum of 6 calibration levels with the lowest being at or below the reporting limit. The coefficient of determination (r^2) must be > 0.990.

10.12. Evaluation of Calibration Curves

10.12.1. The percent relative standard error (% RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.12.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level.

Note: When average calibration factors are used, %RSE is equivalent to %RSD.

10.13. The following requirements must be met for any calibration to be used.

10.13.1. Response must increase with increasing concentration.

10.13.2. If a curve is used, the calculated intercept of the curve at zero response must be less than ± the reporting limit for the analyte.

10.13.3. The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be ≤ 20%.

10.13.4. Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination (COD) may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (*r*) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on *r.* As a result, a curve may have a very good correlation coefficient (>0.990) while also having > 100% error at the low point.

Note: The surrogates must be judged against these same criteria.

10.14. Weighting of Data Points

10.14.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and must be used when an average calibration factor is not appropriate, as long as the data system has this capability.

10.15. Initial Calibration

10.15.1. A minimum five-point calibration of all Aroclors is generated. The low-level standard must be at or below the reporting limit. The other standards define the working range of the detector.

10.15.2. If any Aroclor is determined above the calibration range, the extract must be diluted and re-analyzed.

10.15.3. The surrogate calibration curve is included in the calibration from the Aroclor 1016/1260 mix.

10.16. Initial Calibration Verification (ICV)

10.16.1. The ICVs are analyzed immediately after an initial calibration. The acceptance criterion is ± 20%.

10.16.2. If the overall average percent drift of all analytes is greater than ±20%, corrective action must be taken. This may include clipping the column, changing the liner, or other minor instrument adjustments, followed by re-analyzing the standard. If the overall average percent drift still varies by more than ±20%, a new calibration curve may be required.

10.17. Continuing Calibration Verification (CCV)

10.17.1. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.17.2. Mid-level standards covering all Aroclors of interest are used for the calibration verifications.

10.17.3. CCVs are analyzed for all Aroclors at the beginning of each day, and at the beginning of each 12 hour shift.

10.17.4. Retention times windows are updated daily from the opening CCVs.

10.17.5. Evaluate the resolution of the triplet towards the end of the 1260 chromatogram in the opening CCV. There must be at least 25% resolution on one of the two columns used.

10.17.6. The Aroclor 1016/1260 CCV is analyzed after every 20 injections. Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.

Note: Various programs require a CCV every 10 injections. Analysts are responsible for checking the program requirements.

10.17.7. For Method 8082A, the CCV acceptance criterion is ± 20%. For Method 8082, the CCV acceptance criterion is ±15%.

10.17.8. A bracketing CCV is not required for IS calibrations.

10.17.9. Samples quantitated against an external standard calibration must be bracketed by a 1016/1260 CCV.

10.17.10. Corrective Actions for Continuing Calibration Failures

10.17.10.1. If a CCV fails to meet criteria, corrective action must be taken. This may include clipping the column, changing the liner, or other minor

instrument adjustments, followed by re-analyzing the standard. If the re-analysis still fails to meet criteria, a new calibration curve may be required.

10.17.10.2. Samples quantitated against an external standard calibration must be bracketed with passing CCVs. All samples analyzed immediately prior to, and immediately following the failing CCV must be re-analyzed.

10.17.10.3. Sample results that are below the reporting limit may be reported when a CCV is biased high. Such action must be addressed in the case narrative.

10.18. Retention Time Windows

10.18.1. Retention time (RT) windows must be determined for all analytes.

10.18.2. Initial determination of Retention time windows

10.18.2.1. The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV in the daily analytical sequence, whichever is more recent.

10.18.2.2. Evaluate the deviation from expected retention time for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours. Calculate the standard deviation of these retention times.

10.18.2.3. If three days of analytical data are not available, use a default RT window of 0.01 minutes. At the end of the batch evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.

10.18.2.4. Multiply the standard deviation by 3. This is the retention time window, unless the result is less than 0.01 min, in which case the window is set at 0.01 min.

10.18.2.5. An alternative method to determine the retention time window is to multiply the maximum deviation of all points by 1.5. The minimum retention time window is 0.01 minutes. For example, if the maximum RT deviation for a specific analyte is 0.008 min, then the RT window is set at ± 0.012 min.

Note: For multi-component analytes, like Aroclors, the maximum deviation must be evaluated for each of the 3 to 6 major peaks used for sample calculations.

10.18.2.6. If the retention time windows for analytes of interest overlap, the analyte must be confirmed on a dissimilar column.

10.18.3. Ongoing evaluation of retention time windows

10.18.3.1. Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV of the day and verified every 12 hours. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the retention time window (except as discussed below).

10.18.3.2. Matrix spike analytes may fall outside the retention time window if there is a large non-target peak coeluting with the analyte in the matrix spike.

10.18.3.3. If any analytes fall outside the retention time window in CCVs, LCS or matrix spikes (except as discussed above for matrix spikes) then the RT windows for those analytes shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

10.18.3.4. Retention time windows should be reliably narrower than +/- 0.03 min. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained.

11. PROCEDURE

11.1. Procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

Note: Procedural deviations are not allowed for Ohio VAP Projects.

11.2. Extraction

11.2.1. Extraction procedures are referenced in the SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040, current revisions.

11.3. Suggested gas chromatographic conditions are given in Table 2.

11.4. Allow extracts to warm to ambient temperature before injection.

11.5. Sample Analysis

11.5.1. For samples analyzed by IS calibration models, transfer 100 µL of the extract to an autosampler vial and add 5 µL of the IS solution or equivalent volumes to give an IS concentration of 0.05 ug/mL. The concentration of the internal standard must be the same in all calibration samples, field samples, and QC samples. -.

11.5.2. For samples analyzed by external calibration models, transfer an adequate amount of extract into an autosampler vial and load the vials onto the instrument.

11.5.3. The sample extract must be injected using the same injection volume used for the calibration standards.

11.5.4. If highly contaminated samples are expected, it is acceptable to analyze solvent blanks or primers at any point in the run. Solvent blanks may not be routinely analyzed prior to QC samples.

11.6. Identification of Aroclors

11.6.1. The laboratory performs Update IV's recommended analysis of DDT and analogs DDD and DDE daily to assure there is no interference with major 1254 peaks.

11.6.2. Retention time windows are used for the identification of Aroclor peaks, but the "fingerprint" produced by major peaks of those analytes in the standard is used to differentiate the identity of any Aroclor that may be present. The ratios of the areas of the major peaks are also taken into consideration. Analyst judgement must weigh heavily in the identification of Aroclor patterns. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

11.7. Quantitation of Aroclors

11.7.1. For PCB analysis, the preferred reporting approach is the primary column approach. Dependent upon client program, the higher or lower result may be used for quantitation. Results may be report from the confirmation column when matrix interference is present and impacts either the IS or specific compounds and the RPD between columns.

11.7.2. Use 3-5 major peaks for quantitation

11.7.3. If the analyst believes that a combination of Aroclor 1254 and 1260 or a combination of 1242, 1248 and 1232 is present, then only the predominant

Aroclor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well-separated Aroclor patterns are present, then multiple Aroclors may be quantitated and reported.

11.7.4. Every sample undergoes dual column analysis; however, reporting the second column results will only be performed when requested by the client or regulatory program. The appearance of the multiple characteristic peaks in the sample usually serves as a confirmation of the presence of an Aroclor.

11.8. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is necessary if either DCB or TCMX are outside of acceptance limits. Samples may be reported when there is obvious matrix interference present; however, such action must be included in the case narrative.

Note: For Ohio VAP samples all surrogates must meet acceptance limits, unless the surrogate is biased high and the sample has no detections above the RL.

11.9. Dilutions

11.9.1. Samples may be screened to determine the appropriate dilution for the initial run.

11.9.2. If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and re-analyzed.

11.9.3. Dilutions must target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range when allowed by sample matrix.

11.9.4. It may be necessary to dilute samples due to matrix. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination.

11.9.5. If the sample is run at a dilution and only minor matrix interferences are observed, then the sample should be re-analyzed at a more concentrated dilution in an attempt to target the upper half of the calibration range.

11.9.6. The most concentrated dilution with no target compounds above the calibration range should be reported. Other dilutions may be reported at client request if the lower dilutions will not cause detector saturation, column overload, or carryover. Analyst judgment and client site history will be factors in the reporting of multiple dilutions.

11.10. Interferences

11.10.1. If peak detection is prevented by interferences, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

11.11. Reporting of Data

11.11.1. The preferred reporting approach is the primary column approach, where the analyst evaluates the opening CCVs and designates a primary column to report data from. All data is reported from the primary column in an analytical run, as long as the RPD between columns is less than 40%.

11.11.2. When the RPD between the primary and confirmation column exceeds 40%, it is an indication of likely matrix interference. Every situation is different and the analyst must rely on their experience in choosing which data to report. Two common issues are addressed below:

11.11.2.1. When there is interference with an analyte of interest, the higher result is likely biased due to matrix; therefore, the lower result is reported.

11.11.2.2. When there is interference with the IS, the results on the entire column are biased; therefore, the column without interference in the IS may be the better result. Dilution and reanalysis may be required when there is interference with the IS.

11.12. Analytical Documentation

11.12.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.12.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

Note: When making new standards, it is required that all information entered into TALS is reviewed by another analyst.

11.12.3. Record sample and associated QC information in the LIMs. Level I and Level II technical reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration Calculations

12.1.1. Calibration Factor (CF) for external calibration and Response Factor (RF) internal standard calibration

$$CF = \frac{A_s}{C_s}$$

Where A_s = Peak area (or height) in standard

C_s = Concentration of standard injected

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where: A_x = Peak Area (or height) of the analyte or surrogate

A_{is} = Peak Area (or height) of the internal standard

C_x = Concentration of the analyte or surrogate (µg/L)

C_{is} = Concentration of the internal standard (µg/L)

12.1.2. Evaluating the linearity of the initial calibration using an Average Calibration fit:

$$Mean\ CF = \overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$ (external calibration)

$$Mean\ RF = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$ (internal standard calibration)

Where n = the number of calibration standards

$$Standard\ Deviation\ (SD) = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}}$$ (external calibration)

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}}$$ (internal standard calibration)

Where n = the number of calibration standards

$$\%RSD = \frac{SD}{\overline{CF}} \times 100$$ (external)

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$ (internal standard)

Note: If the RSD of the calibration or response factors is less than or equal to 20%, the average calibration or response factor may be used to determine sample concentrations.

12.1.3. Percent Difference (%D)

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where CF_c = The calibration factor from the CCV or ICV

$\overline{CF}$ = The average calibration factors from the initial calibration

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

Where RF_c = The response factor from the CCV or ICV

$\overline{RF}$ = The average response factors from the initial calibration

12.2. Linear regressions

y = ax + b

Where y = Instrument response (area or height)

a = Slope of the line

x = Concentration of the calibration standard

b = The intercept

12.2.1. For internal standard the equation for weighted or non-weighted linear regression is:

$$C_s = \frac{\left(\frac{A_s C_{is}}{A_{is}} - b\right)}{a}$$

Where A_s = Area (or height) of the peak for the target analyte in the sample

A_{is} = Area (or height) of the peak for the internal standard

C_s = Concentration of the target analyte in the calibration standard

C_{is} = Concentration of the internal standard

a = Slope of the line

b = The intercept

12.2.2. Correlation Coefficient

$$r = \frac{\sum d_x d_y}{\sqrt{\sum d_x^2 \sum d_y^2}}$$

Where:

d_x = deviation of x from the mean

d_y = deviation of y from the mean

12.2.3. Relative Standard Error (%RSE)

$$\%RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{n} \left[\frac{C_i - PC_i}{C_i}\right]^2}{(n-p)}}$$

Where: n = Number of points in the curve
p = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

12.2.4. Percent Drift for CCV and ICV

$$\%Drift = 100\% \times \frac{C_{actual} - C_{found}}{C_{actual}}$$

Where: C_{actaul} = Known concentration in standard

C_{found} = Measured concentration in CCV or ICV

12.2.5. Curve weighting may be beneficial for linear regressions. Curve weighting improves the linearity at the low end of the calibration curve. Weighted curve calculations are similar to the unweighted calculations above, but use 1/x or $1/x^2$ (where x = concentration) to determine the regression instead of the concentration.

12.3. Quadratic calibration fit (only to be used if applicable)

$y = ax^2 + bx + c$

Where: y = Response

x = Concentration

a = Curvature

b = Slope

c = Intercept

12.3.1. Coefficient of Determination (COD)

$$COD = r^2 = \frac{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2}$$

Where: y_{obs} = Observed response (area) for each concentration from each initial calibration standard

$\bar{y}$ = Mean observed response from the initial calibration

y_i = Calculated response at each concentration from the initial calibration

n = Total number of calibration points

p = Number of adjustable parameters in the polynomial equation (2 for second order polynomial)

12.4. Concentration

12.4.1. Aqueous

$$Concentration\ \left(\frac{\mu g}{L}\right)\frac{C_{ex}V_t}{V_o}$$

Where C_{ex} = On-column concentration as determined in sections 12.1-12.3. (ng/µL)

V_t = Final extract volume (µL)

V_o = Initial sample volume (mL)

12.4.2. Non-aqueous

$$Concentration\ \left(\frac{\mu g}{Kg}\right) = \frac{C_{ex}V_t}{W_s D}$$

Where C_{ex} = On-column concentration as determined in sections 12.1-12.3. (ng/µL)

V_t = Final extract volume (µL)

W_s = Initial sample mass (g)

D = (100-%moisture in sample) / 100 for dry weight basis

or

D = 1 for a wet weight basis

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOP CA-Q-S-006.

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure an analyst who has been properly trained in its use and has the required experience performs this procedure.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. Vials containing sample extracts. These vials are placed in the vial waste located in the GC/MS laboratory.

15.2.2. **Tubes containing sample extracts, for PCBs:** these are capped and placed in the PCB/flammable waste located the GC prep laboratory.

15.2.3. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste. PCB containing samples are located through a LIMS query and disposed of as PCB containing.

15.2.4. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane:** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.5. **Discarded samples:** These samples are collected in the solid debris drum.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, and Section 8000B

16.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.4. Corporate Quality Management Plan (CQMP), current versions

16.5. SW846, Update III, December 1996, Method 8082

16.6. SW846, Update IV, Revision 1, February 2007, Method 8082A

16.7. Reporting Results for Methods that Require Dual Column, CA-Q-P-004

16.8. Policy for Determining RT Windows for GC/ECD Tests, CA-T-P-005

16.9. Revision History

Historical File:				
Revision 0: 03/17/14				
Revision 1: 01/14/16				

16.10. Associated SOPs and Policies, current version

16.10.1. QA Policy, QA-003

16.10.2. Glassware Washing, NC-QA-014

16.10.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.10.4. Detection and Quantitation Limits, CA-Q-S-006

16.10.5. Standards and Reagents, NC-QA-017

16.10.6. Cleanup Procedures for Organic Extractable Samples, NC-OP-025

16.10.7. Acceptable Manual Integration Practices, CA-Q-S-002

16.10.8. Calibration Curves (General), CA-Q-S-005

16.10.9. Section of Calibration Points, CA-T-P-002

16.10.10. Continuous Liquid / Liquid Extraction of Organic Compounds from Waters Based on Methods SW846 3520C and 600 Series and Waste Dilution Based on Method 3580A, NC-OP-037

16.10.11. Separatory Funnel Extraction of Organic Compounds from Waters Based on Methods SW846 3510C and 600 Series and Waste Dilution Based on Method, NC-OP-038

16.10.12. Sonication Extraction of Organic Compounds from Soils Based on Method SW846 3550C and Waste Dilution Based on Method 3580A, NC-OP-039

16.10.13. Soxhlet (Traditional) Extraction of Organic Compounds from Soils Based on Method SW846 3540C and Waste Dilution Based on Method 3580A, NC-OP-040

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states the method blank must not contain any analyte of interest at, or above, the Method Detection Limit. This SOP states the Method

Blank must not contain any analyte of interest at, or above, the reporting limit.

17.1.2. The extended hold time for PCBs can be applied to 8082 as per SW846 Update IV. State requirements should be consulted as applicable.

17.2. Tables

Table 1	
Standard Analyte List and CAS Numbers	
Compound	**CAS #**
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

TABLE 2 **Suggested Instrumental Conditions for Methods 8082 and 8082A**	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	CLPesticide I, 30m, 0.53mm ID, 0.5µm
Column 2	CLPesticide II, 30m, 0.53 mm ID, 0.5µm
Injection	1-2 µL, -
Carrier gas	Hydrogen
Make up gas	Nitrogen
Y splitter	Glass, Restek or equivalent

Title: ACID DIGESTION FOR SOLID SAMPLES

[Method: SW846 Method 3050B]

Approvals (Signature/Date):

Technology Specialist	04/19/17 Date	Health & Safety Coordinator	04/18/17 Date
Quality Assurance Manager	07/17/17 Date	Technical Director	06/30/17 Date

This SOP was previously identified as SOP No. NC-IP-010, Rev 6, dated 3/3/16

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of soil samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICPMS) as specified in SW846 Method 3050B.

1.2. Samples prepared by the protocols detailed in this SOP may be analyzed by ICP or ICPMS for the elements listed in Table 1 (Appendix A). Other elements and matrices may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This method is not a total digestion, but will dissolve almost all metals that could become “environmentally available”. By design, metals bound in silicate structures are not dissolved by this procedure, as they are not usually mobile in the environment. This SOP can be applied to metals in solids, sludges, wastes, sediments, biological samples, and wipes.

1.4. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A representative 1 gram (wet weight) portion of sample is digested in nitric acid and hydrogen peroxide. The digestate is refluxed with hydrochloric acid for ICP and ICPMS analysis. The digestates are then filtered and diluted to 100 mL for subsequent analysis.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), latest version.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include metallic or metal-containing lab-ware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination, and take appropriate measures to minimize or avoid them. All glassware is cleaned per SOP NC-QA-014.

4.2. The entire work area, including the bench top and fume hood, must be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental

contamination. Refer to Appendix B for additional contamination control guidelines.

4.3. Boron from the glassware may leach into the sample solution during and following, sample processing. For critical low-level determinations of boron, only quartz and/or plastic lab-ware are recommended.

4.4. Visual interferences or anomalies, such as foaming, emulsions, precipitates, etc., must be documented.

4.5. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric media.

4.6. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table.** A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.5 The acidification of samples containing reactive materials may result in the release of toxic gases such as cyanides or sulfides. Acidification of samples must be done in a fume hood. The analyst must also be aware of the potential for a vigorous reaction.

5.6 Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.7 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8 Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9 Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10 Discard chipped or broken glassware to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, digestion block, steam bath, or other heating source capable of maintaining a temperature of 91-99°C

6.2. Calibrated thermometer that covers a temperature range of 0-110°C

6.3. Vapor recovery device (Watch glasses, ribbed or other device)

6.4. Whatman No. 41 filter paper or equivalent

6.5. Funnels or equivalent filtration apparatus

6.6. Analytical balance capable of accurately weighing to the nearest 0.01 grams

6.7. Repeaters or suitable reagent dispensers

6.8. Calibrated automatic pipettes with corresponding pipette tips: 100uL, 500uL, 1mL-5mL

6.9. Class A volumetric flasks

6.10. Plastic digestate storage bottles, such as Corning Snap Seals™ (may be used if their accuracy is documented and is better than 2%)

6.11. Boiling Stones: Ultra Pure Polytetrafluoroethylene (PTFE) or equivalent

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a DI water purification system that produces DI water approved for use in metals analysis. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks (MB) as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom solutions. All standards must be stored in fluorinated ethylene propylene (FEP) fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017.

7.3. Working ICP LCS/ MS solution: Prepare the ICP LCS/ MS working spike solutions from custom stock standards to the final concentration listed in Table 2. The working

spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS/MS solution must be made fresh every six months. Refer to the reagent module in LIMS for details on standard preparation.

7.4. ICPMS LCS/MS solution: LCS/MS solutions are custom made so the final concentrations after spiking equal the concentrations listed in Table3.

7.4.1. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.5. Nitric acid (HNO_3), concentrated, trace metal grade or better

7.6. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water

Note: When preparing diluted acids, always add acid to water. If the water is added to the acid a violent reaction may occur.

7.7. Hydrochloric acid (HCl), concentrated, trace metal grade or better

7.8. 30% Hydrogen peroxide (H_2O_2), Ultrapure grade

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Solid samples are collected and stored in wide-mouth glass jars with PTFE-lined lids. A minimum of 10 g must be collected.

8.2. Sample holding time for metals included under the scope of this SOP is 180 days from the date of sample collection to the date of analysis.

8.3. Soil samples do not require preservation.

9. QUALITY CONTROL

9.1. Preparation Batch

9.1.1. A preparation batch consists of a group of up to 20 client samples (not counting the batch QC) that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain an MB, an LCS, and an MS/MSD. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of MB are contained within the individual analytical method SOPs. If the MB does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be re-digested.

9.2.2. The MB is prepared by weighing a 1g aliquot of PTFE boiling chips. The MB is then processed as described in Section 11.

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOPs. Tables 2 and 3 provide the details regarding the stock, working standards, and final spike concentrations for ICP and ICPMS. Refer to Section 7 for instructions on preparation of the LCS solutions.

9.3.2. The ICP LCS is prepared by spiking a 1g aliquot of PTFE boiling chips with 2 mL of the working LCS/ MS spike solution (Section 7). The ICPMS LCS is prepared by spiking a 1g aliquot of boiling chips with 1 mL of the LCS/MS solution (Section 7). The LCS is then processed as described in Section 11.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. An MSD is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. Tables 2 and 3 provide the details regarding the stock, working standards and final matrix spike concentrations for ICP and ICPMS. Refer to Section 7

or the LIMS reagent module for instructions on preparation of the working matrix spike solutions.

9.4.3. The ICP MS/MSD is prepared by spiking a 1g aliquot of sample with 2 mL of the working LCS/MS spike solution (Section 7). The ICPMS MS/MSD is prepared by spiking a 1g aliquot of sample with 1 mL of the LCS/MS solution (Section 7). The MS/MSD is then processed as described in Section 11.

9.5. Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.

9.6. Control Limits

9.6.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.6.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.7.2. MDLs are accessible via the LIMs.

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Hot block temperature must be verified daily for each unit used, and must be recorded in a hot block temperature log.

10.2. Laboratory support equipment is calibrated per SOPs NC-QA-004 and NC-QA-015.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo (NCM).

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Deviations are not allowed for Ohio VAP projects.

11.3. The heating procedures are carried out in a properly functioning hood.

11.4. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample. The LIMS provides sample labels to reduce transcription errors.

11.5. Samples are typically logged in as soils. Wastes, such as organic liquids or sludges and tissues (animal/vegetable), are usually logged in as solids. When initiating prep, examine the sample to see if the sample matches the matrix designation.

11.6. If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab.

11.7. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards. Refer to Appendix B for details.

11.8. Preparation of Soils, Sediments, and Sludges for Analysis by ICP and ICPMS

11.8.1. If sample can be mixed easily in the sample jar, mix thoroughly by stirring with a clean plastic or wooden spoon or spatula. If the sample cannot be easily mixed (i.e., clay samples or samples of various and very different particle sizes), use the spoon or spatula to select enough separate portions from locations within the jar to produce a representative sample. Analyst judgment is important in determining how many portions and which locations are used to produce a representative aliquot. If the sample is uniform clay, at least 3 portions should be selected from different locations in the sample jar, if particle sizes or materials indicate a very non-homogenous sample, selection should be made carefully to collect an aliquot that represents the relative percentages of the various particle sizes and types in the sample jar.

11.8.2. For each digestion procedure required (i.e., ICP or ICPMS), weigh a 1g portion of solid and record the exact weight to the nearest 0.01g. A 2g sample size may also be used if needed to meet the reporting limits.

Note: Wipe samples are not weighed. The entire wipe is used.

11.8.3. Measure additional aliquots of the designated sample(s) for the MS/ MSD analyses. MS/MSD samples must be weighed to the exact nominal weight due to a limitation of the LIMS system.

11.8.4. Add 10 mL of 1:1 HNO_3 and mix the sample.

11.8.5. Heat sample to 95° ±4° C and reflux for 10 minutes without boiling, using a vapor recovery device.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.8.6. Add 5 mL of concentrated HNO_3 to all samples and QC. Cover the sample containers with a watch glass or similar device.

11.8.7. Reflux at 95° ±4° C for 30 minutes. (Add reagent water, as needed, to ensure that the volume of solution is not reduced to less than 5 mL.)

Note: If brown fumes are present, repeat steps 11.8.6 and 11.8.7 until brown fumes are no longer present.

11.8.8. Add approximately 2 mL of reagent water and 1 mL of 30 % H_2O_2. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.8.9. Continue adding 30% H_2O_2 in 1 mL aliquots until effervescence is minimal or sample appearance is unchanged. Make sure effervescence subsides before each addition of H_2O_2.

Note: Do not add more than a total of 10 mL of 30 % H_2O_2.

11.8.10. Continue heating at 95° ± 4° C until the volume is reduced by cooking two hours or to approximately 5-10 mL.

11.8.11. Add 10 mL of concentrated HCL and reflux for an additional 15 minutes without boiling.

11.8.12. Allow the sample to cool.

11.8.13. Filter sample through Whatman 41 filter paper or equivalent, that has been rinsed with deionized water, into a measuring bottle (for example, Corning Snap Seals™). These may be used if their accuracy is documented and is better than ± 2%. Rinse sample container and filter paper with reagent water to ensure complete sample transfer.

11.8.14. Dilute sample to 100 mL with reagent water into a 120 mL graduated Snap Seal. The sample is now ready for analysis.

11.9. Incremental Sampling Method (ISM) Solid Preparation Procedure for Analysis by ICP and ICPMS

11.9.1. The laboratory will receive a single sample aliquot containing approximately 10 g from the Solids Lab. The Metals Prep department will divide this aliquot into two separate aliquots for the digestion procedure.

11.9.2. Two approximately 5 g aliquots of a sample are each digested in two separate 130 mL Environment Express tubes (or equivalent) and then combined and diluted to a final volume of 500mL. Because of this, reagents will be entered into TALS at 5X the usual amount, but only 2.5X of each reagent will be added to each tube since one sample is divided between two tubes.

11.9.3. To the two MB tubes, add exactly 5 g of Teflon® boiling chips each.

11.9.4. To the two LCS standard tubes, add exactly 5 g of Teflon® boiling chips each and the appropriate amount of the working standard (see Tables 2 and 3).

11.9.5. To each sample and batch QC bottle carefully add 25 mL of 1:1 HNO3.

11.9.6. Cover the sample containers with a watch glass or similar device. Heat the samples to 95° ±4° C and reflux for 10 minutes without boiling.

Note: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY during any part of the digestion. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.9.7. Add 12.5 mL of concentrated HNO3 to each sample and batch QC digestion tube.

11.9.8. Continue heating at 95° ±4° C and reflux for 30 minutes.

11.9.9. Add approximately 5 mL of reagent water and add 30% H2O2 in 1mL increments to each tube letting the effervescence subside between each addition until a total of 25mL has been added. It important to do this step carefully as the effervescence can be high.

11.9.10. Continue heating at 95° ±4° C and reflux for 2 hours.

11.9.11. Add 25mL of concentrated HCl to each tube. It is important to do this step carefully as the reaction of the hot sample with HCl can be high.

11.9.12. Continue heating at 95° ±4° C and reflux for 15 minutes.

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11.9.13. Remove each sample and batch QC tube from the hotblock and allow the samples to cool.

11.9.14. Transfer one of the sample ID labels to a 500mL plastic bottle that has been marked by pouring out 500mL of water from a graduated cylinder into each empty 500mL plastic bottle.

11.9.15. Take each sample (2 digestate bottles per one sample) and pour the digestates into the appropriate labeled 500 mL plastic bottle. Rinse each digestion bottle twice with DI.

11.9.16. Using reagent water, bring the final volume up to the calibrated 500 mL mark and shake the sample vigorously to mix.

11.9.17. Filter approximately 50 mL to 60 mL of the sample from 11.9.16 through a Whatman #4 filter into a 4 oz. snap seal container. The sample is now ready for analysis.

11.10. Analytical Documentation

11.10.1. Record all analytical information in LIMS including the analytical data from standards, blanks, LCSs, and MS/MSDs, Any corrective actions or modifications to the method must be noted in an NCM.

11.10.2. Record all standards and reagents in the LIMS Reagents module. All standards are assigned a unique number for identification.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability and yearly continuing demonstrations of capability for each individual analyte. This requires analysis of four QC Check samples.

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs.

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13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic waste containing nitric acid generated by the extraction. This waste is disposed of in a designated container labeled "Acid Waste".

15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container labeled "Solid Waste".

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996, Method 3050B

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. Revision History

Historical File:		Revision 2.1: 02/11/00		Revision 6: 03/03/16
(formerly CORP-IP0002NC)		Revision 2.2: 09/25/01		
		Revision 2.3: 01/18/02		
		Revision 2.4: 02/19/03		
		Revision 2.5: 12/02/04		
		Revision 2.6: 07/29/07		
		Revision 0: 07/18/08 (NC-IP-010)		
		Revision 1: 01/07/09		
		Revision 2: 08/12/10		
		Revision 3: 11/23/12		
		Revision 4: 09/04/13		
		Revision 5: 09/30/14		

16.2. Associated SOPs and Policies, current version

16.2.1. Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Methods 6010B and 200.7, NC-MT-012

16.2.2. Inductively Coupled Plasma-Mass Spectrometry, EPA Methods 6020 and 200.8, NC-MT-002

16.2.3. TestAmerica North Canton Quality Control Program, QA-003

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. Subsampling, NC-IP-001

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Method Deviations

17.1.1. The laboratory uses the same preparation procedure for ICP and ICPMS. Hydrochloric acid can be used for ICPMS due to the collision cell technology on newer instruments. Due to the potential chloride interferences, and possible inability to analyze for arsenic and tin, the laboratory must follow the instrument manufacturer guidelines pertaining to the use of HCL and ICP/MS analyses.

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APPENDIX A: TABLES

TABLE1

Method 3050B Analyte List

Element	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Boron	B	7440-42-8
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Lithium	Li	7439-93-2
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Tin	Sn	7440-31-5
Titanium	Ti	7440-32-6
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

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TABLE 2

ICP Soil Matrix Spike (MS) and Laboratory Control Sample (LCS) Levels

Element	Working LCS/MS Standard (mg/L)	Soil MS/LCS Level * (mg/kg)
Aluminum	100	200
Antimony	25	50
Arsenic	100	200
Barium	100	200
Beryllium	2.5	5
Cadmium	2.5	5
Calcium	2500	5000
Chromium	10	20
Cobalt	25	50
Copper	12.5	25
Iron	50	100
Lead	25	50
Magnesium	2500	5000
Manganese	25	50
Molybdenum	50	100
Nickel	25	50
Potassium	2500	5000
Selenium	100	200
Silver	2.5	5
Sodium	2500	5000
Thallium	100	200
Vanadium	25	50
Zinc	25	50
Boron	50	100
Tin	100	200
Titanium	50	100
Silicon	50	100
Silica	107	214

** Final soil spike concentration based on the addition of 2.0 mL working spike (Section 7.3) to 1.0 g of sample/100 mL final volume (assumes 100% solids).*

TABLE 3

ICPMS Soil Matrix Spike (MS) and Laboratory Control Sample (LCS) Levels

Element	Working LCS/MS Standard (mg/kg)	Soil MS/LCS Level * (mg/kg)
Aluminum	1000	1000
Antimony	10	10
Arsenic	10	10
Barium	10	10
Beryllium	10	10
Cadmium	10	10
Calcium	1000	1000
Chromium	10	10
Cobalt	10	10
Copper	10	10
Iron	1000	1000
Lead	10	10
Lithium	10	10
Magnesium	1000	1000
Manganese	10	10
Molybdenum	10	10
Nickel	10	10
Potassium	1000	1000
Selenium	10	10
Silver	10	10
Sodium	1000	1000
Strontium	10	10
Thallium	10	10
Vanadium	10	10
Zinc	10	10
Boron	10	10
Tin	10	10
Titanium	10	10

** Final soil spike concentration based on the addition of 1.0 mL working spike (Section 7.4) to 1.0 g of sample/100 mL final volume (assumes 100% solids).*

APPENDIX B. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware must be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the Metals Lab. All work areas must be kept scrupulously clean.

Powdered gloves must not be used in the Metals Lab since the powder contains zinc, as well as other metallic analytes.

Glassware must be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Title: ACID DIGESTION FOR AQUEOUS SAMPLES

[Methods: SW846 3005A, 3010A, and MCAWW 200 Series]

Approvals (Signature/Date):

Technology Specialist	04/19/17 Date	Health & Safety Coordinator	04/19/17 Date
Quality Assurance Manager	07/24/17 Date	Technical Director	06/30/17 Date

This SOP was previously identified as SOP No. NC-IP-011, Rev 6, dated 2/26/16

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), and Inductively Coupled Plasma-Mass Spectrometry (ICPMS) using the MCAWW 200 series methods (NPDES) and SW846 Methods 3005A, and 3010A.

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables 1 and 2(Appendix A). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved suspended, total recoverable and total elements in ground water, aqueous samples, certain aqueous sludges, and leachates/extracts.

1.4. SW846 Method 3005A / MCAWW Method 200.8 are used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP and ICPMS.

1.5. MCAWW Method 200.7 is used to prepare surface water, domestic and industrial waste samples for total, total recoverable and dissolved metals determination by ICP.

1.6. SW846 Method 3010A is used to prepare aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by ICP.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 / Method 200.8 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP and ICPMS

2.1.1 A representative aliquot of sample is heated with nitric and hydrochloric acids and reduced to a low volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A / Method 200.7 / - Preparation for Total Metals Analysis by ICP

2.2.1 A representative aliquot of sample is refluxed with nitric acid. After the digestate has been reduced to a low volume, it is refluxed with 1:1 hydrochloric acid, filtered (if necessary), and diluted to volume.

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3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include metallic or metal-containing lab ware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. All glassware is cleaned per SOP NC-QA-014.

4.2. The entire work area, including the bench top and fume hood, must be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix B for additional contamination control guidelines.

4.3. Boron from the glassware will migrate into the sample solution during and following sample processing. For critical low-level determinations of boron, it is recommended quartz or plastic lab ware be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrices may not be digested using these methods if they are not soluble with acids.

4.5. Visual interferences or anomalies (such as dilution due to oily matrix) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Samples that contain high concentrations of carbonates, or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in**

the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.5. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples must be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid spills must be neutralized immediately, flushed with water, and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire-polished as an alternative to disposal.

6. EQUIPMENT AND SUPPLIES

EQUIPMENT AND SUPPLIES
Hot plate/digestion block: capable of maintaining a temperature of 90-95º C
Calibrated thermometer: range 0-110º C
Beakers, assorted sizes: Griffen, calibrated digestion beakers, or equivalent
Ribbed watch glasses, or equivalent
Whatman #41 filters, or equivalent
Funnels
Graduated cylinder: 50 mL
Analytical balance capable of weighing to ± 0.01 g
Repeaters or suitable reagent dispensers
Pipettes and disposable tips: various volumes
Volumetric flasks: Class A
pH indicator strips: range 0-6
Plastic digestate storage bottles: Corning snap seals, or equivalent

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks (MB) as defined in the determinative SOPs.

7.2. Reagents

Reagents
Nitric Acid (HNO_3): Concentrated, trace metal grade or better
Hydrochloric Acid (HCl): Concentrated, trace metal grade or better
1:1 Hydrochloric Acid: dilute concentrated HCl with an equal volume of reagent water

Note: When preparing diluted acids, always add acid to water. If the water is added to the acid, a violent reaction may occur.

7.3. Standards

7.3.1. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017.

7.3.2. Working ICP laboratory control sample (LCS)/matrix spike (MS) spike solution: Prepare the ICP LCS/MS working spike solution from custom stock standards to the final concentration listed in Table 3. The working spike must be prepared in a matrix of 5% HNO_3. This acid (5 mL of concentrated HNO_3 per 100 mL) must be added to the volumetric flask before the addition of the stock standard aliquot. The working ICP LCS solution must be made fresh every six months.

7.3.3. The ICPMS LCS/MS solution is provided directly by the vendor. No further standard preparation is necessary.

7.3.4. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary. Refer to Table 5 for final digestate spike concentrations.

7.3.5. The LCS/MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom solution, the individual facility must purchase a solution from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.3.6. Aqueous LCS and MS samples are prepared as described in Sections 9.4 and 9.3. Refer to Tables 3 and 4 (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP and ICPMS LCS and MS preparations.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and must be stored in either plastic or glass. If boron is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

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8.3. Metals samples that are preserved at the laboratory must be held for 24 hours before digestion. For metals samples that require preservation, the Sample Receiving Department must note the time of acid addition.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required

8.4. For dissolved metals analysis, the samples must be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field. In the event that samples are not field filtered, filtration occurs in the laboratory prior to preparation.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike / matrix spike duplicate (MS/MSD) If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. See Policy QA-003 for further definition of the batch. Laboratory generated QC (MB, LCS, MS/MSD) are not included in the sample count.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.2.2. Aqueous and TCLP MBs are prepared by taking 50 mL of reagent water through the appropriate procedure as described in Section 11.

9.2.3. TCLP Leachate Blanks (LBs) are prepared by taking 50 mL of leachate fluid through the appropriate procedure as described in Section 11.

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOPs.

9.3.2. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 1.0 mL for ICP and 0.5 mL for ICPMS of the working LCS/MS spike solution . The LCS is then processed through the appropriate procedure as described in Section 11.

Note: TCLP LCS is prepared by spiking 50 mL of leachate fluid with 1.0 mL for ICP and 0.5 mL for ICPMS of the working LCS/MS solution and taking it through the appropriate procedure as described in Section 11.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the matrix spike) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates (DU) in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis.

Note: For Method 200.7, an MS/MSD pair is required for every 10 samples. 2 MS/MSD pairs must be analyzed if the batch contains more than 10 samples for 200.7 analysis.

9.4.2. The aqueous MS sample is prepared by spiking a 50 mL aliquot of a sample with 1.0 mL for ICP and 0.5 mL for ICPMS of the working LCS/MS spike solution . The MS sample is then processed as described in Section 11.

9.4.3. The ICP TCLP MS/MSD sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution. For ICPMS analysis, the MS/MSD is spiked the same as a water sample. The MS/MSD sample is then processed as described in Section 11.

Note: The TCLP matrix spike standard must be added prior to preservation of the leachate.

Note: If analytes outside of the RCRA list are requested, l mL of additional spiking solution(s) is added.

9.6 Additional information on QC samples can be found in QA Policy QA-003.

9.7 Control Limits

9.7.1 Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMS.

9.8 Method Detection Limits (MDLs) and MDL Checks

9.8.1 MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.8.2 MDLs are easily accessible via the LIMS.

9.9 Nonconformance and Corrective Action

9.9.1 Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Procedural deviations are not allowed for Ohio VAP projects.

10. CALIBRATION AND STANDARDIZATION

10.1. The hot plate/hot block temperature must be verified daily for each hotplate used, and must be recorded on a hotplate/hot block temperature log

10.2. Support equipment used for this procedure will be checked for calibration as per SOP NC-QA-015, current version. .

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file. Procedural deviations are not allowed for Ohio VAP projects.

11.2. All digestion procedures must be carried out in a properly functioning hood.

11.3. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.4. Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment, etc.), contact the lab supervisor or project manager for further instructions. In some cases, it may be more appropriate to process these samples as solids.

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11.5. If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab.

11.6. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.7. The following procedure must be followed for all aqueous sample preparations.

11.7.1. Mix sample by shaking the container.

11.7.2. Measure 50 mL of the sample into a calibrated digestion tube.

Note: For samples with particulate matter, the aliquot may be taken through a repeated series of shake and pour steps.

11.7.3. Measure two extra aliquots of sample selected for the MS/MSD analysis. Spike each aliquot with the appropriate spiking solutions.

11.7.4. Measure 50 mL of reagent water into a calibrated digestion tube for the MB.

11.7.5. Measure 50 mL of reagent water into a calibrated digestion tube for the LCS and add the appropriate spiking solutions.

11.8. Method 3005A / Method 200.7 / Method 200.8 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP / ICPMS

11.8.1. To the sample container, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.8.2. Cover with ribbed watch glass.

11.8.3. Heat at 90-95°C until volume is reduced to less than or equal to 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.8.4. Cool the beaker in a fume hood.

11.8.5. If insoluble materials are present, filter the sample through Whatman 41 filter paper into a plastic storage container, such as a Corning Snap Seal™

Note: If any samples in a preparation batch are filtered, the MB and LCS associated with that batch must also be filtered.

11.8.6. Rinse container and filter paper with reagent water to ensure complete sample transfer.

11.8.7. Adjust the final volume to 50 mL with reagent water in the Snap Seal™ container if the digestate was filtered or in the hot block digestion tube if filtering was not necessary. The sample is now ready for analysis.

11.9. Method 3010A / Method 200.7 - Preparation for Total Metals Analysis by ICP Spectroscopy

11.9.1. To the sample container, add 3.0 mL of concentrated HNO_3.

11.9.2. Cover with ribbed watch glass.

Place container on hot block 90-95°C, and reflux until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing) and the volume is less than or equal to 20 mL. **NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY.** Doing so will result in the loss of analyte and the sample must be re-prepared.

11.9.3. Add 5 mL of 1:1 HCl.

11.9.4. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue. Cool in a fume hood.

11.9.5. Filter sample, if insoluble materials are present, through Whatman 41 filter paper into a plastic storage container, such as a Corning Snap Seal™.

Note: If any samples in the QC batch are filtered, the MB and LCS associated with that batch must also be filtered.

11.9.6. Rinse container and filter paper with reagent water to ensure complete sample transfer.

11.9.7. Adjust final volume to 50 mL with reagent water in the Snap Seal™ container if the digestate was filtered, or in the hot block digestion tube if filtering was not necessary. The sample is now ready for analysis.

11.10. Analytical Documentation

11.10.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.10.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability and yearly continuing demonstrations of capability for each individual analyte. This requires analysis of four QC Check samples.

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs.

13.2. Training Qualification

13.2.1 The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2 Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1 The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic waste containing nitric acid generated by the extraction: This waste is disposed of in the designated container labeled "Acid Waste".

15.2.1.2. Contaminated disposable materials utilized for the analysis. This waste is disposed of in a designated container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A and 3010A

16.1.2 Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983

16.1.3 TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.4 TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.5 Corporate Quality Management Plan (CQMP), current version

16.1.6 Revision History

Historical File:		Revision 1.2: 03/20/00		Revision 5: 08/06/14
(formerly CORP-IP-0003NC)		Revision 1.3: 09/25/01		Revision 6: 02/26/16
		Revision 1.4: 02/19/03		
		Revision 1.5: 12/07/04		
		Revision 1.6: 02/07/07		
		Revision 0: 01/07/09 (NC-IP-011)		
		Revision 1: 01/28/10 (NC-IP-011)		

		Revision 2: 05/17/11		
		Revision 3-A: 06/28/12		
		Revision 4: 06/28/14		

16.2. Associated SOPs and Policies, current version

16.2.1 TestAmerica QC Program, QA-003

16.2.2 Glassware Washing, NC-QA-014

16.2.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4 Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5 Standards and Reagents, NC-QA-017

16.2.6 Subsampling, NC-IP-001

16.2.7 Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW846 Methods 6010B, 6010C, and 200.7, NC-MT-012

16.2.8 Inductively Coupled Plasma – Mass Spectrometry, NC-MT-002

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference methods

17.1.1 Modifications applicable to SW-846 reference methods

17.1.1.1. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "flexibility to alter digestion volumes is addressed and "allowed" by Table 3-1 and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples. EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally,

in written correspondence from the Office of Solid Waste, Oliver Fordham stated “As a “representative sample” can be assured, scaling causes no loss of precision and accuracy in the analysis.”

17.1.1.2. Modifications Specific to Method 3010A

17.1.1.2.1. Section 11.8.3 of this SOP requires the sample be reduced to a volume –less than or equal to 20 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL, but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.1.3. Modifications Specific to MCAWW Methods

17.1.1.3.1. It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness vs. an exact volume).

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APPENDIX A - TABLES

TABLE 1: Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010 A
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	
Arsenic	As	7440-38-2	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element.

Note: *Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.*

TABLE 2: Approved Preparation Method Analytes – NPDES

ELEMENT	Symbol	CAS Number	200.7 (9.4)	200.7 (9.3)
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	X
Arsenic	As	7440-38-2	X	X
Boron	B	7440-42-8	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silicon	Si	7631-86-9	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element

Note: *Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.*

TABLE 3: ICP Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working Laboratory Control Sample (LCS)/Matrix Spike (MS) Standard (mg/L)	Aqueous Laboratory Control Sample (LCS)/ Matrix Spike (MS) Level * (ug/l)
Aluminum	100	2000
Antimony	25	500
Arsenic	100	2000
Barium	100	2000
Beryllium	2.5	50
Cadmium	2.5	50
Calcium	2500	50000
Chromium	10	200
Cobalt	25	500
Copper	12.5	250
Iron	50	1000
Lead	25	500
Magnesium	2500	50000
Manganese	25	500
Molybdenum	50	1000
Nickel	25	500
Potassium	2500	50000
Selenium	100	2000
Silver	2.5	50
Sodium	2500	50000
Thallium	100	2000
Vanadium	25	500
Zinc	25	500
Boron	50	1000
Tin	100	2000
Titanium	50	1000
Lithium	50	1000
Silicon	50	1000
Strontium	50	1000

* *Levels shown indicate the spike concentration in the final digestate of the aqueous laboratory control sample (LCS) or matrix spike (MS) based on the addition of 1.0 mL working spike (7.3) to 50 mL of sample.*

TABLE 4: ICPMS Aqueous Laboratory Control Sample (LCS) and Matrix Spike/Matrix Spike Duplicate (MS/MSD) Levels

ELEMENT	Working Laboratory Control Sample (LCS)/Matrix Spike (MS) Standard (mg/L)	Aqueous Laboratory Control Sample (LCS)/Matrix Spike (MS) Level* (ug/L)
Aluminum	1000	10000
Antimony	10	100
Arsenic	100	1000
Barium	100	1000
Beryllium	100	1000
Cadmium	100	1000
Calcium	1000	10000
Chromium	100	1000
Cobalt	100	1000
Copper	100	1000
Iron	1000	10000
Lead	100	1000
Lithium	10	100
Magnesium	1000	10000
Manganese	100	1000
Molybdenum	10	100
Nickel	100	1000
Potassium	1000	10000
Selenium	100	1000
Silver	10	100
Sodium	1000	10000
Strontium	100	1000
Thallium	25	250
Vanadium	100	1000
Zinc	100	1000
Boron	10	100
Tin	100	1000
Titanium	10	100
Tungsten	10	100

* *Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or MS based on the addition of 0.5 mL working spike (Section 7.4) to 50 mL of sample.*

Note: *Spiking levels may be adjusted as long as the concentrations are documented.*

TABLE 5: TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels for ICP

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)*
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

* *Levels shown indicate the spike concentration in the final digestate of the aqueous MS based on the addition of 0.5 mL working spike (Section 7.5) to 50 mL of sample.*

APPENDIX B

CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware must be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered Latex Gloves must not be used in the metals laboratory since the powder contains zinc, as well as other metallic analytes. Only unpowdered latex or nitrile gloves must be used in the metals laboratory.

Glassware must be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Title: GC/MS Semivolatile Organic Compounds Capillary Column Technique

[Method: EPA Method 625 and 625.1]

Approvals (Signature/Date):

Technology Specialist	02/06/18 Date	Health & Safety Coordinator	02/07/18 Date
Quality Assurance Manager	03/12/18 Date	Technical Director	03/01/18 Date

This SOP was previously identified as SOP No. NC-MS-003, Rev 10, dated 9/28/17

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1. SCOPE AND APPLICATION

1.1. This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Table 1 may be qualitatively and quantitatively determined using this method.

1.2. The method may be extended to include the parameters listed in the Appendix. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. n-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. n-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Benzidine can be subject to oxidative losses during solvent concentration. The preferred method for each of these parameters is listed in Table 2.

1.3. This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Table 1 in water and wastewater, domestic and industrial wastewaters. Method 625 is required for demonstration of compliance with NPDES wastewater discharge permits.

1.4. The reporting limit (RL) for each parameter is listed in Table 1. The RL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix. This method can be applied only to aqueous matrices.

1.5. This SOP applies to the analysis of compounds listed in EPA Method 625. Other compounds may be analyzed by this method with permission from the laboratory. Results for these compounds cannot be reported as certified by Method 625.

1.6. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory.

2. SUMMARY OF METHOD

2.1. A measured volume of sample is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 2 mL to 5 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using the internal standard technique with a single characteristic (m/z).

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.1.1. Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water and rinses with tap water and reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for 15 to 30 minutes. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

4.1.2. The use of high purity reagents and solvents helps to minimize interference problems.

4.2. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

4.3. The base/neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, 3 & 4 methylphenol and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the

Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time, or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzi¬dine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine. Primary standards should be purchased in solution. If neat materials must be obtained, they shall be handled in a hood.

5.5. Exposure to hazardous chemicals must be maintained as low as reasonably achievable. Samples with stickers that read "Caution/Use Hood!" must be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph/Mass Spectrometer System

6.2. Gas Chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories, including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns. The capillary column should be directly coupled to the source.

6.2.1. Column: 30m x 0.25 mm ID, 0.50-μm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent).

6.2.2. Mass Spectrometer: Capable of scanning from 35 to 500 amu every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 2 when the GC/MS tuning standard is injected through the GC.

6.2.3. GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points for each compound of interest and achieves acceptable tuning performance criteria may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

6.2.4. Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances vs. time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

6.3. Syringe: 5 μL Hamilton Laboratory grade syringes or equivalent

6.4. Carrier gas: Ultra high purity helium

7. REAGENTS AND STANDARDS

7.1. Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.2. Methylene chloride, reagent grade

7.3. A minimum three-point calibration curve is prepared for each parameter of interest.

7.4. An 80 µg/mL Internal Standard solution is prepared by adding 1 mL of a 2000 ug/mL I.S. mix to 49 mL of methylene chloride. This solution is added to standards and extracts at a volume to achieve 4 ng I.S. on column. Compounds in the I.S. mix are acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

7.4.1. Internal Standards are added to all standards and extracts at 4 ng on column.

7.5. GC/MS Tuning Standard: A methylene chloride solution containing 25 µg/mL of decafluorotriphenylphosphine (DFTPP) is prepared. Pentachlorophenol, benzidine, and DDT should also be included in the Tuning Standard at 25 µg/mL.

7.6. The working standard listed in Sections 7.2 to 7.5 should be stored per manufacturer's recommendations. Refrigeration at -10°C to -20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. The continuing calibration standard must be replaced every week and is stored at 4°C ± 2°C.

8. SAMPLE, PRESERVATION, AND STORAGE

8.1. Samples must be collected in glass containers. All sampling must be iced or refrigerated at 4°C ± 2°C from the time of collection until extraction.

8.2. Samples are extracted within seven days of sampling, and the extracts must be analyzed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (LCS, MS/MSD, method blanks) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period beginning from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and

process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants: see below).

9.2.2. Corrective Action for MBs

9.2.2.1. If the analyte is a common laboratory contaminant (Dimethyl phthalate, Diethyl phthalate, Di-n-butyl phthalate, Bis(2-ethylhexyl)phthalate, Di-n-octyl phthalate, and Butyl benzyl phthalate), the data may be reported with qualifiers if the concentration of the analyte in the MB is at a concentration up to five times the reporting limit. Such action must be addressed in the project narrative.

9.2.2.2. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.2.2.3. If there is no target analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A full analyte spike is required for Method 625. The spiking levels are given in Table 6.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside the established control limits, the system performance is unacceptable for that parameter. The only exception is if the LCS recovery is biased high and the associated analyte is not detected (ND) for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.2. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. Only the failed parameters are evaluated in the re-preparation and re-analysis.

9.3.3.3. If that parameter is in control in the MS/MSD, data may be reported with client approval. If the parameter is out of control in the MS/MSD, corrective action must be taken.

9.4. Matrix Spike (MS/MSD)

9.4.1. A matrix spike (MS/MSD) is prepared by spiking at least 5% of the samples from each sample site being monitored. At least one sample spiked per month is required. An MS/MSD is a field sample to which known concentrations of all analytes of interest have been added. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, MS/MSD. The MS/MSD is spiked with the same set of analytes as the LCS. Compare the percent recovery to that in the laboratory-specific historically generated limits. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. Corrective Action for MS/MSD

9.4.2.1. If the analyte recovery or Relative Percent Difference (RPD) falls outside the acceptance range, the results should be evaluated to determine the cause of the error.

9.4.2.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability. Re-preparation and /or re-analysis may be necessary.

9.4.2.3. If matrix interference is suspected, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.4.2.4. If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data is reported and flagged with a “4” in LIMS.

NOTE: In cases where a short list or single compound analysis is requested, only the quality control associated with those compounds is required to meet criteria. Examples of these types of analysis are the PAH list and naphthalene only. If the PAH list is requested only the QC associated with this list must pass (continuing calibration, surrogate recoveries, check sample, and MS/MSD). Additional information on method blanks, LCS, and MS/MSD are located in the preparative methods (see SOP NC-OP-032).

9.4.2.5. If client program requirements specify to confirm matrix interferences, re-preparation and re-analysis of the MS/MSD may be necessary.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the recovery limits. One surrogate recovery per fraction can be outside of control limits, as long as surrogate recovery is greater than 10%. Additional information on surrogates is located in the preparative method (see SOPs NC-OP-037 and/or NC-OP-038).

9.5.3. Corrective action is required if the surrogate compound(s) in the blank or samples fall outside the recovery limits. The following corrective action should be taken.

9.5.3.1. Check all calculations to ensure that no errors were made; check internal standard (if applicable) and surrogate spiking solution for degradation, contamination, etc.; also check instrument performance.

9.5.3.2. If the above step fails to reveal a problem, re-analyze the blanks and/or samples. If re-analysis does not confirm original results and is within QC acceptance criteria, then the problem was within the analyst's control and only the re-analyzed data should be reported.

9.5.3.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside the control limits, then the sample and the MS/MSD do not require re-analysis as this phenomenon would indicate a possible matrix problem.

9.5.3.4. If the re-analysis does confirm the original results, then the following steps should be taken.

9.5.3.4.1. For a blank, the analytical system must be considered out of control. The problem must be corrected before continuing. This may include recalibration of the instrument.

9.5.3.4.2. For a sample, the results from the original analyses must be reported and the data flagged as surrogates out due to matrix effect.

9.6. Control Limits

9.6.1. Control limits are established by the method.

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL checks are established by the laboratory as described in SOP NC-QA-021 and CA-Q-S-006.

9.7.2. MDLs are easily accessible via the LIMs.

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is tuned for DFTPP and calibrated with a minimum of a three-point calibration curve.

10.2. Instrument Tuning

10.2.1. At the beginning of each day in which analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP. The tailing factor for benzidine must be less than 3.0. The tailing factor for pentachlorophenol must be less than 5. For Method 625.1, benzidine and pentachlorochlorophenol should not exceed a tailing factor of 2. DDT must be included in the tuning standard, and its breakdown must be < 20%. The tune period for this method is defined as 24 hours for 625 and/12 hours for 625.1. Calculation of the Tailing Factor is illustrated in Appendix A at the end of this document.

10.2.2. These performance tests require the following instrumental parameters.

Electron Energy:	70 volts (nominal)
Mass Range:	35 to 500 amu
Scan Time:	To give at least 5 scans per peak, but not to exceed

10.2.3. DFTPP Performance Test: Inject 0.5 μL (25 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 2 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The

performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3. Initial Calibration

10.3.1. Internal Standard Calibration Procedure: Internal standards are listed in Table 3. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense masses for quantification.

10.3.2. Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding the appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards and dilute to volume with $MeC1_2$. One of the calibration standards should be at a concentration near, but above, the RL; and the other concentrations should define the working range of the GC/MS system.

10.3.3. Using injections of 0.5 μL (5 uL for LVI calibration), analyze each calibration standard and tabulate the area of the primary characteristic masses (m/z) (Table 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using the following equation:

$$\frac{(A_x)(C_{is})}{(A_{is})(C_s)} = Rf$$

Where:

A_x = Area of the characteristic ion for the compound being measured
A_{is} = Area of the characteristic ion for the specific internal standard
C_x = Concentration of the compound being measured (μg/L)
C_{is} = Concentration of the specific internal standard (μg/L)

10.3.4. If the RF value over the working range is constant (□35% RSD), the RF can be assumed to be invariant and the average RF from the initial calibration can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, Ax/Ais vs. RF. If this requirement cannot be met, a regression curve must be constructed for the non-compliant compounds.

10.3.5. Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

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10.3.6. If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve re-analyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

10.3.7. One of the following conditions must be satisfied to allow removal or replacement of a level.

- The data file is corrupted and unusable, or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a bad injection.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made-up standard).
- For external standard methods, the average amount of analyte recovered is less than 70% or greater than 130% of the expected value.

10.3.8. The reason for replacing the level must be documented in the run log. The fact that the curve passes criteria with the level removed is not alone sufficient evidence to document an injection or instrument problem confined to the level.

10.3.9. Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

10.3.10. Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

10.4. Initial Calibration Verification

10.4.1. Method Specification:

10.4.2. A second source initial calibration verification standard must be analyzed subsequent to the initial calibration and prior to sample analysis. The suggested acceptance limit is 70-130% recovery

10.4.3. Approach

10.4.3.1. Laboratories may define alternate limits for initial calibration verification in their SOPs, but the specific analytes and limits must be defined. Most analytes should use the 70-130% guidance from the method. The alternate recovery criterion shall be no less than 50-150% for the following poor performing compounds: 2,4-Dimethylphenol, Hexachlorocyclopentadiene, Famphur, and 2,3,5,6-Tetrachlorophenol

10.4.3.2. Flagging: If the SOP limits are exceeded, for non-detects, no flagging needed. For detects, describe the issue in the narrative, or flag as estimated.

10.5. Continuing Calibration

10.5.1. The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameters varies from the predicted response by more than ± 20% or for 625.1 (refer to table 6 values from the method), the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve may be prepared for that compound.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Samples are prepared using SOP NC-OP-037 or NC-OP-038.

11.4. Summary

11.4.1. The sample extract is injected on a GC column and the eluting compounds are identified by mass spectroscopy.

11.5. Recommended Instrument Conditions

Mass Range:	35 - 500 amu
Scan Time:	≤1 second/scan
Initial Column Temperature/Hold Time:	50°C for 1 minute

Column Temperature Program:	60 - 325°C at 35°C/minute
Final Column Temperature Hold:	325°C for 2 minutes
Injector Temperature:	250 - 300°C
Transfer Line Temperature:	250 - 300°C
Source Temperature:	According to manufacturer's specifications
Injector:	Grob-type, splitless
Sample Volume:	0.5 μL (5 uL for LVI samples)
Carrier Gas:	Helium at 30 cm/second

11.6. Sample Analysis Procedure

11.6.1. Add a known amount of internal standard to the sample extract and mix thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction, or evaporation.

11.6.2. Inject 0.5 μL (5 uL for LVI samples) of the sample extract into the GC/MS system using the same injection volume and injection technique as used for the standards. Record the injection volume used.

11.6.3. If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and re-analyze.

11.6.4. Perform all qualitative and quantitative measurements as described in Sections 12.4 and 12.5. When the extracts are not being used for analyses, refrigerate them at 4°C ± 2°C protected from light in screw cap vials equipped with un-pierced Teflon®-lined septa.

11.7. Qualitative Identification

11.7.1. Obtain EICPs for the primary m/z and the two other masses listed in Table 5. See Section 10.3.1 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification.

11.7.1.1. The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

11.7.1.2. The retention time must fall within ± 30 seconds of the retention time of the authentic compound.

11.7.1.3. The relative peak heights of the three characteristic masses in the EICPs must fall within ± 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

11.7.2. Spectral isomers that have very similar mass spectra and less than 30 seconds difference in retention time can be explicitly identified only if

the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isometric pairs.

Note: For waters, the TIC searches begin with compounds eluting after the first surrogate (2-fluorophenol). Compounds eluting before these are considered volatiles, and would be available in the volatile fraction. A possible exception to this general rule would be if an early eluter was the reason a sample required a dilution. If a client requests ten TICs, the laboratory supplies a minimum of ten. For a request of 20 TICs, the laboratory would supply a minimum of 20 (assuming they are available).

11.7.3. As an alternative to using EICPs, the analyst may use mass spectra for identification.

11.7.3.1. An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained from the same GC/MS. These standard reference spectra are obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: 1) elution of sample component at the same GC retention time as the standard component, and 2) correspondence of the sample component and the standard component mass spectrum.

11.7.3.2. The retention time must fall within ± 30 seconds of the retention time of the standard component.

11.7.3.3. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.7.3.4. The relative intensities of ions must agree within ± 20% between the standard and sample spectra.

11.7.4. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

- The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%)
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.7.5. A screen for 2,3,7,8-TCDD may be performed using selected ion monitoring (SIM) as part of this analytical procedure. This process requires a second injection of the extract under conditions adjusted to look for only the primary masses for this compound and the internal standard compound that elutes most closely (chrysene-d12). The presence or absence of this compound is reported, no quantitative information is provided.

Compound	Masses	RRT
2,3,7,8-TCDD	322, 320, 257	0.99
Chrysene-d12 (IS)	240, 120	------

11.7.6. Analysts evaluating data are trained to know how to handle “problem” compounds. For example, from the TCL list, the problem compounds have been identified as the isomers:

Dichlorobenzenes

Methylphenols

Trichlorophenols

Phenanthrene, Anthracene

Fluoranthene, Pyrene

Benzo (b) and (k) fluoranthene

11.7.6.1. Extra precautions concerning these compounds are to more closely scrutinize retention time vs. standard and also to check for presence of all isomers.

11.7.7. A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid

Chloroanilines

Nitroanilines

2,4-Dinitrophenol

4-Nitrophenol

Hexachlorocyclopentadiene

Pentachlorophenol

3,3'-Dichlorobenzidine

11.7.7.1. Manually checking the integrations would be appropriate for these compounds.

12. DATA ANALYSIS AND CALCULATIONS

12.1. When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in table 5. Use the base peak m/z for internal and surrogate standards. If the sample produces interference for the primary m/z, use a secondary characteristic m/z to quantitate.

12.1.1. Calculate the concentration in the sample using the response factor (RF) determined in Section 10.4.3 and the following equation.

$$\frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)} = \textit{concentration, ug / L}$$

Where:

A_x = Area of characteristic ion for compound being measured

I_s = Amount of internal standard injected (ng)

V_t = Volume of total extract, taking into account dilutions (i.e., a 1:10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half of the base/neutral extract and half of the acid extract are combined, V_t = 2,000.)

A_{is} = Area of characteristic ion for the internal standard

RF = Response Factor for compound being measured (Section 10.4.3)

V_o = Volume of water extracted (mL)

V_i = Volume of extract injected (μL)

12.1.2. Where applicable, an estimate of concentration for non-calibrated components in the sample should be made. The formulas given above should be used with the following modifications. The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

12.1.3. Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

RF = Mean of RFs from intial caibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

RFi = RF for each of the calibration levels

N = Number of RF values

12.1.4. Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.2. Calculation of TICs: The calculation of TICs) is identical to the above calculations with the following exceptions:

Ax = Area of the total ion chromatogram for the compound being measured

Ais= Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

Results for TICs are not quantitative and are always reported as estimated "J."

12.3. Percent DDT breakdown

$$\% \text{ DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDarea}}$$

The total ion current areas are used for this calculation

12.4. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002

12.5. Report Documentation

12.5.1. Record all analytical information in LIMS including any corrective actions or modifications to the method.

12.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

12.5.3. The documentation for each raw data file includes copies of all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs.

12.5.4. Record all sample results and associated QC in LIMS. Level I and Level II reviews are performed in LIMS.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to

minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E_M-001) for "Waste management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

15.3. Waste Streams Produced by the Method

15.3.1. The following waste streams are produced by this method.

15.3.1.1. **Vials containing sample extracts:** These vials are placed in the vial waste located in the GC/MS laboratory.

16. REFERENCES

16.1. Reference

16.1.1. Federal Register - Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

16.1.2. United States Environmental Protection Agency Office of Water EPA 821-R-16-007, Method 625.1: Base / Neutrals and Acids by GC/MS. December 2016

16.1.3. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Revision History

Historical File:		Revision 0: 11/11/96		Revision 6: 08/18/10
		Revision 1: 06/17/03		Revision 7: 09/30/13
		Revision 2: 02/24/04		Revision 8: 04/29/15
		Revision 3: 03/13/06		Revision 9: 04/15/16
		Revision 4: 05/06/08		Revision 10: 09/28/17
		Revision 5: 07/20/10		

16.2. Associated SOPs and Policies, current version

16.2.1. Continuous Liquid/Liquid Extraction of Organic Compounds from Waters Based on Method SW846 3520C NC-OP-037

16.2.2. Separatory Funnel Extraction of Organic Compounds from Waters Based on Method SW846 3510C NC-OP-038

16.2.3. QA Policy, QA-003

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.6. Acceptable Manual Integration Practices, CA-Q-S-002

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Preventative Maintenance Procedures

17.1.1. Daily Instrument Maintenance

17.1.1.1. Clip Column

17.1.1.2. Install new or cleaned injection port line

17.1.2. Major Maintenance

17.1.2.1. When poor pentachlorophenol response is noticed in the DFTPP run, clip the column and change the liner. If response is still poor, a new column is installed. Other times, when a new column might be installed, would be unacceptable response for the SPCC compounds or poor resolution between isomers.

17.1.2.2. Clean source. If overall sensitivity is poor, then the source is removed and cleaned.

17.1.2.3. Replace filaments, replace filters, and change pump oil. All these may be done at the same time as source cleaning. The frequency of changing filters and pump oil is about six months.

17.2. Tables

Table 1 – TestAmerica Canton Base/Neutral and Acid Extractables and Recommended Reporting Limits

Analytes	CAS Number	Water, µg/L
1,1-Biphenyl	92-52-4	10
1,2,3,4-Tetrachlorobenzene	634-66-2	10
1,2,3-Trichlorobenzene	87-61-6	10
1,2,4-Trichlorobenzene	120-82-1	10
1,2-Dichlorobenzene	95-50-1	10
1,3-Dichlorobenzene	541-73-1	10
1,4-Dichlorobenzene	106-46-7	10
1-Methyl Naphthalene	90-12-0	10
2,2'-oxybis(1-chloropropane) [1]	108-60-1	10
2,4,5-Trichlorophenol	95-95-4	10
2,4,6-Trichlorophenol	88-06-2	10
2,4-Dichlorophenol	120-83-2	10
2,4-Dimethylphenol	105-67-9	10
2,4-Dinitrophenol	51-28-5	20
2,4-Dinitrotoluene	121-14-2	10
2,6-Dinitrotoluene	606-20-2	10
2-Chloronaphthalene	91-58-7	10
2-Chlorophenol	95-57-8	10
2-Methylnaphthalene	91-57-6	10
2-Methylphenol	95-48-7	10
2-Nitroaniline	88-74-4	10
2-Nitrophenol	88-75-5	10
3,3'-Dichlorobenzidine	91-94-1	10
3-Nitroaniline	99-09-2	10
3 & 4 Methylphenol	15831-10-4	10
4,6-Dinitro-2-methylphenol	534-52-1	20
4-Bromophenyl phenyl ether	101-55-3	10
4-Chloro-3-methylphenol	59-50-7	10
4-Chloroaniline	106-47-8	10
4-Chlorophenyl phenyl ether	7005-72-3	10
4-Nitroaniline	100-01-6	10
4-Nitrophenol	100-02-7	20
Acenaphthene	83-32-9	10

Analytes	CAS Number	Water, µg/L
Acenaphthylene	208-96-8	10
Aniline	62-53-3	10
Anthracene	120-12-7	10
Atrazine	1912-24-9	10
Azobenzene	103-33-3	1
Benzaldehyde	100-52-7	10
Benzenethiol	108-98-5	10
Benzidine	92-87-5	5
Benzo(a)anthracene	56-55-3	10
Benzo(a)pyrene	50-32-8	10
Benzo(b)fluoranthene	205-99-2	10
Benzo(g,h,i)perylene	191-24-2	10
Benzo(k)fluoranthene	207-08-9	10
Benzoic acid	65-85-0	20
Benzyl alcohol	100-51-6	10
Bis(2-chloroethoxy)methane	111-91-1	10
Bis(2-chloroethyl)ether	111-44-4	10
Bis(2-ethylhexyl)phthalate	117-81-7	10
Butyl benzyl phthalate	85-68-7	10
Caprolactam	105-60-2	10
Carbazole	86-74-8	10
Chrysene	218-01-9	10
Dibenz(a,h)anthracene	53-70-3	10
Dibenzofuran	132-64-9	10
Diethylphthalate	84-66-2	10
Dimethyl phthalate	131-11-3	10
Di-n-butyl phthalate	84-74-2	10
Di-n-octylphthalate	117-84-0	10
Fluoranthene	206-44-0	10
Fluorene	86-73-7	10
Hexachlorobenzene	118-74-1	10
Hexachlorobutadiene	87-68-3	10
Hexachlorocyclopentadiene	77-47-4	10
Hexachloroethane	67-72-1	10
Hexadecane	544-76-3	10
Indeno(1,2,3-cd)pyrene	193-39-5	10
Isodrin	465-73-6	10
Isophorone	78-59-1	10
Methylphenol, Total	1319-77-3	10
Naphthalene	91-20-3	10
Nitrobenzene	98-95-3	10
N-nitrosodimethylamine	62-75-9	1
N-Nitroso-di-n-propylamine	621-64-7	10
N-Nitrosodiphenylamine	86-30-6	10
Pentachlorophenol	87-86-5	10
Phenanthrene	85-01-8	10
Phenol	108-95-2	10
Pyrene	129-00-0	10
Pyridine	110-86-1	10

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Analytes	CAS Number	Water, µg/L
Phenyl Ether	101-84-8	10
Tributyl phosphate	126-73-8	10
1,2,4,5-Tetrachlorobenzene	95-94-3	10
1,3,5-Trinitrobenzene	99-35-4	10
1,3-Dinitrobenzene	99-65-0	10
1,4-Naphthoquinone	130-15-4	10
1-Naphthylamine	134-32-7	10
2,3,4,6-Tetrachlorophenol	58-90-2	10
2,4-Toluene diamine	95-80-7	10
2,6-Dichlorophenol	87-65-0	10
2-Acetylaminofluorene	53-96-3	10
2-Naphthylamine	91-59-8	10
2-Picoline	109-06-8	10
2-secbutyl-4,6-dinitrophenol (Dinoseb2)	88-85-7	10
3,3'-Dimethylbenzidine	119-93-7	10
3-Methylcholanthrene	56-49-5	10
4-Aminobiphenyl	92-67-1	10
4-Nitroquinoline-1-oxide	56-57-5	10
5-Nitro-o-toluidine	99-55-8	10
7,12-Dimethylbenz(a)anthracene	57-97-6	10
a,a-Dimethyl-phenethylamine	122-09-8	10
Acetophenone	98-86-2	10
Aramite	140-57-8	10
Diallate[2]	2303-16-4	10
Dibenz(a,j)acridine	224-42-0	10
Dimethoate	60-51-5	10
Disulfoton	298-04-4	10
Ethyl methanesulfonate	62-50-0	10
Phenylmercaptan - Thiophenol (Benzenethiol)	108-98-5	10
Hexachloropropene	1888-71-7	10
Isosafrole	120-58-1	10
Methapyrilene	91-80-5	10
Methyl methanesulfonate	66-27-3	10
Methyl parathion	298-00-0	10
N-Nitrosodiethylamine	55-18-5	10
n-Nitrosodi-n-butylamine	924-16-3	10
N-Nitrosomethylethylamine	10595-95-6	10
N-Nitrosomorpholine	59-89-2	10
N-Nitrosopiperidine	100-75-4	10
N-Nitrosopyrrolidine	930-55-2	10
o,o,o-Triethyl-Phosphorothioate	126-68-1	10
o-Toluidine	95-53-4	10
p-(Dimethylamino)azobenzene	60-11-7	10
p-Chlorobenzilate	510-15-6	10
Pentachlorobenzene	608-93-5	10
Pentachloroethane	76-01-7	10
Pentachloronitrobenzene	82-68-8	10

Analytes	CAS Number	Water, µg/L
Phenacetin	62-44-2	10
Phorate	298-02-2	10
p-Phenylenediamine	106-50-3	10
Pronamide	23950-58-5	10
Safrole	94-59-7	10
Sulfotepp	3689-24-5	10
Thionazin	297-97-2	10
1-Chloronaphthalene	90-13-1	10
1,4-Dinitrobenzene	100-25-4	10
1,2-Dinitrobenzene	528-29-0	10
4,4'-Methylenebis(2-chloroaniline)	101-14-4	10
Diphenylamine	122-39-4	10
1,2-Diphenylhydrazine	122-66-7	1

1 2,2'oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether.

Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore, these two compounds cannot be distinguished. Diphenylamine is used in the calibration standard to prove a response for both Diphenylamine and N-nitrosodiphenylamine.

Table 2 – DFTTP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 - 80 % of mass 198
68	< 2% of mass 69
69	Mass 69 relative abundance
70	< 2% of mass 69
127	25 - 75 % of mass 198
197	< 1% of mass 198
198	Base peak, 100% of relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	> 0.75% of mass 198
441	Present, but less than mass 443
442	40 - 110% of mass 198
443	15 - 24% of mass 442

Criteria in these tables are for quadrupole and time-of-flight instruments. Alternative tuning criteria from other published EPA reference methods may be used provided method performance is not adversely affected. Alternative tuning criteria specified by an instrument manufacturer may also be used for another type of mass spectrometer, provided method performance is not adversely affected.

Table 3 – Internal and Surrogate Standards

Internal Standards	Surrogate Standards
1,4- Dichlorobenzene-d_4	Nitrobenzene-d_5
Naphthalene-d_8	2-Flurorobiphenyl
Acenaphthene-d_{10}	p-Terphenyl-d_{14}
Chrysene-d_{12}	2-Flurophenol
Perylene-d_{12}	2,4,6-Tribromophenol
Phenanthrene -d_{10}	Phenol-d_5

Table 4: Method 625 Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
1,4-Dioxane	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	N-Nitrosopiperidine	Isosafrole
Pyridine	Isophorone	1,2,4,5-Tetrachlorobenzene
2-Picoline	2-Nitrophenol	2,4,5-Trichlorophenol
N-Nitrosomethylethylamine	2,4-Dimethyphenol	2,4,6-Trichlorophenol
Acrylamide	Benzoic Acid	1,1'-Biphenyl
Methyl methanesulfonate	o,o',o''-Triethylphosphorothioate	2-Chloronaphthalene
N-Nitrosodiethylamine	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Ethyl methanesulfonate	alpha,alpha-Dimethyl phenethylamine	2-Nitroaniline
Benzaldehyde	2,4-Dichlorophenol	1,4-Naphthoquinone
Phenol	1,2,4-Trichlorobenzene	1,4-Dinitrobenzene
Aniline	Naphthalene	Dimethyl phthalate
Bis(2-chloroethyl)ether	4-Chloroaniline	1,3-Dinitrobenzene
Pentachloroethane	2,6-Dichlorophenol	2,6-Dinitrotoluene
2-Chlorophenol	Hexachloropropene	Acenaphthylene
n-Decane	Hexachlorobutadiene	3-Nitroaniline
1,3-Dichlorobenzene	Quinoline	2,4-Dinitrophenol
1,4-Dichlorobenzene	N-Nitrosodi-n-butylamine	Acenaphthene
Benzyl alcohol	Caprolactam	4-Nitrophenol
1,2-Dichlorobenzene	p-Phenylene diamine	2,4-Dinitrotoluene
2-Methylphenol	4-Chloro-3-methylphenol	Pentachlorobenzene
2,2'-oxybis[1-chloropropane]	Safrole, Total	Dibenzofuran
Indene	2,4-Toluene diamine	1-Naphthylamine
N-Nitrosopyrrolidine	2-Methylnaphthalene	2,3,5,6-tetrachlorophenol
3 & 4 Methylphenol	Nitrobenzene-d5	2,3,4,6-Tetrachlorophenol
N-Nitrosodi-n-propylamine		2-Naphthylamine
N-Nitrosomorpholine		Diethyl phthalate
Acetophenone		Hexadecane
2-Toluidine		Thionazin
Hexachloroethane		4-Chlorophenyl phenyl ether
2-Fluorophenol		N-Nitro-o-toluidine
Phenol-d5		4-Nitroaniline
		Fluorene
		2-Fluorobiphenyl (Surr)
		Phenyl Ether
		Hexachlorocyclopentadiene
		2,4,6-Tribromophenol

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4,6-Dinitro-2-methylphenol	Benzidine	Di-n-octyl phthalate
Diphenylamine	Pyrene	7,12-Dimethylbenz(a)anthracene
N-Nitrosodiphenylamine	Aramite, Total	Benzo[b]fluoranthene
Azobenzene	p-Dimethylamino azobenzene	Benzo[k]fluoranthene
Sulfotepp	Chlorobenzilate	Benzo[a]pyrene
1,3,5-Trinitrobenzene		3-Methylcholanthrene
Phenacetin	Butyl benzyl phthalate	Dibenz[a,h]acridine
Diallate	3,3'-Dimethylbenzidine	Indeno[1,2,3-cd]pyrene
Phorate	2-Acetylaminofluorene	Dibenz(a,h)anthracene
4-Bromophenyl phenyl ether	4,4'-Methylene bis(2-chloroaniline)	Benzo[g,h,i]perylene
Dimethoate	3,3'-Dichlorobenzidine	
Hexachlorobenzene	Bis(2-ethylhexyl) phthalate	
Atrazine	Benzo[a]anthracene	
4-Aminobiphenyl	Chrysene	
Pronamide	6-Methylchrysene	
Pentachlorophenol	Terphenyl-d14	
n-Octadecane		
Pentachloronitrobenzene		
Disulfoton		
Dinoseb		
Phenanthrene		
Anthracene		
Carbazole		
Methyl parathion		
Di-n-butyl phthalate		
Ethyl Parathion		
4-Nitroquinoline-1-oxide		
Methapyrilene		
Isodrin		
Fluoranthene		
4,6-Dinitro-2-methylphenol		

TABLE 5a: Analytes (List 1) in Approximate Retention Time Order and Characteristic Ions

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	44
Pyridine	79	52	51
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d_5 (Surrogate Standard)	99	42	71
Benzaldehyde	77	105	106
Aniline	93	66	65
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene-d_4 (Internal Standard)	152	150	115

Analyte	Primary	Secondary	Tertiary
1,4-Dichlorobenzene	146	148	113
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	113
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	79
Indene	115	116	89
3&4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	43	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d_5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d_8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
2,6-Dichlorophenol	162	164	63
Hexachlorobutadiene	225	223	227
Caprolactam	113	55	56
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
Acetophenone	105	77	51
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
1,1'-Biphenyl	154	153	76
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	63	89
Acenaphthene-d_{10} (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	182	77
N-Nitrosodiphenylamine	169	168	167

Analyte	Primary	Secondary	Tertiary
1,2,4,5-Tetrachlorobenzene	216		
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Atrazine	200	173	215
Pentachlorophenol	266	264	268
Phenanthrene-d_{10} (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
1,3-Dinitrobenzene	168	76	75
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
2,3,4,6-Tetrachlorophenol	232	230	131
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d_{14} (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d_{12} (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d_{12} (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 5b: Analytes (List 2) in Approximate Retention Time Order and Characteristic Ions

Analyte	Primary	Secondary	Tertiary
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
1-Chloronaphthalene	162	127	164
N-Nitrosopyrrolidine	100	41	42

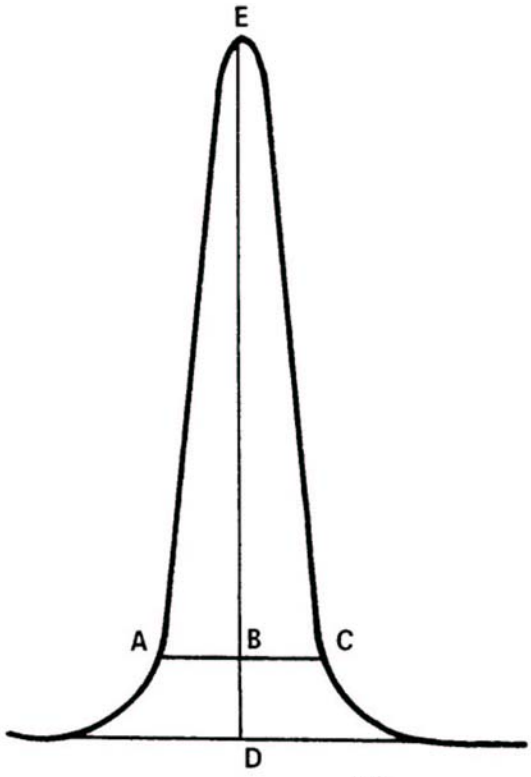
Analyte	Primary	Secondary	Tertiary
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	42
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	107
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	116
2,3,5,6-Tetrachlorophenol	232	230	131
2-Naphthylamine	143	115	116
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	43	234
Dimethoate	87	93	125
4-Aminobiphenyl	169	168	170
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
Ethyl parathion	97	109	291
4-Nitroquinoline-1-oxide	190	128	160
Methapyrilene	58	97	72
Aramite 1	185	63	135
Aramite 2	185	63	135
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	213	211
2-Acetylaminofluorene	181	180	223
Dibenz(a,h)acridine	279	280	278
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 6 – Method 625 LCS and MS/MSD Compounds and Spike Concentrations

LCS Compounds	Spiking Level, ng/µL in extract	Spiking Level, ng/µL in extract LVI Samples
Phenol	20	32
Bis(2-chloroethyl)ether	20	32
2-Chlorophenol	20	32
1,3-Dichlorobenzene	20	32
1,4-Dichlorobenzene	20	32
1,2-Dichlorobenzene	20	32
2,2'-oxybis(1-chloropropane)	20	32
N-Nitroso-di-n-propylamine	20	32
Hexachloroethane	20	32
Nitrobenzene	20	32
Isophorone	20	32
2-Nitrophenol	20	32
2,4-Dimethylphenol	20	32
Bis(2-chloroethoxy)methane	20	32
2,4-Dichlorophenol	20	32
1,2,4-Trichlorobenzene	20	32
Naphthalene	20	32
Hexachlorobutadiene	20	32
4-Chloro-3-methylphenol	20	32
Hexachlorocyclopentadiene	20	32
2,4,6-Trichlorophenol	20	32
2-Chloronaphthalene	20	32
Dimethyl phthalate	20	32
Acenaphthylene	20	32
Acenaphthene	20	32
2,4-Dinitrophenol	40	64
4-Nitrophenol	40	64
2,4-Dinitrotoluene	20	32
2,6-Dinitrotoluene	20	32
Diethylphthalate	20	32
4-Chlorophenyl phenyl ether	20	32
Fluorene	20	32
4,6-Dinitro-2-methylphenol	40	40
N-Nitrosodiphenylamine	20	32
4-Bromophenyl phenyl ether	20	32
Hexachlorobenzene	20	32
Pentachlorophenol	40	64
Phenanthrene	20	32
Anthracene	20	32
Di-n-butyl phthalate	20	32
Fluoranthene	20	32
Benzidine	40	64
Pyrene	20	32
Butyl benzyl phthalate	20	32
3,3'-Dichlorobenzidine	40	64
Benzo(a)anthracene	20	32

LCS Compounds	Spiking Level, ng/µL in extract	Spiking Level, ng/µL in extract LVI Samples
Bis(2-ethylhexyl)phthalate	20	32
Chrysene	20	32
Di-n-octylphthalate	20	32
Benzo(b)fluoranthene	20	32
Benzo(k)fluoranthene	20	32
Benzo(a)pyrene	20	32
Indeno(1,2,3-cd)pyrene	20	32
Dibenz(a,h)anthracene	20	32
Benzo(g,h,i)perylene	20	32
1,2-Diphenylhydrazine	20	32
N-nitrosodimethylamine	20	32
1,1'-Biphenyl	20	32
1,2,4,5-Tetrachlorobenzene	20	32
1,3-Dinitrobenzene	20	32
1,4-Dioxane	20	32
2,3,4,6-Tetrachlorophenol	20	32
2,4,5-Trichlorophenol	20	32
2,6-Dichlorophenol	20	32
2-Methylnaphthalene	20	32
2-Methylphenol	20	32
2-Nitroaniline	20	32
3 & 4-Methylphenol	20	32
3-Nitroaniline	20	32
4-Nitroaniline	20	32
Acetophenone	20	32
Aniline	20	32
Azobenzene	20	32
Benzyl alcohol	20	32
Carbazole	20	32
Dibenzofuran	20	32
n-Decane	20	32
n-Octadecane	20	32
Pyridine	40	64
Atrazine	40	64
Caprolactam	40	64
Benzoic acid	40	64
Diphenylamine	20	32
Benzaldehyde	40	64

Appendix A: Calculation of the DFTPP Tailing Factor



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

Figure 13. Tailing factor calculation.

Title: GC/MS VOLATILE ORGANIC COMPOUNDS

[Method 624]

Approvals (Signature/Date):

Technology Specialist	09/05/17 Date	Health & Safety Coordinator	08/24/17 Date
Quality Assurance Manager	09/27/17 Date	Technical Director	09/08/17 Date

This SOP was previously identified as SOP No. NC-MS-006, Rev 6, dated 3/11/16

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in municipal and industrial wastewater discharges.

1.2. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. A list of compounds routinely quantified by this method is found in Tables 4 and 5.

1.3. This standard operating procedure is based on EPA Method 624, a purge-and-trap gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L. Reporting limits are listed in Table 5.

1.4. This document accurately reflects current laboratory Standard Operating Procedures (SOPs) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Purge-and-Trap Process

2.2.1. An inert gas is bubbled through the sample solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column (trap) is heated and back-flushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components, which are detected with a mass spectrometer.

2.3. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS area response for an appropriate ion characteristic of that compound to the area response for another ion produced by an internal standard

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. The use of ultra-high purity gases, pre-purged purified reagent water, and approved lots of purge-and-trap grade methanol will greatly reduce introduction of contaminants. In extreme cases, the purging vessels may be pre-purged to isolate the instrument from laboratory air that may have become contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.3. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially or in the same purge position on an autosampler. Whenever an unusually concentrated sample is analyzed, it should be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.4. Matrix interferences may be caused by non-target contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.

4.5. Some samples may foam when purged due to surfactants present in the sample. The sample will need to be analyzed at a dilution that will not result in foaming.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.3. There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Materials section. Employees

must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness, and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves **must** be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: various

6.2. Syringes: 5 mL, 25ml, and 50 mL glass with Luerlok tip

6.3. Balance: analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g

6.4. Glassware: beakers, volumetric flasks

6.5. Purge-and-Trap Device: The purge-and-trap device consists of the sample sparger, the trap, and the desorber.

6.5.1. Sample sparger: OI Analytical Model 4560 sample concentrator, OI Analytical Model 4660 sample concentrator, OI Model 4552 Autosampler, or other autosampler capable of reproducible results.

6.5.2. Traps: OI Trap #10, or other equivalent traps that will meet the necessary quality control criteria. Before initial use, the trap must be conditioned by baking for a suitable length of time at 210°C while back-flushing with a helium flow of at least 20 mL/min or follow the trap manufacturer recommendations. Vent the gas to the room--not the analytical column.

6.5.3. Desorber: OI Analytical Model 4560, EST Encon, or equivalent.

6.6. Recommended Gas Chromatograph/Mass Spectrometer System

6.6.1. Gas Chromatograph: The following Gas Chromatographs are used--Agilent 6890, Agilent 7890.

6.6.2. Gas Chromatographic Column 1: 20 m x 0.18mm ID DB624 with 1 μm film thickness.

6.6.3. Mass Spectrometer: Capable of scanning 35-300 amu every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet. The following mass spectrometers are used: Agilent 5973, Agilent 5975.

6.6.4. GC/MS interface: Split injection technique is used.

6.6.5. Data System: A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances vs. time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against user-generated reference library spectra. The most recent release of the NIST/EPA NBS mass spectral library should be used as the reference library for TICs. The computer system must also be capable of backing up data for long-term off-line storage.

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Methanol: Purge-and-Trap grade, high purity

7.1.2. Reagent Water: High purity water that meets the requirements for a method blank when analyzed (see Section 9.2). Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight.

7.2. Standards

7.2.1. Target Calibration Standard

7.2.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon®-sealed screw-cap bottles with minimal headspace at
$<$ -10°C. Stock standards must be replaced after one year or sooner if comparison with check standards indicates a problem. Purchased standards must be replaced upon manufacturer's expiration date.

7.2.1.2. Secondary Dilution Standards: A working solution containing the compounds of interest is prepared monthly or sooner from the stock solutions(s) in methanol. Gases (listed below) are prepared weekly from stock solutions in methanol. These standards are stored with minimal headspace at 4°C $\pm$ 2°C and monitored for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

<u>Gases</u>
Chloromethane
Bromomethane
Chloroethane
Vinyl chloride
Dichlorodifluoromethane
Trichlorofluoromethane

7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.2.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. Prepare the internal standard stock and the working standard solutions in methanol as described in Sections 7.2.1.1 and 7.2.1.2.

7.2.3. Surrogate Standards: The recommended surrogate standards are Toluene-d_8, 4-Bromofluorobenzene, and 1,2-Dichloroethane-d_4. Stock standards and a surrogate standard spiking solution should be prepared as described in Sections

7.2.1.1 and 7.2.1.2. Each sample undergoing GC/MS analysis must be spiked with surrogate standards prior to analysis.

7.2.4. Laboratory Control Sample Spiking Solutions: A midrange standard is prepared as described in Section 7.2.1.2 from a source other than that used for the calibration standards. The LCS containing the compounds listed in Table 6 is prepared in water at a concentration of 20 ug/L.

7.2.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS.

7.2.6. Tuning Standard: A standard containing 50 ng/μL of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. All water samples are preserved with four drops of concentrated hydrochloric acid per 40 mL of sample.

8.1.1. If the sample requires analysis of halogenated compounds, the pH is recorded; and the potential impact of preservation is documented in the project narrative. The analysis is performed on an unpreserved aliquot only if sufficient sample is provided by the client.

NOTE: An unpreserved sample must be analyzed when 2-Chloroethyl vinyl ether and/or acrolein are compounds of interest, as these compounds cannot be reliably recovered from a preserved sample.

8.2. Samples are stored in glass containers with Teflon®-lined caps at 4° C ± 2°C with no headspace.

8.3. The holding time is 14 days [for preserved samples] from sampling to the completion of the analysis.

8.4. The holding time for an unpreserved sample is seven days unless aromatic volatiles (notably benzene, toluene, and ethyl benzene) are not requested, in which case the holding time is 14 days.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (LCS, MB, MS), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB consisting of all reagents added to the samples must be analyzed (prepared) with each batch of samples. The MB is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data. The MB should not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants: see below).

9.2.2. Corrective Action for Blanks

9.2.2.1. If the analyte is a common laboratory contaminant (Methylene chloride, Acetone, 2-Butanone), the data may be reported with qualifiers if the concentration of the analyte in the MB is at a concentration up to five times the reporting limit. **Such action must be addressed in the project narrative.**

9.2.2.2. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.2.2.3. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.2.2.4. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. LCS's are well-characterized laboratory-generated samples used to monitor the laboratory day-to-day performance of routine analytical methods. One aqueous LCS from an independent source must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Corrective Action for LCS

9.3.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.3.2.2. **NOTE:** If the out-of-control analyte exceeds the upper control limit and is not detected (ND) in the associated sample(s), then the system may be considered to be in control; and corrective action may not be necessary. Corrective action will be re-preparation and re-analysis of

the batch unless the client agrees that other corrective action is acceptable

9.4. Matrix Spike (MS)

9.4.1. An MS is analyzed with every batch of 20 samples.

9.4.2. The spiking solution is a full analyte spike added to the sample at a concentration of 20 μg/L.

9.4.2.1. If any individual recovery falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

9.4.2.2. If the recovery for any component is outside QC limits for both the matrix spike and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include re-analysis of the batch.

9.4.2.3. The matrix spike must be analyzed at the same dilution as the un-spiked sample.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Each sample, MB, LCS, and MS is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.5.3. Corrective action is required if the surrogate compound(s) in the blank or samples fall outside the recovery limits. The following corrective action should be taken.

9.5.3.1. Check all calculations to ensure no errors were made. Check internal standard and surrogate spiking solution for degradation, contamination, etc. Also check instrument performance.

9.5.3.2. If the above step fails to reveal a problem, re-analyze the blanks and/or samples. If re-analysis does not confirm original results and is within QC acceptance criteria, then the problem was within the analyst's control, and only the re-analyzed data should be reported.

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9.5.3.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS and the surrogate recoveries in the MS are also outside the control limits, then the sample and the MS do not require re-analysis as this phenomenon would indicate a possible matrix effect.

9.5.3.4. If the sample has surrogate recoveries out high and contains no analyte results above reporting limit, then the sample may be reported without requiring re-analysis. This anomaly must be addressed with a non-conformance narrative.

9.5.3.5. If the re-analysis does confirm the original results, then the following steps should be taken.

9.5.3.5.1. For a blank, the analytical system must be considered out of control. The problem must be corrected before continuing. This may include recalibration of the instrument.

9.5.3.5.2. For a sample, the results from the original analyses must be reported and the data flagged as surrogates out due to matrix effect.

9.6. Control Limits

9.6.1. Control limits are method specified.

9.6.2. Control limits are easily accessible via the LIMs.

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.7.2. MDLs are easily accessible via the LIMs.

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of three concentrations (analyzed under the same BFB tune) to determine the linearity of the response utilizing target

calibration standards. Once the system has been calibrated, the calibration must be verified each 24-hour time period for each GC/MS system.

10.2. Recommended Instrument Conditions

10.2.1. General

Electron Energy:	70 volts (nominal)
Mass Range:	35-300 amu
Scan Time:	To give 5 scans/peak, but not to exceed 2 seconds/scan
Injector Temperature:	200-250°C
Source Temperature:	According to manufacturer's specifications
Transfer Line Temperature:	250-300°C
Max Purge Flow:	40 mL/minute

10.2.2. Gas chromatograph suggested temperature program

10.2.2.1. For column 1, DB-624 Column

10.2.2.1.1. BFB Analysis

Initial Temperature:	100°C
Initial Hold Time:	0.1 minute
Temperature Program:	20°C/minute
Final Temperature:	200°C
Final Hold Time:	None

10.2.2.1.2. Sample Analysis

Initial Temperature:	45°C
Initial Hold Time:	2 minutes
Temperature Program:	15°C/minute
Final Temperature:	200°C
Final Hold Time:	2 minutes

10.3. Instrument Tuning

10.3.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 1 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each 24-hour time period. The 24-hour time period begins at the moment of injection of BFB

10.4. Initial Calibration

10.4.1. A series of at least three initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. The recommended calibration levels are as follows: 1 μg/L, 5 μg/L, 20 μg/L, 50 μg/L, and 100μg/L. Additional concentrations may be necessary depending on working range of the analytes of interest. The internal standard calibration approach uses the following internal standards: Fluorobenzene, Chlorobenzene-d_5, 1,4-Dichlorobenzene-d_4. Each calibration standard is analyzed, and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard using the following equation.

$$RF = \frac{A}{B} x \frac{C}{E}$$

Where:
A = Area of the characteristic ion for the compound to be measured
B = Area of the characteristic ion for the specific internal standard
C = Concentration of the specific internal standard, ng
E = Concentration of the compound being measured, ng

10.4.2. The average RF is also used to check the validity of the initial calibration. The percent relative deviation (% RSD) is calculated for all compounds using the following equation.

$$\%RSD = \frac{A}{B} x\ 100$$

Where:
RSD = Relative Standard Deviation
A = Standard deviation of average RFs for a compound
B = Average of the five initial RFs for a compound

$$A = \sqrt{\sum_{i=1}^{N} \frac{(x_i - x)^2}{N-1}}$$

Where:
X_i = Value of X at I through N
N = Number of points
X = Average value of X

NOTE: If the average RF over the working range is constant (<35% RSD), the initial calibration is valid and can be used for calculations. Alternatively, results can be used to plot a calibration curve of response rations, A_s/A_{is} vs. RF.

10.4.3. Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

10.4.4. If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve re-analyzed. Corrective action may include, but not limited to, instrument maintenance and/or re-preparation of standards.

10.4.5. One of the following conditions must be satisfied to allow removal or replacement of a level.

- The data file is corrupted and unusable, or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made up standard).

10.4.6. The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

10.4.7. Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed, then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event, the number of levels remaining in the calibration must be at least that required by the method.

10.4.8. Removal of the highest or lowest point is permitted on a compound-specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

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10.5. Calibration Check: The initial calibration must be verified every day by the measurement of a calibration check sample.

10.5.1. A 20 μg/L calibration standard is analyzed every 24 hours.

10.5.2. For each parameter, compare the response with the corresponding calibration acceptance criteria found in Table 6. If the responses for all parameters of interest fall within the designated ranges, analysis of samples may begin. If any individual response falls outside the range, corrective action must occur.

NOTE: The large number of parameters in Table 6 present a substantial possibility that one or more will not meet the calibration acceptance criteria when all parameters are analyzed. **Repeat the test only for those parameters that failed to meet the calibration acceptance criteria**. If the response for a parameter does not fall within range in the second analysis, a new calibration curve must be prepared. If the parameter is out of control high, and associated samples are ND for that compound, corrective action is not required. This anomaly must be described with a non-conformance memo.

10.5.3. Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 24 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 24 hours after the BFB is acceptable.)

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Sample Preparation

11.2.1. This method applies to the analysis of waters and wastewaters; therefore, no sample preparation is necessary.

11.3. Sample Analysis

11.3.1. Preliminary Evaluation

11.3.1.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.3.1.2. Dilutions should be done just prior to the GC/MS analysis of the sample. Dilutions are made in volumetric flasks or in a 50 mL Luerlok syringe. Dilutions may also be made in 40 ml vial. Calculate the volume of reagent water required for the dilution. Fill the 50 mL syringe with

reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the 50 mL mark, and inject the proper aliquot of sample into the syringe.

11.3.1.3. The appropriate dilution is determined from the screen, previous runs, and/or historical data. The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.4. Sample Analysis Procedure

11.4.1. All samples and standard solutions must be at ambient temperature before analysis.

11.4.2. Fill a 5 mL syringe with the proper aliquot (as determined in Section 11.4) of the sample. If an autosampler unit, which samples from the VOA vial is used, no further preparation of the vial is needed.

11.4.3. Add a known amount of internal standards and surrogate standards. The internal standards and the surrogate standards may be mixed and added as one spiking solution. Inject the sample into the purging chamber. Autosampler units, which samples from the VOA vial, should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.4.4. Purge the sample for at least 11 minutes. Be sure the trap is cooled below 35°C.

11.4.5. After purging is complete, desorb the sample at 180°C for one minute or per trap manufacturer recommendation, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for 5-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.4.6. Initial Review and Corrective Action

11.4.6.1. If the retention time for any internal standard changes by more than 0.5 minutes from the last calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required.

11.4.6.2. Elution of the compound at the same GC relative retention time (RRT) as the standard compounds; the sample component must compare with 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same tune as the sample. If there is interference, the RRT should be assigned using EICP for ions unique to the compound of interest.

11.4.6.3. If the retention time of any internal standard varies by more than 0.1 minute from the preceding calibration standard, the data must be carefully evaluated to ensure that no analytes have shifted outside their retention time windows.

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11.4.6.4. The mass spectrum of the compound in the sample must correspond with the mass spectrum of the compound in the standard.

11.4.6.4.1. The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

11.4.6.4.2. The retention time must fall within ±30 seconds of the retention time of the authentic compound.

11.4.6.4.3. The relative peak heights of the three characteristic masses in the EICPS must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

11.4.7. Internal Standard References

11.4.7.1. The volatile internal standards with corresponding analytes assigned for quantitation are shown in Table 2.

11.4.8. Tentatively Identified Compounds

11.4.8.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

11.4.8.1.1. Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

11.4.8.1.2. The relative intensities of the major ions should agree within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

11.4.8.1.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

11.4.8.1.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.4.8.1.5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the spectrum because of background contamination or co-eluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

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11.4.8.2. Computer-generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches should the analyst assign a tentative identification.

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

12. DATA ANALYSIS AND CALCULATIONS

12.1. When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification is based on the internal standard technique using the following calculation.

12.1.1. $$\textit{Concentration, } \mu g / L = \frac{A \times B}{C \times E \times RF} \times D$$

Where:

A = Area of characteristic ion for the compound being measured (Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.)

B = Amount of internal standard injected, ng

C = Area of characteristic ion for the internal standard

D = Dilution Factor = $\frac{\textit{Final Dilution Volume, mL}}{\textit{Initial Volume Used for Dilution, mL}}$

E = Volume of water purged, mL

RF = Response Factor for the compound being measured

12.2. When a TIC has been identified, the quantitation of that compound is based on the integrated abundance of the total ion chromatogram for that compound. Calculations are identical to those in Section 12.1.1 with the following exceptions:

A = Area of total ion chromatogram for compound being measured

C = Area of total ion chromatogram for the nearest internal standard without interference

RF = 1.0

12.3. LCS Recovery

$$\text{LCS Recovery, \%} = \frac{SSR}{SA} \times 100$$

Where,

SR = Sample Result
SA = Spiked amount

12.4. MS/MSD (if applicable) Recovery

$$\text{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample result
SR = Sample Result
SA = Spiked amount

12.5. Relative Percent Difference (RPD)

$$\text{RPD} = \frac{|\text{MSR - MSDR}|}{\frac{1}{2}(\text{MSR + MSDR})} \times 100$$

Where: RPD = Relative percent difference
MSR = Matrix spike result
MSDR = Matrix spike duplicate result

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State, and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Used samples: Samples are collected in boxes and removed from the Lab to storage. The Waste Coordinator handles crushing the vials and proper disposal.

15.2.1.2. Methanol waste from rinses and standards: Methanol waste is discarded as a flammable liquid by placing in a waste container identified as "Mixed Flammable Solvent Waste".

15.2.1.3. Laboratory generated aqueous waste: Waste stream must be collected and neutralized before discharge to a sewer system if the pH is less than 5. If not neutralized, it must be placed in a waste container identified as "Acid Waste".

15.2.1.4. Expired standards: Working standards are disposed of in the flammable waste containers located in the Lab. Concentrated standards are disposed of in Lab packs by the Waste Coordinator.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Federal Register - Part VII, Environmental Protection Agency, 40 CFR, Part 136, October 26, 1989, Purgeables, Method 624

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. Revision History

Historical File:		Revision 0: 09/12/96		Revision 4: 06/30/10
		Revision 1: 06/19/03		Revision 5: 11/25/14
		Revision 2: 11/16/04		Revision 6: 03/11/16
		Revision 3: 05/15/08		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.4. Standards and Reagents, NC-QA-017

16.2.5. Acceptable Manual Integration Practices, CA-Q-S-002

16.2.6. Calibration Curves (General), CA-Q-S-005

16.2.7. Selection of Calibration Points, CA-T-P-002

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications from the reference method

17.1.1. Method 624 has been modified in this SOP to use capillary columns rather than the packed columns listed in the reference method. This provides improved separation of the target analytes and improved detection limits.

17.1.2. The quantitation and qualifier ions for some compounds have been changed from those recommended in Method 624 in order to improve the reliability of qualitative identification.

17.1.3. Method 624 provides for the analysis of samples in an unpreserved state and recommends that a separate aliquot of sample is taken and preserved if aromatic volatiles are requested. Unless a second unpreserved aliquot is provided by the client for the analysis of halogenated volatiles, all samples are preserved at the

time of sampling. The pH is recorded, and the potential impact of preservation on the analysis of halogenated compounds is documented in the project narrative.

17.1.4. Xylenes are not listed in Method 624; however, the laboratory has elected to add them to the analyte list.

17.1.5. Two internal standards and one surrogate standard are used that are not listed in the table of suggested surrogate and internal standards.

17.1.6. Samples may also be purged at a temperature above ambient as long as all calibration standards, samples, and QC samples are purged at the same temperature; and acceptable method performance is demonstrated.

17.1.7. Method 624 recommends the surrogate and internal standards be added to samples, quality control, and calibration standards at a concentration of 30 μg/L; however, in order to provide lower reporting limits, the concentration of internal standards added is 20 μg/L and the concentration of surrogate standards is 20 μg/L.

17.2. Reporting limits

17.2.1. For undiluted samples, lower reporting limits (RLs) are listed in Table 5.

17.2.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.3. Troubleshooting guide

17.3.1. Consult the instrument manufacturer's service manuals for guidance.

17.4. Tables

Table 1: BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of mass 95
75	30% to 60% of mass 95
95	Base peak, 100% relative abundance
96	5% to 9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5% to 9% of mass 174
176	Greater than 95%, but less than 101% of mass 174
177	5% to 9% of mass 176

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Table 2: Internal Standards With Corresponding Analytes

Fluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene-d4
Dichlorodifluoromethane	Bromofluorobenzene	1,1,2,2-Tetrachloroethane
Chloromethane	Trans-1,3-Dichloropropene	1,3-Dichlorobenzene
Vinyl Chloride	Tetrachloroethene	1,4-Dichlorobenzene
Bromomethane	Dibromochloromethane	1,2-Dichlorobenzene
Chloroethane	Chlorobenzene	Naphthalene
Trichlorofluoromethane	Ethylbenzene	
Acrolein	M & p-xylenes	
1,1-Dichloroethene	o-Xylene	
Methylene Chloride	Xylenes (total)	
Acrylonitrile	1,1,2-Trichloroethane	
Trans-1,2-Dichloroethene	Bromoform	
1,1-Dichloroethane	Toluene d-8	
Chloroform	Toluene	
1,1,1-Trichloroethane		
Carbon Tetrachloride		
1,2-Dichloroethane-d4		
1,2-Dichloroethane		
Benzene		
Trichloroethene		
1,2-Dichloropropane		
Bromodichloromethane		
2-Chloroethylvinyl ether		
Cis-1,3-Dichloropropene		
MTBE		

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Table 3: Mass Spectral Ions

Compound	Electron Impact		
	Primary*	Secondary	Secondary
Acrolein	56	55	58
Acrylonitrile	53	52	51
Benzene	78	52	77
Fluorobenzene (Internal Standard)	96		
Bromodichloromethane	83	85	129
4-Bromofluorobenzene (Surrogate)	95	174	176
Bromoform	173	171	175, 252
Bromomethane	94	96	
Carbon tetrachloride	117	119	121
Chlorobenzene	112	114	77
Chlorobenzene-d_5 (Internal Standard)	117	82	119
Chlorodibromomethane	129	127	206, 208
Chloroethane	64	66	49
2-Chloroethyl vinyl ether	63	65	106
Chloroform	83	85	47
Chloromethane	50	52	49
Dichlorobenzene (all isomers)	146	148	111
Dichlorodifluoromethane	85	87	50, 101
1,1-Dichloroethane	63	65	83
1,2-Dichloroethane	62	64	98
1,2-Dichloroethane-d_4 (Surrogate)	65	67	102
1,1-Dichloroethene	61	96	98
trans-1,2-Dichloroethene	61	96	98
1,2-Dichloropropane	63	62	41
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	
Ethylbenzene	106	91	

Compound	Electron Impact		
	Primary*	Secondary	Secondary
Methylene chloride	49	84	51, 86
MTBE	73	41	57
Naphthalene	128		
1,1,2,2-Tetrachloroethane	83	85	131, 133
Tetrachloroethene	166	129	131, 164
Toluene	91	92	65
Toluene-d_8 (Surrogate)	98	70	100
1,1,1-Trichloroethane	97	99	117
1,1,2-Trichloroethane	97	83	85, 99
Trichloroethene	130	95	97, 132
Trichlorofluoromethane	101	103	66
Cis-1,2-Dichloroethene	61	96	98
Vinyl chloride	62	64	61
Xylene	106	91	

** The primary ion should be used for quantitation unless interferences are present, in which case a secondary ion may be used.*

Table 4: Approximate Retention Times (in Minutes)

Volatiles	Column 1
Acetone	2.755
Acrolein	2.637
Acrylonitrile	3.311
Benzene	4.897
Bromodichloromethane	5.855
Bromoform	8.600
Bromomethane	2.021
2-Butanone	4.163
Carbon disulfide	2.933
Carbon tetrachloride	4.731
Chlorobenzene	7.831

Volatiles	Column 1
Chloroethane	2.116
Chloroform	4.423
Chloromethane	1.643
Dibromochloromethane	7.263
1,2-Dichlorobenzene	10.435
1,3-Dichlorobenzene	9.973
1,4-Dichlorobenzene	10.056
1,1-Dichloroethane	3.690
1,2-Dichloroethane	4.897
1,1-Dichloroethene	2.731
trans-1,2-Dichloroethene	3.358
1,2-Dichloropropane	5.619
cis-1,3-Dichloropropene	6.234
trans-1,3-Dichloropropene	6.719
Ethylbenzene	7.914
2-Hexanone	7.109
4-Methyl-2-pentanone	6.352
Methylene chloride	3.122
MTBE	3.547
Naphthalene	12.492
Styrene	8.411
1,1,2,2-Tetrachloroethane	9.038
Tetrachloroethene	7.038
Toluene	6.542
1,1,1-Trichloroethane	4.589
1,1,2-Trichloroethane	6.897
Trichloroethene	5.441
Trichlorofluoromethane	2.317
Vinyl acetate	3.713
Vinyl chloride	1.737

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Table 5: Reporting Limits for Volatile Organic Compounds

Compound	CAS No.	Reporting Limit µg/L	Low Level Reporting Limit µg/L
Acrolein[1]	107-02-8	100	20
Acrylonitrile[1]	107-13-1	100	20
Benzene	71-43-2	5	1
Bromodichloromethane	75-27-4	5	1
Bromoform	75-25-2	5	1
Bromomethane	74-83-9	5	1
Carbon tetrachloride	56-23-5	5	1
Chlorobenzene	108-90-7	5	1
Chloroethane	75-00-3	5	1
Chloroform	67-66-3	5	1
Chloromethane	74-87-3	5	1
2-Chloroethyl vinyl ether	110-75-8	10	10
Dibromochloromethane	124-48-1	5	1
1,1-Dichloroethane	75-34-3	5	1
1,2-Dichlorobenzene	95-50-1	5	1
1,3-Dichlorobenzene	541-73-1	5	1
1,4-Dichlorobenzene	106-46-7	5	1
1,1-Dichloroethene	75-35-4	5	1
1,2-Dichloroethane	107-06-2	5	1
1,2-Dichloropropane	78-87-5	5	1
cis-1,3-Dichloropropene	10061-01-5	5	1
Ethylbenzene	100-41-4	5	1
Methylene chloride	75-09-2	5	1
MTBE	1634-04-4	5	1
Naphthalene	91-20-3	5	1
1,1,2,2-Tetrachloroethane	79-34-5	5	1
Tetrachloroethene	127-18-4	5	1
Toluene	108-88-3	5	1
trans-1,2-Dichloroethene	156-60-5	2.5	1

Compound	CAS No.	Reporting Limit µg/L	Low Level Reporting Limit µg/L
trans-1,3-Dichloropropene	10061-02-6	5	1
1,1,1-Trichloroethane	71-55-6	5	1
1,1,2-Trichloroethane	79-00-5	5	1
Trichloroethene	79-01-6	5	1
Trichlorofluoromethane	75-69-4	10	1
Vinyl chloride	75-01-4	10	1
Xylenes (Total)	1330-20-7	5	2

[1] *Method 624 may be used to screen for Acrolein and Acrylonitrile; however, Method 603 is preferred for the analysis of these compounds.*

Table 6: QC Acceptance Criteria

Analytes	Daily QC check acceptance criteria (20µg/L spike)	Matrix spike and LCS acceptance criteria (% recovery)
Benzene	12.8-27.2	37-151
Bromodichloromethane	13.1-26.9	35-155
Bromoform	14.2-25.8	45-169
Bromomethane	2.8-37.2	D-242
Carbon tetrachloride	14.6-25.4	70-140
Chlorobenzene	13.2-26.8	37-160
Chloroethane	7.6-32.4	14-230
2-Chloroethyl vinyl ether	D-44.8	D-305
Chloroform	13.5-26.5	51-138
Chloromethane	D-40.8	D-273
Dibromochloromethane	13.5-26.5	53-149
1,2-Dichlorobenzene	12.6-27.4	18-190
1,3-Dichlorobenzene	14.6-25.4	59-156
1,4-Dichlorobenzene	12.6-27.4	18-190
1,1-Dichloroethane	14.5-25.5	59-155
1,2-Dichloroethane	13.6-26.4	49-155
1,1-Dichloroethene	10.1-29.9	D-234

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Analytes	Daily QC check acceptance criteria (20µg/L spike)	Matrix spike and LCS acceptance criteria (% recovery)
trans-1,2-Dichloroethene	13.9-26.1	54-156
1,2-Dichloropropane	6.8-33.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	D-227
trans-1,3-Dichloropropene	10.0-30.0	17-183
Ethylbenzene	11.8-28.2	37-162
Methylene chloride	12.1-27.9	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	46-157
Tetrachloroethene	14.7-25.3	64-148
Toluene	14.9-25.1	47-150
1,1,1-Trichloroethane	15.0-25.0	52-162
1,1,2-Trichloroethane	14.2-25.8	52-150
Trichloroethene	13.3-26.7	71-157
Trichlorofluoromethane	9.6-30.4	17-181
Vinyl chloride	0.8-39.2	D-251
Naphthalene[1]	10-30	32-141
MTBE[1]	10-30	52-144

1. *Naphthalene and MTBE do not have criteria listed in Method 624. In-house limits are used for these compounds.*

Title: GC/MS ANALYSIS BASED ON METHODS 8270C AND 8270D

[Method: SW846 8270C and 8270D]

Approvals (Signature/Date):

Technology Specialist	03/26/18 Date	Health & Safety Coordinator	02/07/18 Date
Quality Assurance Manager	03/26/18 Date	Technical Director	03/30/18 Date

This SOP was previously identified as SOP NC-MS-018, Rev 6, dated 10/31/17

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1. SCOPE AND APPLICATION

1.1. This method is based upon SW846 8270C and 8270D, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. Direct injection of a sample may be used in limited applications. Refer to Tables 1 and 2 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be analyzed by this method. If non-standard analytes are required, they must be validated by the procedures described in Section 13 before quantitative sample results may be reported.

1.2. The following compounds may require special treatment when being determined by this method:

1.2.1. Benzidine exhibits poor chromatography and can be subject to oxidative losses during solvent concentration. Neutral extraction should be performed if this compound is expected.

1.2.2. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.

1.2.3. N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.

1.2.4. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.2.5. Hexachlorophene is not amenable to analysis by this method.

1.2.6. 3-Methylphenol cannot be separated from 4-methylphenol under the conditions specified in this method.

1.3. Refer to Tables 1 and 2 or the LIMS for specific reporting limits. Reporting limits will be proportionately higher for sample extracts that require dilution.

2. SUMMARY OF METHOD

2.1. Aqueous samples are extracted with methylene chloride using a separatory funnel and/or a continuous extractor. Solid samples are extracted with methylene chloride / acetone using sonication, or soxhlet extractor. The extract is dried, concentrated to a final volume of 2 mL for waters and soils, and analyzed by GC/MS. Extraction

procedures are detailed in SOPs NC-OP-037, NC-OP-038, NC-OP-039, NC-OP-040, NC-OP-042, and NC-OP-043.

2.2. The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) equipped with a narrow-bore fused silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected directly to the GC.

2.3. Identification of target analytes is accomplished by comparing their electron impact mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard (IS), using a calibration curve appropriate to the intended application.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks (MBs) as described in the Quality Control section below. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If interference is detected, it is necessary to determine if the source of interference is in the instrumental analysis, preparation, and/or cleanup of the samples; then take corrective action to eliminate the problem.

4.2. The use of high purity reagents, solvents, and gases helps to minimize interference problems.

4.3. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from sample source to sample source, depending upon the nature of the site.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of solvent to check for cross contamination.

4.5. Phthalate contamination is commonly observed in this analysis and its occurrence must be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5. SAFETY PRECAUTIONS

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.

5.6. Exposure to chemicals must be maintained as low as reasonably achievable. All samples with stickers that read “Caution/Use Hood!” must be opened in the hood.

Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents must be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents must be conducted in a fume hood with the sash closed as far as the operations will permit.

5.9. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported immediately to a Laboratory Supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph/Mass Spectrometer (GC/MS) system: An analytical system complete with a temperature-programmable GC, suitable for split/splitless injection, and all required accessories, including syringes, analytical columns, and gases. The capillary column must be directly coupled to the MS source.

6.2. Column: 30m x 0.25mm ID, 0.5µm film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.

NOTE: A suitable alternative column may be substituted as long as its performance is documented to meet the requirements of the method.

6.3. Mass Spectrometer (MS): Capable of scanning from 35 to 500 AMU every one second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) that meets all of the criteria in Table 4 when the GC/MS tuning standard is injected through the GC.

6.4. GC/MS Interface: Any direct GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.

6.5. Data System: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). Software must also allow integration of the abundances in any EICP

between specified times or scan-number limits. (This is used to quantify TICs: The most recent version of the EPA/NIH Mass Spectral Library is recommended for TIC library searches.)

6.6. Syringes: 5 µL and 10 uL Hamilton Laboratory grade syringes or equivalent.

6.7. Carrier gas: Ultra high purity helium.

6.8. Autosampler vials, inserts, and caps

7. REAGENTS AND STANDARDS

7.1. A minimum five-point calibration curve is prepared. The standard preparation information is detailed in the standards and reagents module in LIMS. If a quadratic regression is used, six points must be analyzed for the calibration curve. The low point must be at or below the reporting limit. Refer to Table 10 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit (RL) and the high standard defines the upper limit or end of the range of the calibration. For Ohio VAP work, the low standard must be at, or below, the RL.

7.2. An IS solution is prepared by diluting a purchased standard. The standard preparation information is detailed in the standards and reagents module in LIMS. Compounds in the IS Mix are acenaphthene-d_{10}, chrysene-d_{12}, 1,4-dichlorobenzene-d_4, naphthalene-d_8, perylene-d_{12}, and phenanthrene-d_{10}.

7.3. Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. Preparation information is detailed in the standards and reagents module in LIMS for the Organic Prep group. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 9.

7.4. GC/MS Tuning Standard: A methylene chloride solution containing decafluorotriphenylphosphine (DFTPP) is prepared. The standard preparation information is detailed in the standards and reagents module in LIMS. Pentachlorophenol, benzidine, and DDT, must also be included in the Tuning Standard to assess chromatographic performance. All components are at 25 ug/mL.

7.5. The standards listed in Sections 7.1 to 7.4 must be refrigerated at $\leq 6^{o}C$ when not in use. Standards may be stored at -10^{o}C to -20^{o}C if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. Additional information on standards preparation, tracking, and storage can be found in SOP NC-QA-017.

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8. SAMPLE PRESERVATION AND STORAGE

8.1. Sample extracts are stored at 4 ± 2°C. Samples and extracts must be stored in suitable glass containers with Teflon®-lined caps. (Extracts will be stored for 30 days after invoicing.)

8.2. Water samples are extracted within seven days of sampling, and the extracts are analyzed within 40 days of extraction. Solids, sludges, and organic liquids are extracted within 14 days of sampling and the extracts are analyzed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / matrix spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank (MB). Batches are defined at the sample preparation stage. Batches must be kept together through the whole extraction process, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the TestAmerica Canton QC Program document (QA-003) for further details of the batch definition.

9.2. Method Blank (MB)

9.2.1. A MB is prepared and analyzed with each batch of samples. The MB consists of reagent water for aqueous samples and sodium sulfate for soil samples. Surrogates are added and the MB is carried through the entire extraction and analysis procedure. The MB must not contain any analyte of interest at or above the reporting limit (except common lab contaminants, see below). Any MB contamination above the RL must be less than 1/10 of the measured concentration of any sample in the associated preparation batch. For Wisconsin the MB must be clean down to ½ the RL.

9.2.2. If the analyte is a common laboratory contaminant the data may be reported with qualifiers if the concentration of the analyte in the MB is less than five times the RL. Such action must be taken in consultation with the client.

9.2.3. Re-analysis of any samples with reportable concentrations of analytes found in the MB is required unless other actions are agreed upon with the client.

9.2.4. If there is no target analyte greater than the RL in the samples associated with an unacceptable MB the data may be reported with qualifiers. Such action should be taken in consultation with the client. NOTE: For Ohio VAP work, there can be no target analyte greater than the RL in the MB. All

samples associated with an unacceptable MB must be re-extracted and re-analyzed. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the analytes detected in the MB are non-detect in the associated samples.

9.2.5. The MB must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the MB has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the MB and affected samples will normally be required. Consultation with the client must take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.

9.2.6. If re-analysis of the batch is not possible due to limited sample volume or other constraints, the MB is reported, all associated samples are flagged with a "B", and appropriate comments must be made in a narrative to provide further documentation.

9.2.7. Refer to the TestAmerica Canton QC Program document (QA-003) for further details of the corrective actions.

9.3. Laboratory Control Sample (LCS)

9.3.1. A LCS is prepared and analyzed with every batch of samples. All control analytes must be within established control limits. The LCS is spiked with the compounds listed in Table 6 unless otherwise specified by a client or agency.

9.3.2. If any control analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. All non-controlling compounds must attain a recovery of 10% or greater if the compound is on the client's list. Corrective action may include re-extraction and re-analysis of the batch. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.

9.3.3. If the batch is not re-extracted and re-analyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not re-analyzing might be that the MS and MSD are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

9.3.4. If re-extraction and re-analysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

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9.3.5. The LCS must have acceptable surrogate recoveries. If surrogate recoveries are low, re-extraction of the LCS and affected samples will normally be required. Consultation with the client should take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted. The exceptions are as follows: (a) insufficient sample for re-extraction (b) expired holding times, or (c) the LCS is biased high and the samples are non-detect for those analytes.

9.3.6. Ongoing monitoring of the LCS over time provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. A MS/MSD is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (see Table 6). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically-generated limits.

9.4.2. If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the laboratory is out of control and corrective action must be taken. For client specific samples, corrective action may include re-preparation and re-analysis of the batch.

9.4.3. The MS/MSD must be analyzed at the same dilution as the un-spiked sample, even if the MS compounds will be diluted out.

9.5. Surrogates

9.5.1. Every sample, MB, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery [%R]) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 9.

9.5.2. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

9.5.2.1. Check all calculations for error.

9.5.2.2. Ensure that instrument performance is acceptable.

9.5.2.3. Recalculate the data and/or re-analyze the extract if either of the above checks reveals a problem.

9.5.2.4. It is only necessary to re-prepare / re-analyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

Note: If all associated QC meets criteria (MB, LCS, MS/D), up to one surrogate per fraction may be outside of acceptance criteria, as long as the recovery is greater than 10%. **Note:** For Ohio VAP all surrogates must be within acceptance criteria. The exceptions for Ohio VAP are as follows: (a) insufficient sample for re-extraction, or (b) the surrogates are biased high and the samples are non-detect.

9.5.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for a MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require re-analysis as this phenomenon would indicate a possible matrix problem.

9.5.4. If the sample is re-analyzed and the surrogate recoveries in the re-analysis are acceptable, then the problem was within the analyst's control and only the re-analyzed data must be reported (unless the re-analysis was outside holding times, in which case, reporting both sets of results may be appropriate).

9.5.5. If the re-analysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.6. Internal Standards

9.6.1. Every sample, MB, and QC sample (including calibration standards, ICV and CCV) is spiked with internal standards.

9.6.2. When compared to the daily CCV, internal standards must be within ± 0.5 minutes and peak area recoveries must be 50% to 200%.

9.6.3. Samples with failing internal standards must be re-analyzed "undiluted" unless matrix interference is apparent. If matrix interference is apparent, dilute the sample with methylene chloride using a syringe for re-analysis. When there is obvious interference causing the IS failure that corrective action will not remedy, data must be flagged with a qualifier indicating matrix interference. If the QC has failing internal standards, the batch must be re-prepped and re-analyzed.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Deviations are not applicable for Ohio VAP projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. The instrument is tuned for decafluorotriphenylphosphine (DFTPP), calibrated initially with a minimum five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 3.

10.2. All standards and extracts are allowed to warm to room temperature before injecting.

10.3. Instrument Tuning

10.3.1. At the beginning of every 12-hour shift, the GC/MS system must be checked to see if acceptable performance criteria (Table 4) are achieved for DFTPP.

10.3.2. Inject the GC/MS tuning standard (Section 7.4). Obtain background-corrected mass spectrum of DFTPP and confirm that all the key m/z criteria in Table 4 are achieved. If all the criteria are not achieved, the analyst must retune the MS and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.3. The GC/MS tuning standard must also be used to evaluate the inertness of the chromatographic system. The tailing factor for benzidine must be less than 3.0. The tailing factor for pentachlorophenol must be less than 5. For Method 8270D, benzidine and pentachlorochlorophenol should not exceed a tailing factor of 2. DDT must be included in the tuning standard, and its breakdown must be < 20%. Refer to Section 12 for the appropriate calculations.

NOTE: Breakdown and trailing factor are not applicable for LVI PAHs.

10.4. Initial Calibration

10.4.1. Internal Standard Calibration Procedure: Internal standards are listed in Table 5. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.

10.4.2. Compounds should be assigned to the IS with the closest retention time. Refer to Table 11 for internal standard corresponding analytes.

10.4.3. Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. Add the appropriate amount of the IS mixture to result in 2 ng on column. (For example, 5 uL of 80 ppm IS mix is added to 100 uL of extract. This results in 2 ng per each 0.5 ul injection). The concentration ranges of all analytes are listed in Table 10. For Ohio VAP work, the low standard must be at or below the reporting limit

10.4.4. For LVI analysis, 2 uL of 8 ppm IS mix is added to 100 uL of extract. The calibration standards are diluted by a factor of 10, however 10x more is injected (5 uL injected rather than the normal 0.5 uL), keeping the on-column amount the same as the non-LVI analytes (2 ng).

10.4.5. Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Table 5 lists the analytes and characteristic ions analyzed in the laboratory. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in Section 12. For Method 8270C, verify that the SPCC and CCC criteria in Sections 10.4.6 and 10.4.8 are met. **No sample analysis maybe performed unless these criteria are met.** See section 10.4.7 for 8270D ICAL criteria.

10.4.6. System Performance Check Compounds (SPCCs) (Method 8270C). The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

SPCC Compounds:
- N-nitroso-di-n-propylamine
- Hexachlorocyclopentadiene
- 2,4-Dinitrophenol
- 4-Nitrophenol

10.4.7. Initial Calibration Criteria for Method 8270D

10.4.7.1. The RSD should be less than 20% for each analyte. For analytes that fail, use linear or quadratic curve with 0.99 correlation coefficient.

NOTE: If compliance with Method 8270C is required, the RSD limit is 15%.

10.4.7.2. No more than 10% of compounds can fail the 20%/0.99 correlation coefficient requirement.

10.4.7.3. If more than 10% of analytes fail both 20% RSD and 0.99 correlation coefficient, then recalibration is necessary.

10.4.7.4. Any individual analyte that fails both 20% RSD and 0.99 correlation coefficient criteria must have any positive result flagged as estimated and must be noted in the narrative.

10.4.7.5. For any analyte non-detect associated with a calibration that fails the 20% RSD/0.99 correlation coefficient/minimum response factor criteria, there must be a demonstration of adequate sensitivity at the quantitation limit. Successful analysis of a LLCCV is considered adequate demonstration for this purpose (see section 10.4.7.7).

10.4.7.6. Minimum response factor should be met, especially for the low level standard to verify the sensitivity.

10.4.7.7. Any individual analyte that fails the minimum response factor set in the SOP must have a demonstration of sensitivity in the analytical batch to report non-detects. The demonstration of sensitivity is analysis of a low level CCV (at or below the reporting limit). The criterion for a passing LLCCV is detection only, and a passing LLCCV allows non-detects to be reported with appropriate flagging. In general, Table 4 in the method should be used as guidance in setting minimum response factors in the SOP; but the RFs may be modified if appropriate (for example, if especially low-level analysis is performed).

10.4.7.8. For Method 8270D, the minimum response factors are listed in Table 12 at the end of this SOP.

10.4.8. Calibration Check Compounds (CCCs) (Method 8270C). The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could also affect the CCCs.

10.4.8.1. If none of the CCCs are required analytes, project-specific calibration specifications must be agreed upon with the client.

10.4.8.2. CCC Compounds

Phenol
Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.9. Continuing Calibration Criteria for Method 8270D

10.4.9.1. At least 80% of analytes must have a %D less than or equal to 20%.

10.4.9.2. Minimum response factors must be evaluated.

10.4.9.3. If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst must evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve, then the appropriate curve with no forced intercept must be used for quantitation.

10.4.9.4. If an analyte in the initial calibration is >15%, then calibration on a curve must be used. Quadratic curve fits must be used if the compound has historically exhibited a nonlinear response. The analyst must consider instrument maintenance to improve the linearity of response where appropriate. Use of $1/Concentration^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. If Relative Standard Error (RSE) is used to evaluate the curve, it must be better than 15%. If the % RSD is >15%, the analyst may drop the low or high points in the ICAL, as long as a minimum of five points are maintained and the quantitation range is adjusted accordingly. If the % RSD is still >15%, a quadratic or linear or quadratic curve must be used. The coefficient of determination (r^2) must be ≥ 0.990. If the coefficient

of determination is < 0.990, then any hits for these compounds must be flagged as estimated. If a curve is not linear for any compound that is found in a sample, the result must be flagged as estimated. Linear is defined as <15% RSD or a coefficient of determination of 0.990.

Note: For Method 8270D, analytes using the linear calibration fit should have the read back concentration of the low level standard evaluated. The read back concentration should be within 50% of the true value. Any sample detects for analytes that fail the read back criterion and are using a linear calibration must be flagged as estimated, and be described in the narrative.

Note: Some of the later-eluting PAH compounds exhibit greater variability at the low end of the calibration curve. Analysts' judgment is critical in assessing the validity of the curve at the low end, if the 50% criterion is exceeded. Any potential effects on sample results will be narrated in the analytical report.

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Note: Several components do not respond well by this method (poor linearity). These compounds are indene, benzoic acid, benzaldehyde, caprolactam, 1,3,5-Trinitrobenzene, dinoseb, p-phenylenediamine, benzidine, alpha alpha-dimethyl phenethylamine, acrylamide, 4-Nitroquinoline-1-oxide, famphur, benzenethiol, kepone, and 2,4-Toluenediamine. If these compounds are requested by a client and hits are found, results will be flagged as estimated. Sensitivity as demonstrated by the low standard is sufficient to substantiate a non-detect.

10.4.9.5. Quantitation is performed using the calibration curve or average response factor from the initial curve.

10.5. Initial Calibration Verification (ICV)

10.5.1. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. The CCC compounds must have $\leq$ 20% difference (%D) from the ICAL. Non-CCC compounds must have $\leq$ 50%D with an allowance of up to six compounds >50%.

10.5.2. If time remains in the 12-hour period initiated by the DFTPP injection before the initial calibration, samples maybe analyzed. (Samples may be analyzed immediately after the ICAL and ICV) Otherwise, proceed to continuing calibration.

10.5.3. For Method 8270D, the suggested acceptance limit is 70-130% for all analytes.

10.6. Continuing Calibration

10.6.1. At the start of each 12-hour period, analyze a GC/MS tuning standard. The injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 4.

10.6.2. Following a successful DFTPP analysis, the continuing calibration standard(s) (CCs) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid-level calibration standard is used for the CC.

10.6.3. For Method 8270C, the following criteria must be met for the CC to be acceptable:

10.6.3.1. The SPCC compounds must have an average response factor of $\geq$ 0.05.

10.6.3.2. The percent difference or drift (both %D) of the CCC compounds from the initial calibration must be $\leq$ 20% (see Section 12 for calculations). In addition, the %D of all analytes must be $\leq$ 50%, with allowance for up to four compounds to be greater than 50%.

10.6.3.3. The IS area response must be within 50-200% of the response in the mid-level of the ICAL.

10.6.3.4. The IS retention times must be within 30 seconds of the retention times in the mid-level standard of the ICAL.

Note: Ohio VAP requires that samples with failing internal standards must be re-analyzed "undiluted" unless matrix interference is apparent. If matrix interference is apparent, dilute the sample with methylene chloride using a syringe for re-analysis. When there is obvious interference causing the IS failure that corrective action will not remedy, data must be flagged with a qualifier indicating matrix interference. If the QC has failing internal standards, the batch must be re-prepped and re-analyzed.

10.6.3.5. If none of the CCCs are required analytes, project specific calibration specifications must be agreed upon with the client.

10.6.3.6. For Method 8270D, any sample non-detects for an analyte that fails the IS criteria low, it must have a low level CC (CC at the RL) in the batch as a sensitivity demonstration. The criterion for a passing

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LLCCV is detection only and a passing LLCCV allows non-detect samples to be reported with appropriate flagging.

10.6.4. Once the above criteria have been met, sample analysis will begin. IC average RFs (or the calibration curve) will be used for sample quantitation, not the CCRFs. Analysis will proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

11. PROCEDURE

11.1. Sample Preparation

11.1.1. Samples are prepared following SOP NC-OP-037, NC-OP-038, NC-OP-039, NC-OP-040, NC-OP-041, or NC-OP-043.

11.2. Sample Analysis Procedure

11.2.1. Calibrate the instrument as described in Section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

11.2.2. Analyze all samples using the same instrument conditions as the preceding CC standard.

11.2.3. Add IS to the extract to result in 2 ng injected on column. Mix thoroughly before injection into the instrument. For LVI samples, the addition should result in 2 ng injected on column.

11.2.4. Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.

11.2.5. The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 12. Quantitation is based on the initial calibration, not the continuing calibration.

11.2.6. Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system. Chromatograms before and after manual integration, as well as the reason for performing the manual integration are required. Additional information on manual integration can be found in SOP CA-Q-S-002.

11.2.7. Target compounds identified by the data system are evaluated using the criteria listed in Section 12.1.

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11.2.8. Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, or TICs) must be performed if required by the client. They are evaluated using the criteria in Section 12.3.

11.3. Dilutions

11.3.1. If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. The diluent used is methylene chloride. An appropriate dilution must be in the upper half of the calibration range. Samples should be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or has hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample should be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range if matrix allows.

11.3.2. Guidance for Dilutions Due to Matrix

11.3.2.1. If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be re-analyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment. For example, samples containing organic acids must be analyzed at a higher dilution to avoid destroying the column.

11.3.3. Reporting Dilutions

11.3.3.1. The most concentrated dilution with target compounds within the calibration range will be reported. Other dilutions will only be reported at client request.

11.3.4. Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at 4 $\pm 2^{o}$C protected from light in screw cap vials equipped with unpierced Teflon®-lined septa.

11.4. Retention Time Criteria for Samples

11.4.1. If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required.

11.4.2. If the retention time of any IS in any sample varies by more than 0.1 minute from the preceding CC standard, the data must be carefully evaluated to ensure no analytes have shifted outside their retention time windows.

11.5. Procedural Variations

11.5.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo (NCM). The NCM must be filed in the project file.

11.6. Troubleshooting Guide

11.6.1. Daily Instrument Maintenance

11.6.1.1. In addition to the checks listed in the instrument maintenance schedule in the TestAmerica Canton Quality Assurance Manual (QAM), current version, the following daily maintenance may be performed as needed.

11.6.1.2. Clip column as necessary.

11.6.1.3. Install new or cleaned injection port liner as necessary.

11.6.1.4. Install new septum as necessary.

11.6.1.5. Perform auto-tune.

11.6.2. Major Maintenance

11.6.2.1. A new ICAL may be necessary following major maintenance. Major maintenance includes changing the column, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards (target compounds) or from the NBS library (TICs). When a good user-generated spectrum for a compound cannot be produced, the NBS library must be used. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the

sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

12.1.1.1. The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same 12 hours as the sample.

12.1.1.2. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

12.1.1.3. The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

12.1.1.4. The relative intensities of ions must agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

12.1.2. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst must report that identification and proceed with quantitation.

12.2. Mass chromatogram searches

12.2.1. Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte, a mass chromatogram (EICP) search is made.

12.2.1.1. Hexachlorophene

12.2.1.1.1. Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d_{12} to at least 4 minutes after chrysene-d_{12}. If peaks for both ions coincide, then the analyst evaluates the spectrum for the presence of hexachlorophene. Quantitation is not possible without calibration. This is a present/not present determination only, no quantitative information can be provided.

12.3. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of

analyses being conducted or by client request. Computer-generated library search routines must not use normalization that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the experienced analyst assign a tentative identification. Guidelines for making tentative identification are:

12.3.1. Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.

12.3.2. The relative intensities of the major ions must agree within ± 20 %. (Example: For an ion with an abundance of 50 % in the standard spectrum, the corresponding sample ion abundance must be between 30 % and 70 %.)

12.3.3. Molecular ions present in the reference spectrum must be present in the sample spectrum.

12.3.4. Ions present in the sample spectrum, but not in the reference spectrum, must be reviewed for possible background contamination or presence of co-eluting compounds.

12.3.5. Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.3.6. Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.

Note: For water samples, the TIC searches begin with compounds eluting after the first surrogate (2-Fluorophenol). For solid samples, the TIC searches begin with compounds eluting after the Aldol Condensation Product. Any compounds eluting before these analytes are considered volatile analytes are reported in the volatile analysis. A possible exception to this general rule would be if an early eluting compound were the reason for a sample dilution.

12.3.7. If a client requests 10 TICs, the laboratory supplies a minimum of 10. Choosing the largest non-target peaks present in the sample chromatogram. For a request of 20 TICS, the laboratory would supply a minimum of 20, assuming that number of compounds was available.

12.4. Anyone evaluating data must be trained to handle isomers with identical mass spectra and close elution times. These include target compounds:

Dichlorobenzenes
Methylphenols
Trichlorophenols

Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

12.4.1. Extra precautions concerning these compounds include closely scrutinizing retention time vs. the calibration standard and also checking that all isomers have distinct retention times.

12.4.2. A second category of problem compounds would be the poor responders or compounds that chromatograph poorly (or exhibit erratic response). Included in this category are:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

12.4.3. Manually checking the integrations is appropriate for these compounds.

12.5. Calculations

12.5.1. Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{\overline{RF}} \times 100$$

$RF =$ Mean of RFs from intial caibration for a compound

$SD =$ Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^{N} \frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

$RFi =$ RF for each of the calibration levels

$N =$ Number of RF values

12.5.2. Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.5.3. Concentration in the extract

12.5.3.1. The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.4. Average Response Factor

12.5.4.1. If the average of all the %RSDs of the response factors in the initial calibration is $\leq$ 15%, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} \overline{RF}}$$

12.5.5. Linear fit

$$X_s = \frac{\left(\frac{A_s \times C_{is}}{A_{is}}\right) - b}{a} \times C_{is}$$

Where: X_s = Concentration in extract, µg/mL
A_s = Response for analyte
A_{is} = Concentration of internal standard
C_{is} = Intercept

12.5.6. Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}}{R_{is}}^2\right)$$

Where: C = Curvature

12.5.7. The concentration in the sample is then calculated.

12.5.7.1. Aqueous Calculation

$$\text{Concentration, } \mu g / L = \frac{C_{ex} V_t}{V_o}$$

Where: V_t = Volume of total extract, µL, taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean V_t = 10,000 µL. If half the base/neutral extract and half the acid extract are combined, V_t=2,000)

V_o = Volume of water extracted (mL)

12.5.7.2. Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis

$$\text{Concentration, } \mu g / kg = \frac{C_{ex} V_t}{W_s D}$$

Where: W_s = Weight of sample extracted or diluted in grams

D = (100 - % moisture in sample)/100, for a dry weight basis or one for a wet weight basis

12.5.8. MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where: S_{SR} = Spike sample result

S_R = Sample result

S_A = Concentration equivalent of spike added

12.5.9. Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1/2(MS_R + MSD_R)} \times 100$$

Where: RPD = Relative percent difference

MS_R = Matrix spike result

MSD_R = Matrix spike duplicate result

12.5.10. Relative response factor calculation

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where: A_x = Area of the characteristic ion for the compound being measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_x = Concentration of the compound being measured (µg/L)

C_{is} = Concentration of the specific internal standard (µg/L)

12.6. Calculation of TICs: The calculation of TICs) is identical to the above calculations with the following exceptions:

A_x = Area of the total ion chromatogram for the compound being measured

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

Results for TICs are not quantitative and are always reported as estimated "J."

12.7. Percent DDT breakdown

$$\%\ \text{DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDDarea}}$$

The total ion current areas are used for this calculation

12.8. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002

13. METHOD PERFORMANCE

13.1. Method Detection Limit (MDL)

13.1.1. Each laboratory must generate a valid MDL for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Policy CA-Q-S-006 and SOP NC-QA-021.

13.2. Lower Limit of Quantitation Verification – The lowest calibration standard analyzed establishes the LLOQ or Reporting Limit. The capability to reliably detect this concentration through the preparation, clean-up and analytical procedure is verified through the annual analysis of a standard at the LLOQ/RL. The LLOQ verification

shall also be performed whenever significant changes are made to the preparation and/or analytical procedure.

13.2.1. The LLOQ verification standard shall be prepared at a concentration 0.5-2 times the LLOQ/RL, and be taken through all preparation and clean-up methods which samples would be.

13.2.2. The LLOQ verification standard for aqueous matrix shall be prepared using laboratory deionized water and for the solid matrix using clean Ottawa sand. Other clean matrices may be used in addition, for project specific requirements.

13.2.3. The LLOQ shall be verified annually on each instrument used for client sample analysis.

13.2.4. Recovery of each analyte must meet the laboratory established LCS recovery limits + 20%. (For example, if the LCS recovery limits are 70-130%, the LLOQ verification must meet recovery limits of 50-150%.) Once sufficient points have been generated, LLOQ based statistical limits may be used in place of limits based on LCS recovery. NOTE: The lower recovery limit for the LLOQ can be no lower than 10%.

13.2.5. If the LLOQ cannot be verified, it will be necessary to raise the RL to a concentration level that can be carried through the preparation and cleanup steps to meet recovery limits.

13.3. Initial Demonstration of Capability (IDOC)

13.3.1. Each analyst must make an IDOC for each individual analyte. Demonstrations of capability (DOCs) for both soil and water matrices is required. This requires analysis of four LCSs containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.3.1.1. Four aliquots of the LCS are analyzed using the same procedures used to analyze samples, including sample preparation.

13.3.1.2. Calculate the average recovery and standard deviation of the recoveries for each analyte of interest.

13.3.1.3. If any analyte does not meet the LCS acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

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13.4. Training Qualification

13.4.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.4.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

15.3. Waste Streams Produced by the Method

15.3.1. Vials containing sample extracts: These vials are placed in the vial waste located in the GC/MS laboratory.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), 8270D, Rev. 4, 2007

16.1.3. SW846, Test Methods for Evaluating Solid Waste, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), 8270D, Rev. 5, 2014

16.1.4. J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File:		Revision 2.1: 01/25/99		Revision 0: 05/28/08 (NC-MS-018)
(formerly CORP-MS-0001NC)		Revision 2.2: 03/27/00		Revision 1: 12/16/08
		Revision 2.3: 02/15/01		Revision 2: 10/26/10
		Revision 2.4: 05/29/01		Revision 3: 04/25/13
		Revision 2.5: 04/25/02		Revision 4: 07/24/14
		Revision 2.6: 08/15/02		Revision 5: 03/01/16
		Revision 2.7: 11/12/02		Revision 6: 10/31/17
		Revision 2.8: 01/23/03		
		Revision 2.9: 06/18/03		
		Revision 2.10: 02/24/04		
		Revision 2.11: 02/03/06		
		Revision 2.12: 03/01/07		

16.2. Associated SOPs and policies, current version

16.2.1. Continuous Liquid/Liquid Extraction of Organic Compounds from Waters Based on Method SW-846 3520C and 600 Series, NC-OP-037

16.2.2. Separatory Funnel Extraction of Organic Compounds from Waters Based on Method SW-846 3510C and 600 Series, NC-OP-038

16.2.3. Sonication Extraction of Organic Compounds from Soils Based on Method SW-846 3550C, NC-OP-039

16.2.4. Soxhlet (Traditional) Extraction of Organic Compounds from Soils Based on Method SW-846 3540C, NC-OP-040

16.2.5. Microextraction of Organic Compounds from Waters Based on Method 3511, NC-OP-042

16.2.6. Waste Dilution, NC-OP-043

16.2.7. QA Policy, QA-003

16.2.8. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.9. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.10. Standard and Reagents, NC-QA-017

16.2.11. Acceptable Manual Integration Practices, CA-Q-S-002

16.2.12. Calibration Curves (General), CA-Q-S-005

16.2.13. Section of Calibration Points, CA-T-P-002

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2. The quantitation and qualifier ions from compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.2. Tables and Appendices

TABLE 1: TestAmerica Canton Standard Reporting Limits				
Analytes	**CAS Number**	**Water, µg/L**	**Soil, µg/kg**	**TCLP, mg/L**
1,1-Biphenyl	92-52-4	1	50	
1,2,3,4-Tetrachlorobenzene	634-66-2	1	30	
1,2,3-Trichlorobenzene	87-61-6	1	50	
1,2,4-Trichlorobenzene	120-82-1	1	50	
1,2-Dichlorobenzene	95-50-1	1	50	
1,3,5-Trichlorobenzene	108-70-3	1	50	
1,3-Dichlorobenzene	541-73-1	1	50	
1,4-Dichlorobenzene	106-46-7	1	50	0.004
1-Methyl Naphthalene	90-12-0	0.2	6.67	
2,2'-oxybis(1-chloropropane) [1]	108-60-1	1	100	
2,4,5-Trichlorophenol	95-95-4	5	150	0.02
2,4,6-Trichlorophenol	88-06-2	5	150	0.02
2,4-Dichlorophenol	120-83-2	2	150	
2,4-Dimethylphenol	105-67-9	2	150	
2,4-Dinitrophenol	51-28-5	5	330	
2,4-Dinitrotoluene	121-14-2	5	200	0.02
2,6-Dinitrotoluene	606-20-2	5	200	
2-Chloronaphthalene	91-58-7	1	50	
2-Chlorophenol	95-57-8	1	50	
2-Methylnaphthalene	91-57-6	0.2	6.67	
2-Methylphenol	95-48-7	1	200	
2-Nitroaniline	88-74-4	2	200	
2-Nitrophenol	88-75-5	2	50	
3,3'-Dichlorobenzidine	91-94-1	5	100	
3-Nitroaniline	99-09-2	2	200	
3 & 4 Methylphenol	15831-10-4	2	400	0.04
4,6-Dinitro-2-methylphenol	534-52-1	5	150	
4-Bromophenyl phenyl ether	101-55-3	2	50	
4-Chloro-3-methylphenol	59-50-7	2	150	
4-Chloroaniline	106-47-8	2	150	
4-Chlorophenyl phenyl ether	7005-72-3	2	50	
4-Nitroaniline	100-01-6	2	200	
4-Nitrophenol	100-02-7	5	330	
6-Methylchrysene	1705-85-7	5	330	
Acenaphthene	83-32-9	0.2	6.67	
Acenaphthylene	208-96-8	0.2	6.67	
Acrylamide	79-06-1	20	100	
Aniline	62-53-3	5	330	
Anthracene	120-12-7	0.2	6.67	
Atrazine	1912-24-9	1	200	
Azobenzene	103-33-3	10	330	

TABLE 1: TestAmerica Canton Standard Reporting Limits				
Analytes	**CAS Number**	**Water, µg/L**	**Soil, µg/kg**	**TCLP, mg/L**
Benzaldehyde	100-52-7	1	100	
Benzenethiol	108-98-5	10	330	
Benzidine	92-87-5	5	660	
Benzo(a)anthracene	56-55-3	0.2	6.67	
Benzo(a)pyrene	50-32-8	0.2	6.67	
Benzo(b)fluoranthene	205-99-2	0.2	6.67	
Benzo(g,h,i)perylene	191-24-2	0.2	6.67	
Benzo(k)fluoranthene	207-08-9	0.2	6.67	
Benzoic acid	65-85-0	25	660	
Benzyl alcohol	100-51-6	5	330	
Bis(2-chloroethoxy)methane	111-91-1	1	100	
Bis(2-chloroethyl)ether	111-44-4	1	100	
Bis(2-ethylhexyl)phthalate	117-81-7	2	50	
Butyl benzyl phthalate	85-68-7	1	50	
Caprolactam	105-60-2	5	330	
Carbazole	86-74-8	1	50	
Chrysene	218-01-9	0.2	6.67	
Dibenz(a,h)acridine	226-36-8	50	330	
Dibenz(a,h)anthracene	53-70-3	0.2	6.67	
Dibenzofuran	132-64-9	1	50	
Diethylphthalate	84-66-2	1	50	
Dimethyl phthalate	131-11-3	1	50	
Di-n-butyl phthalate	84-74-2	1	50	
Di-n-octylphthalate	117-84-0	1	50	
Ethyl methacrylate	97-63-2	2	330	
Fluoranthene	206-44-0	0.2	6.67	
Fluorene	86-73-7	0.2	6.67	
Hexachlorobenzene	118-74-1	0.2	6.67	0.02
Hexachlorobutadiene	87-68-3	1	50	0.02
Hexachlorocyclopentadiene	77-47-4	10	330	0.05
Hexachloroethane	67-72-1	1	50	
Hexadecane	544-76-3	10	330	
Indene	95-13-6	5	330	
Indeno(1,2,3-cd)pyrene	193-39-5	0.2	6.67	
Isophorone	78-59-1	1	50	
Methylphenol, Total	1319-77-3	5	400	
N,n-Dimethylacetamide	127-19-5	10	330	
Naphthalene	91-20-3	0.2	6.67	
Nitrobenzene	98-95-3	1	100	0.004
N-nitrosodimethylamine	62-75-9	1	100	
N-Nitroso-di-n-propylamine	621-64-7	1	50	
N-Nitrosodiphenylamine	86-30-6	1	50	
Pentachlorophenol	87-86-5	5	150	0.04
Phenanthrene	85-01-8	0.2	6.67	
Phenol	108-95-2	1	50	

TABLE 1: TestAmerica Canton Standard Reporting Limits				
Analytes	**CAS Number**	**Water, µg/L**	**Soil, µg/kg**	**TCLP, mg/L**
Pyrene	129-00-0	0.2	6.67	
Pyridine	110-86-1	1	100	0.02
Quinoline	91-22-5	5	330	
Tributyl phosphate	126-73-8	10	330	
1,2,4,5-Tetrachlorobenzene	95-94-3	1	100	
1,3,5-Trinitrobenzene	99-35-4	5	1600	
1,3-Dinitrobenzene	99-65-0	2	330	
1,4-Naphthoquinone	130-15-4	50	330	
1-Naphthylamine	134-32-7	2	330	
2,3,4,6-Tetrachlorophenol	58-90-2	10	100	
2,6-Dichlorophenol	87-65-0	5	150	
2-Acetylaminofluorene	53-96-3	10	330	
2-Naphthylamine	91-59-8	2	200	
2-Picoline	109-06-8	5	330	
2-secbutyl-4,6-dinitrophenol (Dinoseb2)	88-85-7	2	330	
3,3'-Dimethylbenzidine	119-93-7	5	330	
3-Methylcholanthrene	56-49-5	5	200	
4-Aminobiphenyl	92-67-1	5	330	
4-Nitroquinoline-1-oxide	56-57-5	5	330	
5-Nitro-o-toluidine	99-55-8	2	330	
7,12-Dimethylbenz(a)anthracene	57-97-6	2	330	
a,a-Dimethyl-phenethylamine	122-09-8	5	660	
Acetophenone	98-86-2	1	100	
Aramite	140-57-8	5	330	
Diallate[2]	2303-16-4	10	330	
Dibenz(a,j)acridine	224-42-0	5	330	
Dimethoate	60-51-5	2	330	
Disulfoton	298-04-4	2	330	
Ethyl methanesulfonate	62-50-0	2	330	
Famphur	52-85-7	10	3300	
Hexachloropropene	1888-71-7	5	0.02	
Isosafrole	120-58-1	5	330	
Methapyrilene	91-80-5	2	330	
Methyl methanesulfonate	66-27-3	2	330	
N-Nitrosodiethylamine	55-18-5	2	100	
n-Nitrosodi-n-butylamine	924-16-3	2	100	
N-Nitrosomethylethylamine	10595-95-6	2	100	
N-Nitrosomorpholine	59-89-2	2	330	
N-Nitrosopiperidine	100-75-4	2	330	
N-Nitrosopyrrolidine	930-55-2	2	50	
o,o,o-Triethyl-Phosphorothioate	126-68-1	2	330	
o-Toluidine	95-53-4	2	330	
p-(Dimethylamino)azobenzene	60-11-7	2	330	

TABLE 1: TestAmerica Canton Standard Reporting Limits				
Analytes	**CAS Number**	**Water, µg/L**	**Soil, µg/kg**	**TCLP, mg/L**
p-Chlorobenzilate	510-15-6	2	330	
Pentachlorobenzene	608-93-5	2	100	
Pentachloroethane	76-01-7	20	330	
Pentachloronitrobenzene	82-68-8	2	330	
Phenacetin	62-44-2	2	330	
Phorate	298-02-2	2	330	
p-Phenylenediamine	106-50-3	40	660	
Pronamide	23950-58-5	2	330	
Safrole	94-59-7	2	330	
Sulfotepp	3689-24-5	5	330	
Thionazin	297-97-2	2	330	
1,3-Dinitrobenzene	99-65-0	2	330	
1,4-Dinitrobenzene	100-25-4	2	100	
1,2-Dinitrobenzene	528-29-0	1	50	0.05
4,4'-Methylenebis(2-chloroaniline)	101-14-4	2		0.05
Diphenylamine	122-39-4	1	100	0.05
1,2-Diphenylhydrazine	122-66-7	1	50	0.05

1 2,2'oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether.

Skinner List Compound

Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram (see Section 12.2.1).

Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore, these two compounds cannot be distinguished. Diphenylamine is used in the calibration standard to prove a response for both Diphenylamine and N-nitrosodiphenylamine.

TABLE 1-A: TestAmerica Canton Standard Reporting Limits for LVI PAH				
Analytes	**CAS Number**	**Water, µg/L**	**Soil, µg/kg**	**TCLP, mg/L**
1,1-Biphenyl	95-52-4	1	50	0.01
1-Methylnaphthalene	90-12-120	0.2	6.67	0.05
2-Chloronaphthalene	91-58-7	1	50	0.05
2-Methylnaphthalene	91-57-6	0.2	6.67	0.05
Acenaphthylene	208-96-8	0.2	6.67	0.05
Acenaphthene	83-32-9	0.2	6.67	0.05
Anthracene	120-12-7	0.2	6.67	0.05
Benzo(a)anthracene	56-55-3	0.2	6.67	0.05
Benzo(b)fluoranthene	205-99-2	0.2	6.67	0.05
Benzo(k)fluoranthene	207-08-9	0.2	6.67	0.05
Benzo(a)pyrene	50-32-8	0.2	6.67	0.05
Benzo(g,h,I)perylene	191-24-2	0.2	6.67	0.05
Chrysene	218-01-9	0.2	6.67	0.05
Dibenzofuran	132-64-9	1	50	0.05
Dibenz(a,h)Anthracene	53-70-3	0.2	6.67	0.05
Fluoranthene	206-44-0	0.2	6.67	0.05
Fluorene	86-73-7	0.2	6.67	0.05
Hexachlorobenzene	118-74-1	0.2	6.67	0.02
Ideno(1,2,3-cd)pyrene	193-39-5	0.2	6.67	0.05
Phenanthrene	85-01-8	0.2	6.67	0.05

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TABLE 2: TestAmerica Canton Michigan Program[1]			
Semivolatile	**CAS Number**	**Michigan Reporting Limits**	
		Aqueous µg/L	**Low Soil/Sediment µg/kg**
Acenaphthene	83-32-9	5	330
Acenaphthylene	208-96-8	5	330
Acetophenone	98-86-2	5	330
Anthracene	120-12-7	5	330
Atrazine	1912-24-9	5	330
Benzaldehyde	100-52-7	10	330
Benzo(a)anthracene	56-55-3	1	330
Benzo(a)pyrene	50-32-8	2	330
Benzo(b)fluoranthene	205-99-2	2	330
Benzo(g,h,i)perylene	191-24-2	5	330
Benzo(k)fluoranthene	207-08-9	5	330
1,1'-Biphenyl	92-52-4	10	330
4-Bromophenylphenyl ether	101-55-3	5	330
Butylbenzylphthalate	85-68-7	5	330
di-n-Butylphthalate	84-74-2	5	330
Caprolactam	105-60-2	10	330
Carbazole	86-74-8	10	330
4-Chloroaniline	106-47-8	20	1700
bis(2-Chloroethoxy)methane	111-91-1	5	330
bis(2-Chloroethyl)ether	111-44-4	4	330
bis(2-Chloroisopropyl)ether	108-60-1	5	330
4-Chloro-3-Methylphenol	59-50-7	5	330
2-Chloronaphthalene	91-58-7	5	330
2-Chlorophenol	95-57-8	5	330
4-Chlorophenyl phenyl ether	7005-72-3	5	330
Chrysene	218-01-9	5	330
Dibenz(a,h)anthracene	53-70-3	2	330
Dibenzofuran	132-64-9	5	330
3,3'-Dichlorobenzidine	91-94-1	4	2000
2,4-Dichlorophenol	120-83-2	10	330
Diethylphthalate	84-66-2	5	330
2-4-Dimethylphenol	105-67-9	5	330
Dimethylphthalate	131-11-3	5	330

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
4,6-Dinitro-2-methylphenol	534-52-1	20	1700
2,4-Dinitrophenol	51-28-5	20	1700
2,4-Dinitrotoluene	121-14-2	5	330
2,6-Dinitrotoluene	606-20-2	5	330
bis(2-Ethylhexyl)phthalate	117-81-7	5	330
Fluoranthene	206-44-0	5	330
Fluorene	86-73-7	5	330
Hexachlorobenzene	118-74-1	5	330
Hexachlorobutadiene	87-68-3	5	330
Hexachlorocyclopentadiene	77-47-4	5	330
Hexachloroethane	67-72-1	5	330
Indeno(1,2,3-cd)pyrene	193-39-5	2	330
Isophorone	78-59-1	5	330
2-Methylnapthalene	91-57-6	5	330
2-Methylphenol	95-48-7	5	330
3&4-Methylphenol	15831-10-4	5	330
Naphthalene	91-20-3	5	330
2-Nitroaniline	88-74-4	20	1700
3-Nitroaniline	99-09-2	20	1700
4-Nitroaniline	100-01-6	20	1700
Nitrobenzene	95-95-3	4	330
2-Nitrophenol	88-75-5	5	330
4-Nitrophenol	100-02-7	20	1700
N-Nitroso-di-n-propylamine	621-64-7	5	330
N-Nitrosodiphenylamine (diphenylamine)	62-75-9	5	330
di-n-Octylphthalate	117-84-0	5	330
Pentachlorophenol	87-86-5	20	800
Phenanthrene	85-01-8	5	330
Phenol	108-95-2	5	330
Pyrene	129-00-0	5	330
2,4,5-Trichlorophenol	95-95-4	5	330
2,4,6-Trichlorophenol	88-06-2	4	330

[1] *Reporting Limits are only for samples performed under the Michigan program.*

TABLE 3: Suggested Instrument Conditions	
Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	60°C for 1 minutes, 50°C for 1 minute for LVI
Column Temperature Program	60 - 320°C at 35°C/min for 3 min 50 - 320°C at 35°C/min for 3 min for LVI
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's Specifications
Injector	Grob-type, split / splitless
Sample Volume	0.5 µl, or 5.0 ul for LVI
Carrier Gas	Helium at 30 cm/sec

TABLE 4: DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 – 80% of mass 198
68	<2% of mass 69
69	Present
70	<2% of mass 69
127	25 - 75% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	> 0.75% of mass 198
441	Present, but less than mass 443
442	40 - 110% of mass 198
443	15 - 24% of mass 442

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TABLE 5a: Analytes (List 1) in Approximate Retention Time Order and Characteristic Ions			
Analyte	**Primary**	**Secondary**	**Tertiary**
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d_5 (Surrogate Standard)	99	42	71
Benzaldehyde	77	105	106
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene-d_4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	113
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	113
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane)[1]	45	77	79
Indene	115	116	89
3&4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d_5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d_8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
2,6-Dichlorophenol	162	164	63
Hexachlorobutadiene	225	223	227
Caprolactam	113	55	56
4-Chloro-3-methylphenol	107	144	142
1-Methylnaphthalene	142	141	115
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
Acetophenone	105		
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
1,1'-Biphenyl	154	153	76
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153
2,6-Dinitrotoluene	165	63	89

Acenaphthene-d_{10} (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	182	77
N-Nitrosodiphenylamine	169	168	167
1,2,4,5-Tetrachlorobenzene	216		
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Atrazine	200	173	215
Pentachlorophenol	266	264	268
Phenanthrene-d_{10} (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
1,3-Dinitrobenzene	168		
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
2,3,4,6-Tetrachlorophenol	232		
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d_{14} (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d_{12} (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d_{12} (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277

Table 5b: Analytes (List 2) in Approximate Retention Time Order and Characteristic Ions			
2-Picoline	93	66	92
N-Nitrosomethylethylamine	88	42	43
Acrylamide	71	44	55

Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
1-Chloronaphthalene	162	127	164
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2,3,5,6-Tetrachlorophenol	232	230	131
2-Naphthylamine	143	115	
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
Ethyl parathion	97	109	291
4-Nitroquinoline-1-oxide	190	128	160
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,h)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

Table 6: Method 8270C LCS Control Compounds	
LCS Compounds	**Spiking Level, Concentration Added = 20 ug/L**
1,1'-Biphenyl	20
1,2,4,5-Tetrachlorobenzene	20
1,2,4-Trichlorobenzene	20
1,2-Dichlorobenzene	20
1,3-Dichlorobenzene	20
1,3-Dinitrobenzene	20
1,4-Dichlorobenzene	20
1,4-Dioxane	20
1-Methylnaphthalene	20
2,2'-oxybis[1-chloropropane]	20
2,3,4,6-Tetrachlorophenol	20
2,4,5-Trichlorophenol	20
2,4,6-Trichlorophenol	20
2,4-Dichlorophenol	20
2,4-Dimethylphenol	20
2,4-Dinitrophenol	40
2,4-Dinitrotoluene	20
2,6-Dichlorophenol	20
2,6-Dinitrotoluene	20
2-Chloronaphthalene	20
2-Chlorophenol	20
2-Methylnaphthalene	20
2-Methylphenol	20
2-Nitroaniline	20
2-Nitrophenol	20
3&4-Methylphenol	20
3,3'-Dichlorobenzidine	40
3-Nitroaniline	20
4,6-Dinitro-2-methylphenol	40
4-Bromophenyl phenyl ether	20
4-Chloro-3-methylphenol	20
4-Chloroaniline	20
4-Chlorophenyl phenyl ether	20
4-Nitroaniline	20
4-Nitrophenol	40
Acenaphthene	20
Acenaphthylene	20
Acetophenone	20
Aniline	20

Anthracene	20
Atrazine	40
Azobenzene	20
Benzaldehyde	40
Benzidine	40
Benzoic acid	40
Benzo[a]anthracene	20
Benzo[a]pyrene	20
Benzo[b]fluoranthene	20
Benzo[g,h,i]perylene	20
Benzo[k]fluoranthene	20
Benzyl alcohol	20
Bis(2-chloroethoxy)methane	20
Bis(2-chloroethyl)ether	20
Bis(2-ethylhexyl) phthalate	20
Butyl benzyl phthalate	20
Caprolactam	40
Carbazole	20
Chrysene	20
Dibenz(a,h)anthracene	20
Dibenzofuran	20
Diethyl phthalate	20
Dimethyl phthalate	20
Di-n-butyl phthalate	20
Di-n-octyl phthalate	20
Fluoranthene	20
Fluorene	20
Hexachlorobenzene	20
Hexachlorobutadiene	20
Hexachlorocyclopentadiene	20
Hexachloroethane	20
Hexadecane	20
Indene	40
Indeno[1,2,3-cd]pyrene	20
Isophorone	20
Naphthalene	20
n-Decane	20
Nitrobenzene	20
N-Nitrosodimethylamine	20
N-Nitrosodi-n-propylamine	20
N-nitrosodiphenylamine	40
n-Octadecane	20
Pentachlorophenol	40
Phenanthrene	20

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Phenol	20
Pyrene	20
Pyridine	40

TABLE 7: TCLP LCS Compounds	
LCS Compounds	**Spiking Level, mg/L in extract**
1,4-Dichlorobenzene	0.08
2,4-Dinitrotoluene	0.08
Hexachlorobenzene	0.08
Hexachlorobutadiene	0.08
Hexachloroethane	0.08
2-Methylphenol	0.08
3-Methylphenol	0.08
4-Methylphenol	0.08
Nitrobenzene	0.08
Pentachlorophenol	0.08
Pyridine	0.08
2,4,5-Trichlorophenol	0.08
2,4,6-Trichlorophenol	0.08

Recovery limits for the LCS and for matrix spikes are generated historical data, and are maintained by the QA Dept.

TABLE 8: Method 8270C Surrogate Compounds	
Surrogate Compounds	**Spiking Level, Conc. Added = 20 ug/L / 30 ug/L**
Nitrobenzene-d_5	20
2-Fluorobiphenyl	20
Terphenyl-d_{14}	20
Phenol-d_5	30
2-Fluorophenol	30
2,4,6-Tribromophenol	30

Recovery limits for surrogates are generated from historical data, and are maintained by the QA department.

TABLE 9: Calibration Ranges

Analyte	Calibration Range	LVI Calibration Range
1,1'-Biphenyl	0.1-25 ug/mL	0.01-2.5 ug/mL
1,2,4,5-Tetrachlorobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
1,2,4-Trichlorobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
1,2-Dichlorobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
1,3-Dichlorobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
1,3-Dinitrobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
1,4-Dichlorobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
1,4-Dioxane	0.5-25 ug/mL	0.05-2.5 ug/mL
1-Methylnaphthalene	0.1-25 ug/mL	0.01-2.5 ug/mL
2,2'-oxybis(1-chloropropane)[1]	0.5-25 ug/mL	0.05-2.5 ug/mL
2,3,4,6-Tetrachlorophenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2,4,5-Trichlorophenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2,4,6-Trichlorophenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2,4-Dichlorophenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2,4-Dimethylphenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2,4-Dinitrophenol	1-50 ug/mL	0.1-5.0 ug/mL
2,4-Dinitrotoluene	0.5-25 ug/mL	0.05-2.5 ug/mL
2,6-Dichlorophenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2,6-Dinitrotoluene	0.5-25 ug/mL	0.05-2.5 ug/mL
2-Chloronaphthalene	0.1-25 ug/mL	0.01-2.5 ug/mL
2-Chlorophenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2-Methylnaphthalene	0.1-25 ug/mL	0.01-2.5 ug/mL
2-Methylphenol	0.5-25 ug/mL	0.05-2.5 ug/mL
2-Nitroaniline	0.5-25 ug/mL	0.05-2.5 ug/mL
2-Nitrophenol	0.5-25 ug/mL	0.05-2.5 ug/mL
3&4-Methylphenol	0.5-25 ug/mL	0.05-2.5 ug/mL
3,3'-Dichlorobenzidine	1-50 ug/mL	0.1-5 ug/mL
3-Nitroaniline	0.5-25 ug/mL	0.05-2.5 ug/mL
4,6-Dinitro-2-methylphenol	1-50 ug/mL	0.1-5.0 ug/mL
4-Bromophenyl phenyl ether	0.5-25 ug/mL	0.05-2.5 ug/mL
4-Chloro-3-methylphenol	0.5-25 ug/mL	0.05-2.5 ug/mL
4-Chloroaniline	0.5-25 ug/mL	0.05-2.5 ug/mL
4-Chlorophenyl phenyl ether	0.5-25 ug/mL	0.05-2.5 ug/mL
4-Nitroaniline	0.5-25 ug/mL	0.05-2.5 ug/mL
4-Nitrophenol	1-50 ug/mL	0.1-5 ug/mL
Acenaphthene	0.1-25 ug/mL	0.01-2.5 ug/mL
Acenaphthylene	0.1-25 ug/mL	0.01-2.5 ug/mL
Acetophenone	0.5-25 ug/mL	0.05-2.5 ug/mL

TABLE 9: Calibration Ranges		
Analyte	**Calibration Range**	**LVI Calibration Range**
Aniline	0.5-25 ug/mL	0.05-2.5 ug/mL
Anthracene	0.1-25 ug/mL	0.01-2.5 ug/mL
Atrazine	1-50 ug/mL	0.1-5 ug/mL
Azobenzene[2]	0.5-25 ug/mL	0.05-2.5 ug/mL
Benzaldehyde	0.2-50 ug/mL	0.02-5.0 ug/mL
Benzidine	1-50 ug/mL	0.1-5.0ug/mL
Benzo(a)anthracene	0.1-25 ug/mL	0.01-2.5 ug/mL
Benzo(a)pyrene	0.1-25 ug/mL	0.01-2.5 ug/mL
Benzo(b)fluoranthene	0.1-25 ug/mL	0.01-2.5 ug/mL
Benzo(g,h,i)perylene	0.1-25 ug/mL	0.01-2.5 ug/mL
Benzo(k)fluoranthene	0.1-25 ug/mL	0.01-2.5 ug/mL
Benzoic acid	1-50 ug/mL	0.1-5.0 ug/mL
Benzyl alcohol	0.5-25 ug/mL	0.05-2.5 ug/mL
Bis(2-chloroethoxy)methane	0.5-25 ug/mL	0.05-2.5 ug/mL
Bis(2-chloroethyl)ether	0.5-25 ug/mL	0.05-2.5 ug/mL
Bis(2-ethylhexyl)phthalate	0.5-25 ug/mL	0.05-2.5 ug/mL
Butyl benzyl phthalate	0.5-25 ug/mL	0.05-2.5 ug/mL
Caprolactam	1-50 ug/mL	0.1-5.0 ug/mL
Carbazole	0.5-25 ug/mL	0.05-2.5 ug/mL
Chrysene	0.1-25 ug/mL	0.01-2.5 ug/mL
Dibenz(a,h)anthracene	0.1-25 ug/mL	0.01-2.5 ug/mL
Dibenzofuran	0.1-25 ug/mL	0.01-2.5 ug/mL
Diethylphthalate	0.5-25 ug/mL	0.05-2.5 ug/mL
Dimethyl phthalate	0.5-25 ug/mL	0.05-2.5 ug/mL
Di-n-butyl phthalate	0.5-25 ug/mL	0.05-2.5 ug/mL
Di-n-octylphthalate	0.5-25 ug/mL	0.05-2.5 ug/mL
Fluoranthene	0.1-25 ug/mL	0.01-2.5 ug/mL
Fluorene	0.1-25 ug/mL	0.01-2.5 ug/mL
Hexachlorobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
Hexachlorobutadiene	0.5-25 ug/mL	0.05-2.5 ug/mL
Hexachlorocyclopentadiene	0.5-25 ug/mL	0.05-2.5 ug/mL
Hexachloroethane	0.5-25 ug/mL	0.05-2.5 ug/mL
Hexadecane		
Indene	1-50 ug/mL	0.1-5 ug/mL
Indeno(1,2,3-cd)pyrene	0.1-25 ug/mL	0.01-2.5 ug/mL
Isophorone	0.5-25 ug/mL	0.05-2.5 ug/mL

TABLE 9: Calibration Ranges		
Analyte	**Calibration Range**	**LVI Calibration Range**
Naphthalene	0.1-25 ug/mL	0.01-2.5 ug/mL
n-Decane		
Nitrobenzene	0.5-25 ug/mL	0.05-2.5 ug/mL
N-nitrosodimethylamine	0.5-25 ug/mL	0.05-2.5 ug/mL
N-Nitroso-di-n-propylamine	0.5-25 ug/mL	0.05-2.5 ug/mL
N-Nitrosodiphenylamine	1-50 ug/mL	0.1-5 ug/mL
n-Octane		
Parathion (ethyl)	0.5-25 ug/mL	0.05-2.5 ug/mL
Pentachlorophenol	1-50 ug/mL	0.1-5.0 ug/mL
Phenanthrene	0.1-25 ug/mL	0.01-2.5 ug/mL
Phenol	0.5-25 ug/mL	0.05-2.5 ug/mL
Pyrene	0.1-25 ug/mL	0.01-2.5 ug/mL
Pyridine	0.5-25 ug/mL	0.05-2.5 ug/mL

[1] *2,2'oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether.*

[2] *Azobenzene is formed by decomposition of 1,2-diphenyhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.*

Note: *Nine calibrations standards are prepared varying in concentration from 0.01 ug/mL to 25 ug/mL. A minimum of 5 calibration concentrations will be used for initial calibration.*

Table 10: Method 8720C and 8270D Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
1,4-Dioxane	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	N-Nitrosopiperidine	Isosafrole

Pyridine	Isophorone	1,2,4,5-Tetrachlorobenzene
2-Picoline	2-Nitrophenol	2,4,5-Trichlorophenol
N-Nitrosomethylethylamine	2,4-Dimethyphenol	2,4,6-Trichlorophenol
Acrylamide	Benzoic Acid	1,1'-Biphenyl
Methyl methanesulfonate	o,o',o''-Triethylphosphorothioate	2-Chloronaphthalene
N-Nitrosodiethylamine	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Ethyl methanesulfonate	alpha,alpha-Dimethyl phenethylamine	2-Nitroaniline
Benzaldehyde	2,4-Dichlorophenol	1,4-Naphthoquinone
Phenol	1,2,4-Trichlorobenzene	1,4-Dinitrobenzene
Aniline	Naphthalene	Dimethyl phthalate
Bis(2-chloroethyl)ether	4-Chloroaniline	1,3-Dinitrobenzene
Pentachloroethane	2,6-Dichlorophenol	2,6-Dinitrotoluene
2-Chlorophenol	Hexachloropropene	Acenaphthylene
n-Decane	Hexachlorobutadiene	3-Nitroaniline
1,3-Dichlorobenzene	Quinoline	2,4-Dinitrophenol
1,4-Dichlorobenzene	N-Nitrosodi-n-butylamine	Acenaphthene
Benzyl alcohol	Caprolactam	4-Nitrophenol
1,2-Dichlorobenzene	p-Phenylene diamine	2,4-Dinitrotoluene
2-Methylphenol	4-Chloro-3-methylphenol	Pentachlorobenzene
2,2'-oxybis[1-chloropropane]	Satrole, Total	Dibenzofuran
Indene	1-Methylnaphthalene	1-Naphthylamine
N-Nitrosopyrrolidine	2-Methylnaphthalene	2,3,5,6-tetrachlorophenol
3 & 4 Methylphenol	Nitrobenzene-d5	2,3,4,6-Tetrachlorophenol
N-Nitrosodi-n-propylamine		2-Naphthylamine
N-Nitrosomorpholine		Diethyl phthalate
Acetophenone		Hexadecane
2-Toluidine		Thionazin
Hexachloroethane		4-Chlorophenyl phenyl ether
2-Fluorophenol		N-Nitro-o-toluidine
Phenol-d5		4-Nitroaniline
		Fluorene
		2-Fluorobiphenyl (Surr)
		Hexachlorocyclopentadiene
		2,4,6-Tribromophenol

Phenanthrene-d_{10}	**Chrysene-d_{12}**	**Perylene-d_{12}**
4,6-Dinitro-2-methylphenol	Benzidine	Di-n-octyl phthalate
Diphenylamine	Pyrene	7,12-Dimethylbenz(a)anthracene
N-Nitrosodiphenylamine	Aramite, Total	Benzo[b]fluoranthene
Azobenzene	p-Dimethylamino azobenzene	Benzo[k]fluoranthene
Sulfotepp	Chlorobenzilate	Benzo[a]pyrene
1,3,5-Trinitrobenzene	Famphur	3-Methylcholanthrene
Phenacetin	Butyl benzyl phthalate	Dibenz[a,h]acridine
Diallate	3,3'-Dimethylbenzidine	Indeno[1,2,3-cd]pyrene
Phorate	2-Acetylaminofluorene	Dibenz(a,h)anthracene
4-Bromophenyl phenyl ether	4,4'-Methylene bis(2-chloroaniline)	Benzo[g,h,i]perylene
Dimethoate	3,3'-Dichlorobenzidine	
Hexachlorobenzene	Bis(2-ethylhexyl) phthalate	
Atrazine	Benzo[a]anthracene	
4-Aminobiphenyl	Chrysene	
Pronamide	6-Methylchrysene	
Pentachlorophenol	Terphenyl-d14	
n-Octadecane		

Pentachloronitrobenzene		
Disulfoton		
Dinoseb		
Phenanthrene		
Anthracene		
Carbazole		
Methyl parathion		
Di-n-butyl phthalate		
Ethyl Parathion		
4-Nitroquinoline-1-oxide		
Methapyrilene		
Isodrin		
Fluoranthene		
4,6-Dinitro-2-methylphenol		

Table 11: Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Actophenone	0.010
3&4-Methylphenol	0.600
N-Nitros-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroanaline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroanaline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900

Table 11: Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification	
Semivolatile Compounds	**Minimum Response Factor (RF)**
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Dithyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phananthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,I)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

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SOP Amendment Form

SOP NUMBER: NC-MS-019 Rev. 5

SOP TITLE: Determination of Volatile Organics by GC/MS Based on Methods 8260C, 8260B, and 8260A

REASON FOR ADDITION OR CHANGE: Addition of analytes to Table 1

CHANGE EFFECTIVE FROM: (DATE): 10/18/16

Change(s) Made:

Added the following analytes with CAS# and RLs to Table 1:

Butadiene
Ethyl acrylate
n-Butyl acetate

EDITED BY/DATE: Melissa A. Fuller-Gustavel 10/18/16

Title: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHODS 8260C, 8260B, AND 8260A

[Method: EPA Methods 8260A, 8260B, and 8260C]

Approvals (Signature/Date):

Technology Specialist	03/10/16 Date	Health & Safety Coordinator	03/02/16 Date
Quality Assurance Manager	03/09/16 Date	Technical Director	03/02/16 Date

This SOP was previously identified as SOP No. NC-MS-019, Rev 4, dated 5/21/14

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges, and other solid matrices.

1.2. This SOP is applicable to Methods 8260B and 8260C. It may also be used for analysis following Method 8260A.

1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.

1.4. The method is based upon a purge and trap sample delivery, gas chromatograph/mass spectrometric (GC/MS) separation and detection procedure. Reporting limits are listed in Tables 1 and 3 and are available in the LIMS. Reporting limits will be proportionately higher for samples that require a dilution.

1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates (MS/MSD), and laboratory control spike (LCS) samples.

2. SUMMARY OF METHOD

2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.2. Aqueous samples are purged directly. Soils are preserved (in the field or in the laboratory) by extracting the volatile analytes into methanol. Soil samples may also be preserved with sodium bisulfate or by freezing for storage, then thawing and purging directly.

2.3. In the purge and trap process, an inert gas is bubbled through the sample at ambient temperature or at 40°C (40°C required for low-level soils) and the volatile components are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and back-flushed with inert gas to desorb the components onto a GC column. The GC column is gradually heated to separate the components; when they elute they are detected with a mass spectrometer.

2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response ratio for a characteristic ion produced by that compound to the response of the

applicable internal standard (IS) in the sample, compared against the same ratio for the target compound and IS in the calibration standards.

3. DEFINITIONS

3.1. Refer to the TestAmerica Canton Quality Assurance Manual (QAM), current version, for definitions of terms used in this document.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks (MBs) as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. The use of ultra-high purity (UHP) gases pre-purged, purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases, the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.

4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination. Refer to SOP NC-QA-020 for additional information on holding blanks.

4.3. Matrix interferences may be caused by non-target contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from sample to sample depending upon the nature of the sample matrix and diversity of the site being sampled.

4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially on an autosampler. Whenever an unusually concentrated sample is analyzed, it must be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.

4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered, the sample must be diluted.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately. Cut-resistant gloves MUST be worn when opening VOA vials and when doing any other task that presents a strong possibility of getting cut.

5.3. Primary Materials Used

5.3.1. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material [(1)]	**Hazards**	**Exposure Limit** [(2)]	**Signs and symptoms of exposure**
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with a sticker that reads "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made. MS VOA samples may be prepared outside of the hood, unless it is known that concentrations are high.

5.6. The preparation of standards and reagents must be conducted in a fume hood with the sash closed as far as the operations will permit. MS VOA standards may be prepared outside of the hood due to low concentrations of analytes.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the laboratory Group Leader.

5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the TestAmerica Corporate Environmental Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by annual refresher training.

5.9. Specific Safety Concerns or Requirements

5.9.1. The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.9.2. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.9.3. There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.9.4. Sodium bisulfate creates Sulfuric Acid when mixed with water.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes: 10 µL and larger

6.2. Syringe: 5, 25, or 50 mL glass with luerlok tip, if applicable to the purging device.

6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.01 g

6.4. Glassware

6.4.1. Vials: 20 and 40 mL with screw caps and Teflon® liners.

6.4.2. Volumetric flasks: 10 mL, 100 mL, and 500 mL class A with ground-glass stoppers.

6.5. Spatula: Wood splints, small and large.

6.6. Disposable pipettes: Pasteur, 5 ¾ in.

6.7. Pipetters: Drummond, 30 uL to 100 uL, and 10 uL to 25 uL

6.8. Waste Dilution Pipette: 1 mL capacity

6.9. Methanol Dispensers: 5 mL, 10 mL, and 50 mL

6.10. pH paper: Wide range, pH 0-14.

6.10.1. Chlorine Test Paper: 0 ppm to 10 ppm

6.11. Gases

6.11.1. Helium: UHP, gr. 5, 99.999%.

6.11.2. Nitrogen: UHP from cylinders or gas generators may be used as an alternative to helium for purge gas.

6.12. Purge and Trap Device: The purge and trap device consists of the sparger, trap, and desorber.

6.12.1. Sparger: The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low-level soils are purged directly from a VOA vial.

6.12.2. Trap: A variety of traps may be used, depending on the target analytes required. Vocarb 3000 trap, OI 10, or an equivalent may be used if the Quality Control criteria are met. (Refer also to instrument operating manuals located within the laboratory).

6.12.3. Desorber: The desorber must be capable of rapidly heating the trap to at least 180°C.

6.12.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low-level soil analysis.

6.13. GC/MS System – HP (Agilent) GC/MSD 5973/5975 or equivalent

6.13.1. Autosampler – Archon or OI

6.13.2. The GC system must be capable of temperature programming.

6.13.3. GC Columns: Capillary Column: 20m x 0.18 ID DB-624 or equivalent, with 1 µm film thickness.

6.13.4. Mass Spectrometer: The mass spectrometer must be capable of scanning 35-300 amu every two seconds or less, using 70 volts electron (eV) energy in the electron impact (EI) mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) is injected into the gas chromatograph column inlet.

6.13.5. GC/MS Interface: Direct introduction to the mass spectrometer is used in the Canton MS VOA laboratory, but any interface that achieves all acceptance criteria may be used.

6.13.6. Data System: A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST/EPA mass spectral library must be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

6.13.7. Chemstation software is used in Canton MS VOA laboratory for data acquisition.

6.13.8. CHROM software is used in Canton MS VOA laboratory for data processing.

7. REAGENTS AND STANDARDS

7.1. Reagents and standards information is recorded and available in the laboratory LIMS system. Preparation dates and expiration dates, concentrations, and stock standard identifications are all stored in the LIMS system.

7.2. Reagents

7.2.1. Methanol: Purge and Trap grade, high purity

7.2.2. Reagent Water: High purity water that meets the requirements for an MB when analyzed (see Section 9.4). Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight.

7.2.3. Hydrochloric Acid: Reagent grade or equivalent

7.2.4. Sodium bisulfate: Reagent grade or equivalent

7.3. Standards

7.3.1. Calibration Standard

7.3.1.1. Stock Solutions: Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon®-sealed screw-cap bottles with minimal headspace at -10° to -20°C. Note that standard/spiking concentrations or vendors are subject to change.

7.3.1.2. Working standards: A working solution containing the compounds of interest is prepared from the stock solution(s) in methanol on a weekly basis. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored daily by comparison to the initial calibration curve at the beginning of each 12 hour tune sequence. If any of the calibration check compounds drift in the continuing calibration standard response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem, then a new initial calibration must be performed.

7.3.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.

7.3.1.4. If stock or secondary dilution standards are purchased in sealed ampoules, they may be used up to the manufacturer's expiration date.

7.3.1.5. Additional information can be found in SOP NC-QA-017.

7.3.2. Internal Standards: Internal standards are added to all samples, standards, and blank analyses. Refer to Table 5 for internal standard components.

7.3.3. Surrogate Standards: Refer to Table 6 for surrogate standard components and spiking levels.

7.3.4. Laboratory Control Sample Spiking Solutions: Refer to Table 7 for LCS components and spiking levels. One LCS is included in every batch.

7.3.5. Matrix Spiking Solutions: The matrix spike contains the same components as the LCS. Refer to Table 7. A MS/MSD is included in every batch.

7.3.6. Tuning Standard: A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 50 ng/µL of 4-Bromofluoro-benzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.

7.3.7. All standard preparation information is detailed in the LIMS standards and reagents module.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection to analysis.

8.2. Water samples are normally preserved at pH $\leq$ 2 with hydrochloric acid. Unpreserved water samples must be analyzed within seven days of sampling.

8.3. Solid samples are field preserved with sodium bisulfate solution or by freezing upon receipt at the laboratory for low-level analysis, or with methanol for medium-level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. Analysis must be completed 14 days from sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. Following shipment back to the lab, the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes), then it will be necessary to collect three use two additional 5g EnCore™ samples, one for methanol and two for low-level soils.

8.5. Sample collection for medium level analysis using EnCore™ samplers

8.5.1. When the samples are received at the lab, extrude each (nominal) 5g sample into a tared VOA vial containing 5 mL methanol. Obtain the weight of the soil added to the vial and record in LIMS prep batch.

8.5.2. Add the correct amount of surrogate spiking mixture. 5 µL for a nominal 5g sample.) Refer to Section 17.2 for Michigan project criteria.

8.5.3. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 50 µg/mL solution for a nominal 5 g sample). Reduce the volume of methanol added to ensure the final volume is 5 mL methanol for a nominal 5g sample. Refer to Section 17.2 for Michigan project criteria.

8.5.4. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL spike to 5 mL methanol). Refer to Section 17.2 for Michigan project criteria.

8.5.5. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6. Sample collection for medium-level analysis using field methanol preservation

8.6.1. At client request, the methanol addition and weighing may be performed in the field.

8.6.2. When the samples are returned to the lab, obtain the weight of the soil added to the vial and record in LIMS prep batch.

8.6.3. Add the correct amount of surrogate spiking mixture. (Add 5 µL of 2500 ug/mL solution for a nominal 5g sample.) Refer to Section 17.2 for Michigan project criteria.

8.6.4. Add the correct amount of matrix spiking solution to the MS and MSD samples. (Add 100 µL of 50 µg/mL solution for a nominal 5g sample.) Reduce the volume of methanol added to ensure the final volume is 5 mL methanol for a nominal 5g sample. Refer to Section 17.2 for Michigan project criteria.

8.6.5. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 5 mL methanol. Refer to Section 17.2 for Michigan project criteria.

8.6.6. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.7. Low-level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg), low-level soil preservation must be used. However, it is also necessary to take a sample for the medium-level (field methanol preserved or using the EnCore™ sampler) procedure in case the concentration of analytes in the soil is above the calibration range of the low-level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method (Varian Archon, O.I. 4552, or equivalent).

8.7.3. The soil sample is taken using a 5g EnCore™ sampling device and returned to the lab. It is recommended that two EnCore™ samplers be used for each

field sample location to allow for reruns if necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials for sodium bisulfate preservation by adding a magnetic stir bar, approximately 1g of sodium bisulfate, and 5 mL of reagent water. Prepare vials for preservation by freezing by adding a stir bar and 5 mL reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.01g, and record the weight in the LIMS prep batch.

8.7.7. Extrude the soil sample from the EnCore™ sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil.

Note: Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at <-10^{o}C within 48 hours. The sample must be analyzed within 14 days after sampling and stored at a 45 degree angle in the freezer.

8.8. Unpreserved Soils

8.8.1. At specific client request, unpreserved soils packed into glass jars or brass tubes may be accepted and sub-sampled in the lab. This is the old procedure based on Method 5030A and Method 8260A. It is no longer included in SW846 and is likely to generate results that are biased low, possibly by more than an order of magnitude.

8.9. Aqueous samples are stored in glass containers with Teflon®-lined septa at 4^{o}C ± 2^{o}C with no headspace.

8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14-day holding time. However, they should be analyzed as soon as possible. The lack of preservation must be addressed in the case narrative). Maximum holding time for the EnCore™ sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.11. A holding blank is stored with the samples. Holding blanks are used in all refrigerators used to store samples for volatile compound analyses. Holding blanks are held in storage for a minimum of seven days. These holding blanks are analyzed weekly. The holding blanks are replaced every seven days.

Note: An unpreserved sample must be analyzed when 2-Chloroethyl vinyl ether (2-

CEVE) is a compound of interest, as it cannot be reliably recovered from a preserved sample. If an unpreserved sample is received with 2-CEVE requested as a target analyte, the sample must be analyzed within 7 days of collection. If 2-CEVE is reported from an acid-preserved sample, or from an unpreserved sample past the 7-day holding time, the PM must be notified. The analyst must generate the appropriate NCM to explain that 2-CEVE cannot be reliably recovered from acidified samples.

9. QUALITY CONTROL

9.1. Batch

9.1.1. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort must be made to keep the samples together.

9.1.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Refer to the TestAmerica QC program document (QA-003) for further details of the batch definition.

9.2. Control Limits

9.2.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.2.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.2.3. Control limits may also be project or site specific.

9.3. Surrogates

9.3.1. Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 6. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure instrument performance is acceptable.
- Recalculate the data and/or re-analyze if either of the above checks reveal a

problem.

- Re-prepare and re-analyze the sample if there is sufficient volume. If there is insufficient volume, the surrogate is narrated.

9.3.2. It is only necessary to re-prepare/re-analyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

9.3.3. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then re-analysis or flagging of the data is required.

9.3.4. For concrete matrix, Dibromofluoromethane may have poor recovery in samples and matrix spikes. If the surrogate does not meet criteria, no further action is required due to matrix effect.

9.3.5. Refer to the TestAmerica QC Program document (QA-003) for further details of the corrective actions.

9.4. Method Blanks (MBs)

9.4.1. For each batch of samples, analyze a MB. The MB is analyzed after the calibration standards, normally before any samples. For low-level volatiles, the MB consists of reagent water. For medium-level samples, the MB consists of the same volume of methanol that was used to prepare the samples. Surrogates are added and the MB is carried through the entire analytical procedure. The MB must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below). The method blank is acceptable if any compound detected in the blank is present in the associated samples at ten times the blank level.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, or 2-butanone; chloroform is a common laboratory contaminant for SPLP), the data may be reported with qualifiers, if the concentration of the analyte is less than five times the reporting limit. Such action may only be taken after consultation with and agreement from the client.

- Re-analysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers.

9.4.2. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is

free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client must take place.

9.4.3. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated sample results are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

9.4.4. Refer to the TestAmerica QC Program document, Policy QA-003, for further details of the corrective actions.

9.5. Laboratory Control Samples (LCS)

9.5.1. For each batch of samples, analyze an LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest (see Table 7), and must contain the same analytes as the matrix spike. If any analyte or surrogate is outside established control limits in the sample, the system is out of control and corrective action must occur. Corrective action will normally be re-preparation and re-analysis of the batch. The exceptions are as follows: (a) insufficient sample for re-preparation (b) expired holding times, or (c) the LCS is biased high and the samples are non-detect for those analytes.

- If the batch is not re-extracted and re-analyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.
- If re-extraction and re-analysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation and explanation.

9.5.2. Refer to the TestAmerica QC Program document (Policy QA-003) for further details of the corrective action.

9.5.3. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be

expected statistically. These requirements must be negotiated with the client. n-Hexane must be spiked and reported for the LCS for Ohio VAP samples.

9.5.4. If full analyte spike lists are used at the client request, it is possible some compounds in the LCS may interfere with each other. In that case, the lab will quantitate those compounds in the LCS with a secondary ion which is free from interferences.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. For each QC batch, analyze an MS and MSD. Spiking compounds and levels are given in Table 7. Compare the percent recovery and relative percent difference (RPD) to that from the laboratory-specific, historically-generated limits.

9.6.2. If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the LCS. Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

9.6.2.1. If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include re-analysis of the batch.

9.6.2.2. The matrix spike/duplicate must be analyzed at the same dilution as the un-spiked sample, even if the matrix spike compounds will be diluted out.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. See Canton SOP NC-QA-029.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system with a continuing calibration verification (CCV) standard.

10.1.2. General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 amu
Scan Time:	To give at least 5 scans/peak, but not to exceed 2 seconds/scan
Injector Temperature:	200–250°C
Source Temperature:	According to manufacturer's specifications

Transfer Line	Temperature: 250–300°C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 0.4 – 0.6 mL/minute

10.2. Gas chromatograph suggested temperature program

10.2.1. BFB Analysis

Initial Temperature:	100°C
Initial Hold Time:	0.1 minute
Temperature Program:	20°C/minute
Final Temperature:	200°C

10.2.2. Sample Analysis

Initial Temperature:	40°C
Initial Hold Time:	2minutes
Temperature Program:	15°C/minute
Final Temperature:	200°C
Final Hold Time:	3 minutes

10.3. Instrument Tuning

10.3.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 8 for a maximum of a 50 ng injection or purge of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each 12-hour time period. The 12-hour time period begins at the moment of injection of BFB.

10.4. Initial Calibration (IC)

10.4.1. A series of at least five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Six standards must be used for a quadratic least squares calibration. Suggested calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Suggested calibration levels for a low level 5mL purge are 1, 5, 10, 20, and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 2, 2A, and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. (For example, adequate sensitivity can be obtained by using a 5 mL purge volume to reach the same reporting limits that once required a 25 mL purge. The calibration levels will still be the same 1, 5, 10, 20, 40 µg/L.) However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

NOTE: For Method 8260C. Historically the surrogate compounds have been included in the multi-point initial calibration at variable concentrations in order to

evaluate the linear response as with any target analyte. However, with improvements in instrumentation and more reliance on the autosampler, an option is available depending on the project-specific data quality requirements for allowing the autosampler (or using a manual technique) to spike the initial calibration standards with surrogates in the same manner as the samples are spiked. With this option the surrogate standards in the initial calibration can be averaged to develop a response factor and an effective one point calibration with the sole purpose to measure the surrogate recovery using the same concentration for each sample analysis. For this calibration option the surrogate linear response is less important, since multiple concentrations of surrogates are not being measured. Instead, the surrogate concentration remains constant throughout and the recovery of this known concentration can easily be attained without demonstrating if the response is linear. Under a second calibration option, the surrogates can be calibrated in the same manner as the target analytes, however, the laboratory should have the latitude to employ either option given the instrument system limitations and the ability to meet the project's data quality objectives.

10.4.2. It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests.

10.4.3. Internal standard calibration is used. The internal standards are listed in Table 5. Target compounds must reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See Table 12 for a list of characteristic ions. See Equation 1, Section 12, for calculation of response factor.

10.4.4. For Method 8260B, the % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 11 for the CCCs. This criterion must be met before sample analysis begins.

10.4.4.1. Calibration Check Compound (CCC) (Method 8260B only)

10.4.4.1.1. CCCs are a representative group of compounds, which are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

10.4.4.2. System Performance Check Compounds (SPCC) (Method 8260B only)

10.4.4.2.1. SPCCs are compounds, which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the

continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

10.4.5. The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 9 for the SPCC compounds for Method 8260B and required minimum response factors. Refer to Table 10 for the recommended minimum average relative response factor criteria for initial and continuing calibration verification for Method 8260C.

10.4.6. Weighting of Data Points

10.4.6.1. In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and must be used if the data system has this capability. The Y-intercept is evaluated to determine calibration acceptability.

10.4.7. For any analyte with % RSD >15%, linear or quadratic curve fits may be used if the compounds have historically exhibited a non-linear response. The analyst must consider instrument maintenance to improve the linearity of response. Nonlinear calibration models cannot be used to extend the calibration range for compounds that normally exhibit a linear response, but in a narrower calibration range. If the % RSD is > 15%, the analyst may drop the low or high in the ICAL , as long as a minimum of five points are maintained (six points for quadratic) and the quantitation range is adjusted accordingly. Otherwise, the coefficient of determination r^2 must be $\geq$ 0.99. For Method 8260C, % RSD is ± 20% for each target analyte.

10.4.8. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9. The calibration standards for the initial five-point calibration for low-level soils must be heated to 40ºC for purging. Using this calibration curve for water samples is acceptable as long as all calibration, QC, and samples are also heated to 40°C. A separate five-point calibration must be prepared for analysis of low level soils that are preserved with sodium bisulfate. Low-level soils analysis requires the use of a closed vial autosampler. Each standard for analysis of sodium bisulfate preserved samples is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1g sodium bisulfate. The standards are heated to 40ºC for

purging. All low-level soil samples, standards, and blanks must also be heated to 40ºC for purging.

10.4.10. Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five-point initial calibration. Detection of the non-standard analytes at the low concentration is required. If the analyte is detected in any of the samples, a five-point initial calibration must be generated and the sample(s) re-analyzed for quantitation. However, if the analyte is not detected, the non-detect is reported and no further action is necessary.

10.4.11. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. For Method 8260B, the recovery for CCC compounds must be ≤ 20%. The recovery for non-CCC compounds must be ≤ 50% with an allowance of up to six compounds > 50%.

10.4.11.1. For Method 8260C, the acceptance criteria is 70-130% for each target analyte, with the exception of the analytes listed in section 17.4 that have acceptance criteria of 50- 150%:

10.4.11.2. Continuing Calibration

10.4.12. The initial calibration must be verified every 12 hours.

10.4.13. Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. A midpoint calibration standard is used as the continuing calibration.

10.4.14. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in Equation 4, Section 12.3.4.

10.4.15. For Method 8260B, the % difference or % drift of the CCCs must be ≤ 20% for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 9. In addition, the percent drift of all analytes must be ≤ 50% with allowance for up to six target analytes to have percent drift > 50%.

10.4.15.1. For Method 8260C, all compounds of interest must be verified at 20%, with the exception of the compounds listed in section 17.4 that must be verified with percent difference or percent drift of 50%.

10.4.16. If the CCCs and/or the SPCCs do not meet the criteria in Section 10.5.3 and Table 9, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis

begins. Extensive corrective action such as a different type of column will require a new initial calibration. For Method 8260C, any sample non-detects for an analyte that fails the SOP criteria low, must have a low level CCV (CCV at the RL) in the batch as a sensitivity demonstration. The criterion for a passing LLCCV is detection only, and a passing LLCCV allows non-detect samples to be reported without flagging.

10.4.17. Once the above criteria have been met, sample analysis may begin. Initial calibration average RFs (or the calibration equation) will be used for sample quantitation, not the continuing calibration RFs. Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11. PROCEDURE

11.1. Procedural Variations

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation must be completely documented using a Nonconformance Memo and approved by a Supervisor or Group Leader. The Nonconformance Memo must be filed in the project file.

11.1.2. Any unauthorized deviations from this procedure must also be documented as a non-conformance with a cause and corrective action described. See SOP NC-QA-029.

11.2. Preliminary Evaluation

11.2.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.2.2. Where available, the project manager's notes and historical information available in the LIMS system must be consulted for details on sample matrix, special instructions, and/or dilutions.

11.2.3. Aqueous samples must be checked for proper preservation. Sample vials used for screening purposes are checked prior to being placed on the instrument. Any sample with a pH greater than 2 is considered unpreserved and must be analyzed within 7 days of sampling. Sample vials used for the analysis are checked for proper preservation after analysis has been completed. Both the screening vial pH and the analysis vial pH will be noted.

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11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain an MS/MSD, an LCS, and a method blank. See Section 9.4 for method blank preparation.

11.3.2.1. It is not necessary to re-analyze batch QC with re-analyses of samples. However, any reruns must be part of a valid batch.

11.3.3. Dilutions must be done just prior to the GC/MS analysis of the sample. Dilutions are made in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 µL of sample, then serial dilutions must be made in volumetric flasks. Dilutions may also be prepared in a 40 mL vial. An appropriate amount of water is added to the vial. The sample is added using an appropriate syringe.

11.3.3.1. Estimate a dilution that will give analyte concentrations in the upper half of the calibration range.

11.4. Methanol Extract Soils

11.4.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Sections 8.5 or 8.6) to the syringe. If less than 1µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1µL will be added to the water in the syringe. Refer to Section 17.2 for Michigan project requirements.

Note: All soil samples prepared as a methanol extraction will be corrected for moisture content using the factor in the equation 12.3.6.

11.5. Liquid wastes that are soluble in methanol and insoluble in water.

11.5.1. Pipette 1 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1g.

11.5.2. Quickly add 4 mL of methanol, then add 5µL of a 2500 µg/mL surrogate spiking solution to bring the final volume to 5 mL. Cap the vial and shake for two minutes to mix thoroughly. For an MS/MSD or LCS, 4.9 mL of methanol, 5µL of a 2500 µg/mL surrogate spiking solution, and 0.1 mL of matrix spike solution is used.

11.5.3. Rinse a gas-tight syringe with organic-free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Sections 8.5 or 8.6) to the syringe. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1µL will be added to the water in the syringe.

11.6. Aqueous and low-level soil sample analysis (Purge and Trap units that sample directly from the VOA vial)

11.6.1. Units which sample from the VOA vial must be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.6.2. If the autosampler uses automatic IS/SS injection no further preparation of the VOA vial is needed. Otherwise, the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to be analyzed as soils.

11.6.3. Soil samples, which are preserved with sodium bisulfate, must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1g in 5 mL).

11.6.4. Soil samples, which are preserved by freezing, must be allowed to thaw completely before sample analysis begins.

11.6.5. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.7. Aqueous Samples Not Directly Sampled from VOA Vials

11.7.1. All samples and standard solutions must be at ambient temperature before analysis.

11.7.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq$ 5 µL. Check and document the pH of the remaining sample.

11.7.3. Add 50 ng of each internal and surrogate standard. The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 10 µg/L solution for a 5 mL sample). Inject the sample into the purging chamber. Alternately, the internal and surrogate standards can be added automatically by the autosampler.

11.7.3.1. For TCLP samples, use 1.0 mL of TCLP leachate with 4 mL reagent water. (Note: TCLP reporting limits will be five times higher than the corresponding aqueous limits.)

11.7.4. Purge the sample for 11 minutes (trap must be below 35ºC).

11.7.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for approximately 3-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.7.6. Desorb and bake time and temperature are optimized for the type of trap in use (see vendor's instructions). The same conditions must be used for all samples and standards.

11.8. Analyzing aqueous samples in the soil mode

11.8.1. Measure out 10 mL of aqueous sample using a gas tight syringe

11.8.2. Expel into a clean 40 mL VOC vial

11.8.3. Load into autosampler

11.8.4. Autosampler adds 5 mL of reagent water and 1 µl each of surrogate and internal standard

11.8.5. Analyze as described in Section 11.6.

11.9. *Low-Level Solids Analysis using discrete autosamplers, Methods 8260A and 5030A*

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

11.9.1. This method is based on purging a heated soil/sediment sample mixed with reagent water containing the surrogates and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40^{o}C.

11.9.2. Weigh out 5g (or other appropriate aliquot) of sample into a 40 mL vial. Record the weight to the nearest 0.1g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 0.5g. If the sample is contaminated with analytes such that a purge amount less than 0.5g is appropriate, use the medium level method. Add 5 mL of organic free water to the VOA vial. Add surrogate/internal standard (and matrix spike solutions if required.). Analyze as described in Section 11.6.

11.9.3. For the medium level method, add 5g soil to 5 mL methanol containing the surrogates, mix for two minutes, allow to settle, and store in a clean Teflon®-capped vial at 4°C until analysis. Analyze as described in Section 11.4.

11.9.4. The above steps must be performed rapidly and without interruption to avoid loss of volatile organics.

11.10. Medium-Level Soil/Sediment and Waste Samples

11.10.1. Sediments/soils and waste that are insoluble in methanol

11.10.1.1. Weigh 5 g (wet weight) into a tared vial. Use a top-loading balance. Record the weight to 0.1 gram. Do not discard any supernatant liquids.

11.10.1.2. Quickly add 5 mL of methanol, and 5µL of 2500 µg/mL surrogate spiking solution to bring the final volume of methanol to 5 mL. For an LCS or MS/MSD sample, add 4.9 mL of methanol, 5µL of surrogate spike solution, and 0.1 mL of matrix spike solution. Cap the vial and shake or vortex to mix thoroughly.

Note: Sections 11.10.1.1 and 11.10.1.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.11. Initial review and corrective actions

11.11.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required.

11.11.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required. Re-analysis must be at the same dilution, if matrix interference is not observed.

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11.11.2.1. The internal standard response in samples is compared to the associated continuing calibration standard. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect, the sample is re-analyzed to confirm. If the change in sensitivity is due to instrumental problems, all affected samples must be re-analyzed after the problem is corrected.

11.12. Dilutions

11.12.1. If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution must be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.12.2. Guidance for Dilutions Due to Matrix

11.12.2.1. If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample must be re-analyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgment.

11.12.3. Reporting Dilutions

11.12.3.1. The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Target compound mass spectra for standard reference must be obtained on the user's GC/MS by analysis of the calibration standards.

12.1.2. Two criteria must be satisfied to verify target compound identification: (1) elution of sample component at the same GC retention time as the same component in the standard, and (2) correspondence of the sample component and the standard component characteristic ions. See Table 12 for a list of the

characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

12.1.2.1. The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same 12 hours as the sample.

12.1.2.2. The relative intensities of ions must agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.3. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst must report that identification and proceed with quantitation.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

12.2.1.1. Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) must be present in the sample spectrum.

12.2.1.2. The relative intensities of the major ions must agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum must be present in the sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of co-eluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual

inspection of the sample with the nearest library searches must the analyst assign a tentative identification.

12.3. Calculations

12.3.1. Response Factor (RF)

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_{is} = Amount of the internal standard, ng

C_x = Amount of the compound being measured, ng

12.3.2. Standard Deviation (SD)

Equation 2

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(Xi - X)^2}{N - 1}}$$

Where:

X_i = Value of X at i through N

N = Number of points

X = Average value of X_I

12.3.3. Percent Relative Standard Deviation (%RSD)

Equation 3

$$\%RSD = \frac{\text{Standard Deviation}}{\overline{RF_i}} \times 100$$

$\overline{RF_i}$ = Mean of RF values in the curve

12.3.4. Percent Drift Between the Initial Calibration and the Continuing Calibration

Equation 4

$$\%\ \text{Drift} = \frac{C_{expecte} - C_{found}}{C_{expecte}} \times 100$$

Where:

$C_{expecte}$ = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3.5. Target Compound and Surrogate Concentrations

12.3.5.1. Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is ≤ 15% (< 20% for method 8260C).

12.3.5.2. Calculation of Concentration Using Average Response Factors

Equation 5

$$\text{Concentration } \mu g / L = \frac{x}{\overline{RF}}$$

12.3.5.3. Calculation of Concentration using Linear Fit

Equation 6

$$\textbf{Concentration } \mu\textbf{g / L} = A + Bx$$

12.3.5.4. Calculation of Concentration Using Quadratic Fit

Equation 7

$$\textbf{Concentration } \mu\textbf{g / L} = A + Bx + Cx^2$$

Where:

x is defined in Equations 8, 9, and 10

A is a constant defined by the intercept

B is the slope of the curve

C is the curvature

12.3.5.5. Calculation of ***x*** for Water and water-miscible waste:

Equation 8

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

X = ug/L

A_x = Area of characteristic ion for the compound being measured (secondary ion quantitation is allowed only when there are sample interferences with the primary ion)

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

V_o = Volume of water purged, mL

12.3.5.6. Calculation of ***x*** for Medium level soils:

Equation 9

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

X = ug/kg

A_x, I_s, D_f, A_{is}, same as for water

V_t = Volume of total extract, mL

V_a = Volume of extract added for purging, µL

W_s = Weight of sample extracted, g

$$D = \frac{100 - \%moisture}{100}$$

12.3.5.7. Calculation of ***x*** for Low level soils:

Equation 10

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

X = ug/kg

A_x, I_s, A_{is}, same as for water

D = as for medium level soils

W_s = Weight of sample added to the purge vessel, g

12.3.5.8. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x = Area in the total ion chromatogram for the compound being measured

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference

RF = 1

In other words, the concentration is equal to *x* as defined in Equations 5 through 10.

12.3.6. Calculation for solids with methanol correction applied

12.3.6.1. SW-846 8000C, Section 11.10.5 states the following: Solid samples with a significant moisture content (>10%), designated for volatile organic analysis, that are extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the solvent/water mixture. The total mixture volume can only be calculated based on the sample moisture present as determined by the % moisture determination. This total volume is then expressed as Vt in the sample concentration calculations provided. Therefore, in order to report results for volatiles analysis of samples containing significant moisture content on an "as received" basis, the calculated concentration needs to be corrected using the total solvent/water mixture volume represented as Vt. The total solvent/water volume is calculated as follows:

Equation 11

uL solvent/water V_t = *[mL of solvent + ((%moisture/100) x g of sample)] x 1000 uL/mL*

V_t solvent/water is then used in the formula in section 12.3.5.6.

12.3.7. MS/MSD Recovery

Equation 12

$$\textbf{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample result
SR = Sample Result
SA = Spiked amount

12.3.8. Relative % Difference (RPD) calculation for the MS/MSD:

Equation 13

$$\textbf{RPD} = \frac{|\textbf{MSR - MSDR}|}{\frac{1}{2}(\textbf{MSR + MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result
MSDR = Matrix spike duplicate result

12.4. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is defined in QA SOPs NC-QA-021 and CA-Q-S-006. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method. The non-standard compound must be detected in the reporting limit standard to be acceptable.

13.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client.

13.2. Initial Demonstration

13.2.1. Each analyst must have initial demonstration of competence (IDOC) data on file for each method he or she performs. A continuing DOC (CDOC) must be performed annually as evidence of on-going competence to perform these analyses.

13.2.2. An MDL study must be performed and documented for each analysis method and each matrix.

13.3. Training Qualification

13.3.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Specific training requirements are outlined in the Quality Assurance Manual.

13.3.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

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14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

15.2. All waste will be disposed of in accordance with Federal, State, and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.3. The following waste streams are produced when this method is carried out.

15.3.1. **Acidic material from the auto-sampler**: Waste stream must be collected and neutralized before discharge to a sewer system if the pH is less than 5.

15.3.2. **Methanol waste from rinses and standards:** Methanol waste is discarded as a flammable liquid in a solvent waste container identified as "Flammable Liquid Waste".

15.3.3. **All samples including purged and extracted soils and waters:** Samples are collected in boxes and removed from the lab to storage. The Waste Coordinator handles crushing the vials and proper disposal.

16. REFERENCES

16.1. References

16.1.1. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

16.1.2. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260A, Update II, September 1994

16.1.3. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Purge-and-Trap for Aqueous Samples, Method 5030C, Rev 3, May 2003

16.1.4. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Purge-and-Trap for Aqueous Samples, Method 5030B, Rev 2, December 1996

16.1.5. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Purge-and-Trap for Aqueous Samples, Method 5030A, Rev 1, July 1992

16.1.6. SW846, *Test Methods for Evaluating Solid Waste,* Third Edition, Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035, Rev 0, December 1996

16.1.7. SW846, Test Methods for Evaluating Solid Waste Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035A, Draft Revision 1, July 2002

16.1.8. SW846, Test Methods for Evaluation Solid Waste, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Method 8260C, Revision 3, August 2006.

16.1.9. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.10. TestAmerica Corporate Environmental Health and Safety Manual, **CW-E-M-001** and TestAmerica **Canton Facility Addendum And Contingency Plan**, current version

16.1.11. Corporate Quality Management Plan (CQMP), current version

16.1.12. Revision History

Historical File:		Revision 2.0: 12/15/97		Revision 0: 06/30/08 (NC-MS-019)
(formerly CORP-MS-0002NC)		Revision 2.1: 03/06/00		Revision 1: 01/07/09
		Revision 2.2: 11/28/00		Revision 2: 02/17/12
		Revision 2.3: 05/23/01		Revision 3: 06/29/12
		Revision 2.4: 09/27/04		Revision 4: 05/21/14
		Revision 2.5: 04/03/07		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection LimitsNC-QA-021 and CA-Q-S-006

16.2.5. Standards and Reagents, NC-QA-017

16.2.6. Laboratory Holding Blanks, NC-QA-020

16.2.7. Selection of Calibration Points, CA-T-P-002

16.2.8. Calibration Curves (General), CA-Q-S-005

16.2.9. Acceptable Manual Integration Practices, CA-Q-S-002

17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW846 in order to improve the reliability of qualitative identification.

17.2. The following are protocols that must be followed to achieve the lower reporting limits required when analyzing Michigan projects.

17.2.1. Modify Sections 8.5.4 and 8.6.8 (add 5 uL of 2500 ug/mL surrogate solution for a nominal 10g sample).

17.2.2. Modify Sections 8.5.5 and 8.6.9 (add 200 uL of 50 ug/mL spike solution for a nominal 10g sample).

17.2.3. Modify Sections 8.5.6 and 8.6.10 (add 200 uL of 50 ug/mL spike solution for a nominal 10g sample).

17.2.4. Michigan reporting limits for methanol preserved soils are achieved by injecting 100 uL of the methanol extract in a 5 mL purge. The instrument is calibrated using the recommended calibration range for water of 0.5 ug/L to 100 ug/L. Some analytes are prepared at higher concentrations.

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17.3. Analysis of aqueous samples in the soil mode: A 10 mL aliquot of the sample is poured into a 40 mL vial, 5 mL of reagent water is added, and the sample is loaded in the autosampler.

17.4. The minimum response factors recommended by Method 8260C were modified to define the performance of analytes on the columns and conditions used.

The initial calibration verification criteria and continuing calibration acceptance criteria were modified to define acceptance limits for the following poor performing compounds, which include a) compounds that do not purge well, b) compounds that have erratic response, and c) compounds that are common lab contaminants whose contribution to reference standard peak areas can adversely affect the calibration causing the potential for high or low bias to calclulated results and recoveries.

Acetone

Acrolein

1,2-Dibromo-3-chloropropane

1,4-Dioxane

Ethyl acetate

2-Methyl-2-propanol

Methylene Chloride

Naphthalene

1,2,4-Trichlorobenzene

Vinyl acetate

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Table 1 - TestAmerica Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Dichlorodifluoromethane	75-71-8	5	1	5	250	250
Chloromethane	74-87-3	5	1	5	250	250
Bromomethane	74-83-9	5	1	5	250	250
Vinyl chloride	75-01-4	5	1	5	250	250
Chloroethane	75-00-3	5	1	5	250	250
Trichlorofluoromethane	75-69-4	5	1	5	250	250
Acrolein	107-02-8	100	20	100	5,000	5,000
Acetone	67-64-1	20	10	20	1,000	1,000
Trichlorotrifluoroethane	76-13-1	5	1	5	250	250
Iodomethane	74-88-4	5	1	5	250	250
Carbon disulfide	75-15-0	5	1	5	250	250
Methylene chloride	75-09-2	5	1	5	250	250
tert-Butyl alcohol	75-65-0	200	50	200	10,000	10,000
1,1-Dichloroethene	75-35-4	5	1	5	250	250
1,1-Dichloroethane	75-34-3	5	1	5	250	250
Trans-1,2-Dichloroethene	156-60-5	5.0	1.0	5.0	250	250
Acrylonitrile	107-13-1	100	20	100	5,000	5,000
Methyl *tert*-butyl ether (MTBE)	1634-04-4	5	1	5	250	250
Hexane	110-54-3	5	1	5	250	250
cis-1,2-Dichloroethene	156-59-2	5	1	5	250	250
1,2-Dichloroethene (Total)	540-59-0	10	2	10	500	500
Tetrahydrofuran	109-99-9	20	5	20	1,000	1,000
Chloroform	67-66-3	5	1	5	250	250
1,2-Dichloroethane	107-06-2	5	1	5	250	250
Dibromomethane	74-95-3	5	1	5	250	250
2-Butanone	78-93-3	20	5	20	1,000	1,000
1,4-Dioxane	123-91-1	500	200	500	25,000	25,000
1,1,1-Trichloroethane	71-55-6	5	1	5	250	250
Carbon tetrachloride	56-23-5	5	1	5	250	250
Bromodichloromethane	75-27-4	5	1	5	250	250
1,2-Dichloropropane	78-87-5	5	1	5	250	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250	250
Trichloroethene	79-01-6	5	1	5	250	250
1,2-Dibromoethane	106-93-4	5	1	5	250	250

Table 1 - TestAmerica Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
1,2,3-Trichloropropane	96-18-4	5	1	5	250	250
1,1,2-Trichloroethane	79-00-5	5	1	5	250	250
Benzene	71-43-2	5	1	5	250	250
Ethylmethacrylate	97-63-2	5	1	5	250	250
Trans-1,3-Dichloropropene	10061-02-6	5	1	5	250	250
Bromoform	75-25-2	5	1	5	250	250
4-Methyl-2-pentanone	108-10-1	20	5	20	1000	1,000
2-Hexanone	591-78-6	20	5	20	1000	1,000
Tetrachloroethene	127-18-4	5	1	5	250	250
Toluene	108-88-3	5	1	5	250	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250	250
2-Chloroethyl vinyl ether	110-75-8	N/A[2]	N/A	50	1000	1,000
Vinyl acetate	108-05-4	10	2	10	500	500
Chlorobenzene	108-90-7	5	1	5	250	250
Ethylbenzene	100-41-4	5	1	5	250	250
Styrene	100-42-5	5	1	5	250	250
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250	250
m and p Xylenes		10	2	10	500	500
o-xylene	95-47-6	5.0	1	5	250	250
Total xylenes	1330-20-7	10	2	10	500	500
1,3-Dichlorobenzene	541-73-1	5	1	5	250	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250	250
2,2-Dichloropropane	590-20-7	5	1	5	250	250
Bromochloromethane	74-97-5	5	1	5	250	250
1,1-Dichloropropene	563-58-6	5	1	5	250	250
Bromodichloromethane	75-27-4	5	1	5	250	250
1,2-Dichloropropane	78-87-5	5	1	5	250	250
1,3-Dichloropropane	142-28-9	5	1	5	250	250
Isopropylbenzene	98-82-8	5	1	5	250	250
Bromobenzene	108-86-1	5	1	5	250	250
n-Propylbenzene	103-65-1	5	1	5	250	250
2-Chlorotoluene	95-49-8	5	1	5	250	250
4-Chlorotoluene	106-43-4	5	1	5	250	250
1,3,5-Trimethylbenzene	108-67-8	5	1	5	250	250
Tert-Butylbenzene	98-06-6	5	1	5	250	250

Table 1 - TestAmerica Reporting Limits

Compound	CAS Number	Reporting Limits[1]				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
1,2,4-Trimethylbenzene	95-63-6	5	1	5	250	250
Sec-butylbenzene	135-98-8	5	1	5	250	250
4-Isopropyltoluene	99-87-6	5	1	5	250	250
n-Butylbenzene	104-51-8	5	1	5	250	250
1,2,4-Trichlorobenzene	120-82-1	5	1	5	250	250
Napthalene	91-20-3	5	1	5	250	250
Hexachlorobutadiene	87-68-3	5	1	5	250	250
1,2,3-Trichlorobenzene	87-61-6	5	1	5	250	250
Cyclohexane	110-82-7	10	1	10	500	500
Methyl Acetate	79-20-9	10	10	10	500	500
Methyl cyclohexane	108-87-2	10	1	10	500	500
Epichlorohydrin	106-89-8	50		25	1250	
Propylene Oxide	75-56-9	20		100	5000	
2-Ethyltoluene	611-14-3	1		5	250	
3-Ethyltoluene	620-14-4	1		5	250	
1-Chlorohexane	544-10-5	1		5	250	
Ethylene Oxide	75-21-8	200		250		
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250	
1,2-Dibromo-3-chloropropane	96-12-8	10	2	10	500	
3-Chloro-1-propene	107-05-1	10	2	10	500	
Dichlorofluoromethane	75-43-4	10	2	10	500	
Ethyl ether	60-29-7	10	2	10	500	
Isobutanol	78-83-1	200	50	200	10,000	
n-Heptane	142-82-5	1	5	5	250	
1,3-Dichloropropene, Total	542-75-6	2	10	10	500	
Butadiene	106-99-0	1			250	
Ethyl acrylate	140-88-5	1			500	
n-Butyl acrylate	123-86-4	1			250	
Trihalomethanes, Total		1				

[1] Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

[2] 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

Table 2 - TestAmerica Recommended Primary Standard Calibration Levels, 5 mL purge Solid

Compound	Calibration Level ug/kg				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	10	50	100	200
Toluene-d8 (Surrogate)	5	10	50	100	200
4-Bromofluorobenzene (Surrogate)	5	10	50	100	200
Dichlorodifluoromethane	5	10	50	100	200
Chloromethane	5	10	50	100	200
Bromomethane	5	10	50	100	200
Vinyl chloride	5	10	50	100	200
Chloroethane	5	10	50	100	200
Dichlorofluoromethane	5	10	50	100	200
Trichlorofluoromethane	5	10	50	100	200
Ethyl ether	5	10	50	100	200
Acrolein	50	100	500	1000	2000
Acetone	10	20	100	200	400
Trichlorotrifluoroethane	5	10	50	100	200
Iodomethane	5	10	50	100	200
Carbon disulfide	5	10	50	100	200
3-Chloro-1-propene	5	10	50	100	200
Methylene chloride	5	10	50	100	200
tert-Butyl alcohol	100	200	1,000	2,000	4,000
1,1-Dichloroethene	5	10	50	100	200
1,1-Dichloroethane	5	10	50	100	200
trans-1,2-Dichloroethene	5	10	50	100	200
Acrylonitrile	50	100	500	1000	2000
Methyl *tert*-butyl ether (MTBE)	5	10	50	100	200
Hexane	5	10	50	100	200
cis-1,2-Dichloroethene	5	10	50	100	200
Tetrahydrofuran	5	10	50	100	200
Chloroform	5	10	50	100	200
1,2-Dichloroethane	5	10	50	100	200
Dibromomethane	5	10	50	100	200
2-Butanone	10	20	100	200	400
1,4-Dioxane	250	500	2,500	5,000	10,000
1,1,1-Trichloroethane	5	10	50	100	200
Carbon tetrachloride	5	10	50	100	200
Isobutyl alcohol	125	250	1250	2500	5000
Bromodichloromethane	5	10	50	100	200
1,2-Dichloropropane	5	10	50	100	200

Table 2 - TestAmerica Recommended Primary Standard Calibration Levels, 5 mL purge Solid

Compound	Calibration Level ug/kg				
	Level 1	Level 2	Level 3	Level 4	Level 5
cis-1,3-Dichloropropene	5	10	50	100	200
Trichloroethene	5	10	50	100	200
Dibromochloromethane	5	10	50	100	200
1,2-Dibromoethane	5	10	50	100	200
1,2,3-Trichloropropane	5	10	50	100	200
Acetonitrile	50	100	500	1000	2000
1,1,2-Trichloroethane	5	10	50	100	200
Benzene	5	10	50	100	200
n-Heptane	5	10	50	100	200
Ethylmethacrylate	5	10	50	100	200
trans-1,3-Dichloropropene	5	10	50	100	200
Bromoform	5	10	50	100	200
4-Methyl-2-pentanone	10	20	100	200	400
2-Hexanone	10	20	100	200	400
Tetrachloroethene	5	10	50	100	200
Toluene	5	10	50	100	200
1,1,2,2-Tetrachloroethane	5	10	50	100	200
2-Chloroethyl vinyl ether	10	20	100	200	400
Vinyl acetate	5	10	50	100	200
Chlorobenzene	5	10	50	100	200
1,1,1,2-Tetrachloroethane	5	10	50	100	200
Ethylbenzene	5	10	50	100	200
Styrene	5	10	50	100	200
t-1,4-Dichloro-2-butene	5	10	50	100	200
m and p Xylenes	10	20	100	200	400
o-xylene	5	10	50	100	200
1,3-Dichlorobenzene	5	10	50	100	200
1,4-Dichlorobenzene	5	10	50	100	200
1,2-Dichlorobenzene	5	10	50	100	200
1,2-Dibromo-3-chloropropane	5	10	50	100	200
2,2-Dichloropropane	5	10	50	100	200
Bromochloromethane	5	10	50	100	200
1,1-Dichloropropene	5	10	50	100	200
Bromodichloromethane	5	10	50	100	200
1,2-Dichloropropane	5	10	50	100	200
1,3-Dichloropropane	5	10	50	100	200
Isopropylbenzene	5	10	50	100	200
Bromobenzene	5	10	50	100	200
n-Propylbenzene	5	10	50	100	200
2-Chlorotoluene	5	10	50	100	200
4-Chlorotoluene	5	10	50	100	200

Table 2 - TestAmerica Recommended Primary Standard Calibration Levels, 5 mL purge Solid

Compound	Calibration Level ug/kg				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,3,5-Trimethylbenzene	5	10	50	100	200
tert-Butylbenzene	5	10	50	100	200
1,2,4-Trimethylbenzene	5	10	50	100	200
sec-butylbenzene	5	10	50	100	200
4-Isopropyltoluene	5	10	50	100	200
n-Butylbenzene	5	10	50	100	200
1,2,4-Trichlorobenzene	5	10	50	100	200
Napthalene	5	10	50	100	200
Hexachlorobutadiene	5	10	50	100	200
1,2,3-Trichlorobenzene	5	10	50	100	200
Epichlorohydrin	50	100	500	1000	2000
Propylene oxide	50	100	500	1000	2000
2-Ethyltoluene	5	10	50	100	200
3-Ethyltoluene	5	10	50	100	200
1-Chlorohexane	5	10	20	50	200
Ethylene oxide	50	100	500	1000	2000

Table 2A - TestAmerica Primary Standard Recommended Calibration Levels, Low Level [1(Water)]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Dibromofluoromethane (Surrogate)	1	2	10	20	40
1,2-Dichloroethane-d4 (Surrogate)	1	2	10	20	40
Toluene-d8 (Surrogate)	1	2	10	20	40
Bromofluorobenzene (Surrogate)	1	2	10	20	40
Dichlorodifluoromethane	1	2	10	20	40
Chloromethane	1	2	10	20	40
Vinyl Chloride	1	2	10	20	40
Bromomethane	1	2	10	20	40
Chloroethane	1	2	10	20	40
Dichlorofluoromethane	1	2	10	20	40
Trichlorofluoromethane	1	2	10	20	40
Ethyl ether	1	2	10	20	40
Acrolein	10	20	100	200	400
Acetone	2	4	20	40	80
1,1-Dichloroethene	1	2	10	20	40
Trichlorotrifluoroethane	1	2	10	20	40
Iodomethane	1	2	10	20	40
Carbon Disulfide	1	2	10	20	40
3-Chloro-1-propene	1	2	10	20	40
Methylene Chloride	1	2	10	20	40
Acetonitrile	10	20	100	200	400
Acrylonitrile	10	20	100	200	400
Methyl tert-butyl ether	1	2	10	20	40
trans-1,2-Dichloroethene	1	2	10	20	40
Hexane	1	2	10	20	40
Vinyl acetate	1	2	10	20	40
1,1-Dichloroethane	1	2	10	20	40
tert-Butyl Alcohol	20	40	200	400	800
2-Butanone	2	4	20	40	80
cis-1,2-dichloroethene	1	2	10	20	40
2,2-Dichloropropane	1	2	10	20	40
Bromochloromethane	1	2	10	20	40

Table 2A - TestAmerica Primary Standard Recommended Calibration Levels, Low Level [1(Water)]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Chloroform	1	2	10	20	40
Tetrahydrofuran	1	2	10	20	40
1,1,1-Trichloroethane	1	2	10	20	40
1,1-Dichloropropene	1	2	10	20	40
Carbon Tetrachloride	1	2	10	20	40
Isobutyl alcohol	25	50	250	500	1000
1,2-Dichloroethane	1	2	10	20	40
Benzene	1	2	10	20	40
n-Heptane	1	2	10	20	40
Trichloroethene	1	2	10	20	40
1,2-Dichloropropane	1	2	10	20	40
1,4-Dioxane	50	100	500	1000	2000
Dibromomethane	1	2	10	20	40
Bromodichloromethane	1	2	10	20	40
2-Chloroethyl vinyl ether	2	4	20	40	80
cis-1,3-Dichloropropene	1	2	10	20	40
4-Methyl-2-pentanone	2	4	20	40	80
Toluene	1	2	10	20	40
trans-1,3-Dichloropropene	1	2	10	20	40
Ethyl Methacrylate	1	2	10	20	40
1,1,2-Trichloroethane	1	2	10	20	40
1,3-Dichloropropane	1	2	10	20	40
Tetrachloroethene	1	2	10	20	40
2-Hexanone	2	4	20	40	80
Dibromochloromethane	1	2	10	20	40
1,2-Dibromoethane	1	2	10	20	40
Chlorobenzene	1	2	10	20	40
1,1,1,2-Tetrachloroethane	1	2	10	20	40
Ethylbenzene	1	2	10	20	40
m + p-Xylene	2	4	20	40	80
Xylene-o	1	2	10	20	40
Styrene	1	2	10	20	40
Bromoform	1	2	10	20	40
Isopropylbenzene	1	2	10	20	40
1,1,2,2-	1	2	10	20	40

Table 2A - TestAmerica Primary Standard Recommended Calibration Levels, Low Level [1(Water)]

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Tetrachloroethane					
1,4-Dichloro-2-butene	1	2	10	20	40
1,2,3-Trichloropropane	1	2	10	20	40
Bromobenzene	1	2	10	20	40
n-Propylbenzene	1	2	10	20	40
2-Chlorotoluene	1	2	10	20	40
1,3,5-Trimethylbenzene	1	2	10	20	40
4-Chlorotoluene	1	2	10	20	40
tert-Butylbenzene	1	2	10	20	40
1,2,4-Trimethylbenzene	1	2	10	20	40
sec-Butylbenzene	1	2	10	20	40
4-Isopropyltoluene	1	2	10	20	40
1,3-Dichlorobenzene	1	2	10	20	40
1,4-Dichlorobenzene	1	2	10	20	40
n-Butylbenzene	1	2	10	20	40
1,2-Dichlorobenzene	1	2	10	20	40
1,2-Dibromo-3-chloropropane	1	2	10	20	40
1,2,4-Trichlorobenzene	1	2	10	20	40
Hexachlorobutadiene	1	2	10	20	40
Naphthalene	1	2	10	20	40
1,2,3-Trichlorobenzene	1	2	10	20	40
Cyclohexane	1	2	10	20	40
Methyl Acetate	2	4	20	40	80
Methylcyclohexane	1	2	10	20	40
1,3,5-Trichlorobenzene	1	2	10	20	40
Epichlorohydrin	10	20	100	200	400
Propylene oxide	10	20	100	200	400
2-Ethyltoluene	1	2	10	20	40
3-Ethyltoluene	1	2	10	20	40
1-Chlorohexane	1	2	10	20	40
Ethylene oxide	50	100	500	1000	2000

[1] *25 mL purge samples analyzed at 5 mL purge on more sensitive equipment.*

Table 3 - TestAmerica Appendix IX Standard and Reporting Limits, 5 mL purge

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	Low Level 5mL purge water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Acetonitrile	75-05-8	100	20	100	5000
Isopropyl ether	108-20-3	10	2	10	500
Chloroprene	126-99-8	5	1	5	250
n-Butanol	71-36-3	200	50	200	10,000
Propionitrile	107-12-0	50	10	50	2500
Methacrylonitrile	126-98-7	50	10	50	2500
Methyl methacrylate	80-62-6	5	1	5	250
Ethyl Acetate	141-78-6	20	4	20	1,000
2-Nitropropane	79-46-9	10	4	10	500
Cyclohexanone	108-94-1	50	20	50	2500
Isopropylbenzene	98-82-8	5	1	5	250
1,2,3-Trimethylbenzene	526-73-8	5	5	5	250
1,3,5-Trichlorobenzene	108-70-3	5	1	5	250
Benzyl chloride	100-44-7	5	1	5	250
Pentachloroethane	76-01-7	10	2	10	500
Tert-Amyl methyl ether	994-05-8	10	5	10	500
Tert-Butyl ethyl ether	637-92-3	10	5	10	500
2-Methylnaphthalene (Michigan only)	91-57-6	25	5	10	1250

Table 4

Recommended TestAmerica Appendix IX Standard Calibration Levels, µg/kg

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Acetonitrile	50	100	500	1000	2000
Isopropyl ether	5	10	50	100	200
Chloroprene	5	10	50	100	200
n-Butanol	125	250	1250	2500	5000
Propionitrile	50	100	500	1000	2000
Methacrylonitrile	50	100	500	1000	2000
Methyl methacrylate	10	40	100	200	400
Ethyl Acetate	10	40	100	200	400
2-Nitropropane	10	40	100	200	400
Cyclohexanone	50	100	500	1000	2000
Ethyl tert-butyl ether	5	10	50	100	200
tert-Amyl methyl ether	5	10	50	100	200
1,2,3-Trimethylbenzene	5	10	50	100	200
Benzyl chloride	5	10	50	100	200
1,3,5-Trichlorobenzene	5	10	50	100	200
2-Methylnaphthalene (Low Level Soil)	10	40	100	200	400

Table 5 - Internal Standards

Compound	Standard Concentration µg/mL (may vary per matrix)	Quantitation ion
Fluorobenzene	50 – 250	96
Chlorobenzene-d5	50 – 250	117
1,4-Dichlorobenzene-d4	50 – 250	152

Notes:

1) Except for medium level soils, the surrogate and internal standards may be combined in one solution.

Table 6 - Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL (may vary per matrix)
1,2-Dichloroethane-d_4	50 – 250
Dibromofluoromethane (not required for Method 8260C)	50 – 250
Toluene-d_8	50 - 250
4-Bromofluorobenzene	50 – 250

Notes:

1) *Except for medium level soils, the surrogate and internal standards may be combined in one solution.*
2) *Recovery limits for surrogates are g enerated from historical data and are maintained by the QA Dept.*
3) *There is no corrective action for Dibromofluoromethane for Method 8260C.*

Table 7 - Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
1,1,1,2-Tetrachloroethane	50
1,1,1-Trichloroethane	50 – 250
1,1,2,2-Tetrachloroethane	50
1,1,2-Trichloro-1,2,2-trifluoroethane	50
1,1,2-Trichloroethane	50
1,1-Dichloroethane	50
1,1-Dichloroethene	50
1,1-Dichloropropene	50
1,2,3-Trichlorobenzene	50
1,2,3-Trichloropropane	50
1,2,4-Trichlorobenzene	50
1,2,4-Trimethylbenzene	50
1,2-Dibromo-3-chloropropane	50
1,2-Dibromoethane	50
1,2-Dichlorobenzene	50
1,2-Dichloroethane	50
1,2-Dichloroethene (total)	100
1,2-Dichloropropane	50
1,3,5-Trimethylbenzene	50
1,3-Dichlorobenzene	50
1,3-Dichloropropane	50
1,4-Dichlorobenzene	50
1,4-Dioxane	1000
2,2-Dichloropropane	50
2-Butanone	50
2-Chloroethyl Vinyl Ether	100 – 500
2-Chlorotoluene	50
2-Methyl-2-propanol	500
2-Hexanone	50
3-Chloro-1-propene	50
4-Chlorotoluene	50
4-Methyl-2-pentanone	50
Acetone	50
Acetonitrile	500 – 2500
Acrolein	500
Acrylonitrile	100 – 500
Benzene	50
Bromobenzene	50
Bromochloromethane	50
Bromodichloromethane	50
Bromoform	50
Bromomethane	50
Carbon disulfide	50
Carbon tetrachloride	50
Chlorobenzene	50
Chloroethane	50
Chloroform	50
Chloromethane	50
cis-1,2-Dichloroethene	50
cis-1,3-Dichloropropene	50
Cyclohexane	50

Table 7 - Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
Dibromochloromethane	50
Dibromomethane	50
Dichlorodifluoromethane	50
Dichlorofluoromethane	50
Ethylbenzene	50
Ethyl ether	50
Ethyl methacrylate	50
Hexachlorobutadiene	50
Iodomethane	50
Isobutyl alcohol	1250
Isopropylbenzene	50
Methyl acetate	50
Methyl tert-butyl ether (MTBE)	50
Methylcyclohexane	50
Methylene chloride	50
Naphthalene	50
n-Butylbenzene	50
n-Heptane	50
n-Hexane (Ohio VAP only)	50
n-Propylbenzene	50
p-Isopropyltoluene	50
sec-Butylbenzene	50
Styrene	50
tert-Butylbenzene	50
Tetrachloroethene	50
Toluene	50
trans-1,2-Dichloroethene	50
Tetrahydrofuran	100
trans-1,3-Dichloropropene	50
trans-1,4-Dichloro-2-butene	50
Trichloroethene	50
Trichlorofluoromethane	50
Vinyl Acetate	50
Vinyl chloride	50
Xylenes (total)	150 – 750

Notes: 1) 5 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.

2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by QA Dept.

Table 8 - BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 9 - SPCC Compounds and Minimum Response Factors for Method 8260B

Compound	Methods 8260B and 8260A Min. RF
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	0.100
1,1,2,2-Tetrachloroethane	0.300
Chlorobenzene	0.300

Table 10 - Method 8260C. Recommended Average Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification		
Volatile Compound	**Minimum Response Factor**	**Typical Response Factor**
Dichlorodifluoromethane	0.100	0.327
Chloromethane	0.100	0.537
Vinyl chloride	0.100	0.451
Bromomethane	0.050	0.255
Chloroethane	0.050	0.254
Trichlorofluoromethane	0.100	0.426
1,1-Dichloroethene	0.100	0.313
1,1,2-Trichloro-1,2,2-trifluoroethane	0.050	0.302
Acetone	0.010	0.151
Carbon disulfide	0.100	1.163
Methyl Acetate	0.100	0.302
Methylene chloride	0.100	0.380
trans-1,2-Dichloroethene	0.100	0.351
cis-1,2-dichloroethene	0.100	0.376
Methyl tert-Butyl Ether	0.100	0.847
1,1-Dichloroethane	0.200	0.655
2-Butanone	0.010	0.216
Chloroform	0.200	0.557
1,1,1-Trichloroethane	0.100	0.442
Cyclohexane	0.100	0.579
Carbon tetrachloride	0.100	0.353
Benzene	0.500	1.368
1,2-Dichloroethane	0.100	0.443
Trichloroethene	0.150	0.338
Methylcyclohexane	0.100	0.501
1,2-Dichloropropane	0.100	0.382
Bromodichloromethane	0.150	0.424
cis-1,3-Dichloropropene	0.150	0.537
trans-1,3-Dichloropropene	0.100	0.515
4-Methyl-2-pentanone	0.050	0.363
Toluene	0.400	1.577
1,1,2-Trichloroethane	0.100	0.518
Tetrachloroethene	0.150	0.606
2-Hexanone	0.050	0.536
Dibromochloromethane	0.100	0.652
Styrene	0.300	1.916
Bromoform	0.100	0.413
Isopropylbenzene	0.100	2.271
1,1,2,2-Tetrachloroethane	0.300	0.782
1,3-Dichlorobenzene	0.600	1.408

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Table 10 - Method 8260C: Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification (cont'd)		
Volatile Compound	**Minimum Response Factor**	**Typical Response Factor**
1,4-Dichlorobenzene	0.500	1.427
1,2-Dichlorobenzene	0.400	1.332
1,2-Dibromo-3-chloropropane	0.050	0.129
1,2,4-Trichlorobenzene	0.200	0.806

Table 11 - CCC Compounds for Method 8260B

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	30	20
1,1-Dichloroethene	30	20
Chloroform	30	20
1,2-Dichloropropane	30	20
Toluene	30	20
Ethylbenzene	30	20
n-Hexane (Ohio VAP only)	30	20

Table 12 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d_4 (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101,103
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Acetone	43	58	
Methylene chloride	84	49	51, 86
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl *tert* butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131

Table 12 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d_8 (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo-3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	
Cyclohexane	56	69	84
Methyl Acetate	43	74	
Methyl cyclohexane	83	55	98
Epichlorohydrin	57	49	
Propylene oxide	58	43	
2-Ethyltoluene	105	120	
3-Ethyltoluene	105	120	
1-Chlorohexane	91	55	

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Table 12 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Ethylene oxide	44	43	

** The primary ion must be used for quantitation unless interferences are present, in which case a secondary ion may be used.*

*** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.*

Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE

[Method: 1631E]

Approvals (Signature/Date):

Technology Specialist	09/19/17 Date	Health & Safety Coordinator	08/08/17 Date
Quality Assurance Manager	09/27/17 Date	Technical Director	09/08/17 Date

This SOP was previously identified as SOP No. NC-MT-001, Rev 8, dated 4/28/16

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) using Method 1631E.

1.2. CVAFS analysis provides for the determination of total mercury (organic and inorganic). The oxidant, bromine monochloride (BrCl), has been found to give quantitative recovery with both types of analytes. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.

1.3. Method 1631E (hereafter abbreviated to Method 1631 in this SOP) is applicable to the preparation and analysis of mercury in ground water, surface water, effluents, and other aqueous samples. Appendix A to Method 1631 is applicable to the preparation and analysis of mercury in sediments, soils, biological media and other solid samples. All matrices require sample preparation prior to analysis.

1.4. The laboratory instrumentation uses the flow injection process. Any method criteria applying to the bubbler method is not applicable to 1631E prep or analysis as performed according to this SOP.

1.5. The TestAmerica Canton reporting limit for mercury in aqueous matrices is 0.5 ng/L. The reporting limit for mercury in solid matrices is 1.0 ug/kg.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solids, biological, and aqueous solutions. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor and fluorescence at 253.7 nm. For aqueous samples, a representative portion of the sample is digested and oxidized in BrCl. For solid or biological samples, 1 gram of sample is digested with matrix appropriate acid solution, diluted, and further oxidized with BrCl (except as detailed in work instruction WI-NC-0165 Sample Preparation Guidelines for Digestion of Micro Volume Tissues). Excess free halogens in the digestate are then reduced with hydroxylamine hydrochloride. The mercury (Hg^{+2}) is reduced to its elemental state with stannous chloride ($SnCl_2 \bullet 2H_2O$) and purged from solution with argon in a gas / liquid separator. The mercury vapor is collected on a gold trap and then thermally desorbed to the detector. The mercury vapor passes through a cell positioned in the light path of an atomic fluorescence spectrometer. Fluorescence is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample fluorescence to the calibration curve (fluorescence vs. concentration).

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2. Gold, silver, and iodide are known interferences. At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced dramatically.

4.3. The use of a brominating digestion coupled with atomic fluorescence detection overcomes many of the interferences. No interferences have been noted for sulfide concentrations below 24 mg/L.

4.4. Water vapor may collect in the gold traps (Method 1631), and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by pre-drying the gold trap and by discarding those traps that tend to absorb large quantities of water.

4.5. The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause *quenching* of the excited atoms.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. All glassware is cleaned per SOP NC-QA-014. Be aware of potential sources of contamination, and take appropriate measures to minimize or avoid them. The analytical instrument and sample / standards preparation area should be protected from mercury vapor or particulates in the laboratory air. Samples, standards, and blanks should only be opened in a clean area. Gloves must be powder free, and should be checked for mercury contamination. Do not use powdered nitrile gloves as they have been shown to contribute both low-level mercury contamination and interferences. Only clean gloves should touch the instrument and all other equipment used to process blanks, standards, and samples.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety

Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Bromine Monochloride	Corrosive Poison Oxidizer	0.1 (Br) ppm TWA	May be fatal if inhaled. Causes severe eye and skin burns. Causes damage to the following organs: Lungs, mucous membranes, respiratory tract, skin, central nervous system, eyes, lens or cornea.
Potassium Bromate	Oxidizer	0.1 mg/m^3 TWA	Irritates respiratory tract. May cause coughing and shortness of breath. Causes irritation to the skin. May cause redness, itching, and pain. In the presence of liquids, it is slowly absorbed in toxic amounts. Prolonged exposure may cause burns. Causes irritation to eyes with redness, pain. May cause eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and cleanup techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion, or absorption through skin. All lines should be checked for leakage, and

the mercury vapor must be vented into a hood or passed through a mercury–absorbing media such as a carbon filter.

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAFS apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Atomic Fluorescence Spectrophotometer equipped with:

6.1.1. Fluorescence Cell with quartz ends. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.1.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.1.3. Peristaltic pump

6.1.4. Flowmeter

6.1.5. Recorder or printer

6.1.6. Gas /Liquid separator

6.1.7. Drying devices: Nafion Dryer soda lime trap

6.1.8. Gold trap (1): Quartz tube containing gold-coated sand

6.1.9. Hotblock maintaining a temperature of 50-110°C

6.2. Sample bottles, 40 mL borosilicate glass VOC vials, QEC or equivalent, < 0.5 ng/L contamination when used for Method 1631 samples. In actual practice, should contribute less than 0.1 ng/L to facilitate meeting method blank criteria. Unless tested by the manufacturer for cleanliness and accuracy, four vials from each lot must be gravimetrically tested in triplicate at the 40 mL point. Cleanliness is assessed by adding 0.2 mL BrCl (Section 7.15). Store the test vials at room temperature for at least 12 hours and analyze as samples. All vial results must be less than the reporting limit.

6.3. Class A glass volumetric flasks: various volumes

6.4. Starch Paper Test Strips

6.5. Argon gas supply, high purity, or equivalent: A gold trap may be used in-line to further purify the argon.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a US Filter PureLab Plus deionized water system or equivalent. Reagent water must be free of mercury and interferences as demonstrated through the analysis of reagent and method blanks.

7.2. Stock (10 mg/L) mercury standards (in 5-10% HCL) are purchased. All standards must be stored in glass volumetric flasks or glass 40 mL VOC vials. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year, and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 µg/L): Fill a 100 mL volumetric flask about half full with reagent water. Add 0.5 mL of BrCl solution (Section 7.15). Add 0.10 mL of the stock mercury standard (Section 7.2) and dilute to 100 mL with reagent water. The intermediate mercury standard should be replaced every six months.

7.4. Working mercury standard (1 µg/L): Fill a 40 mL vial about half full with reagent water. Add 0.2 mL of BrCl solution (Section 7.15). Add 4.0 mL of the intermediate mercury standard (Section 7.3) and dilute to 40 mL with reagent water. The working mercury standard should be replaced every six months. Additional information can be found in SOP NC-QA-017.

7.5. The calibration standards listed in Table I must be prepared fresh from the working standard (Section 7.4) by adding 0, 0.02, 0.04, 0.08, 0.2, 0.4,1.0, and 4.0 mL of a mercury standard to 40 mL vials and diluting to volume with reagent water. BrCl (Section 7.15) and $NH_2OH•HCl$ (Section 7.12) reagent solutions are also added.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

7.6. The initial calibration verification standard (QCS or ICV) must be made from a different manufacturer or lot than that of the calibration standards.

7.7. The LCS is generally spiked with the ICV standard solution, however, alternate sources may be used for the LCS.

7.8. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, and spiking solutions. All standards must be processed with the same reagents that are used for sample preparation.

7.9. Stannous Chloride ($SnCl_2 • 2H_2O$): ACS Reagent grade suitable for mercury determination (< 1 ppb) is recommended.

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade.

Note: Ultra trace mercury HCl should be used to prepare the BrCl solution Trace metal grade HCl may be used to prepare the $SnCl_2$ and 2% HCl rinse solutions provided that these solutions are purged with argon prior to use.

7.11. Autosampler rinse solution (2%): Add 1 mL of stannous chloride working solution and purge with argon (0.5 L/min) for at least 1 hour.

7.12. $SnCl_2•2H_2O$ Solution Concentrate: Add 500 g of $SnCl_2•2H_2O$ to 2.4 L trace metals concentrated HCl. Allow the $SnCl_2•2H_2O$ to completely dissolve.

7.13. $SnCl_2•2H_2O$ Working Solution: Fill a 2.5 L glass bottle (HCl leached) with 2.25 L of reagent water. Add 250ml stannous chloride concentrate (Section 7.10) to bring the total volume to 2.5 L. This produces a reductant solution that is 10% HCl and 2% $SnCl_2•2H_2O$. Purge with argon (0.5 L/min) for at least 1 hour. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.7).

7.14. Hydroxylamine Hydrochloride Solution: Typically purchased

7.15. Bromine monochloride, intermediate solution: Typically purchased 10 mL tubes

7.16. BrCl, working solution: Place 10 mL of Bromine monochloride intermediate solution (1 tube) into 90 mL of concentrated Hydrochloric acid. Invert to mix.

Note: Prior to placing a new lot of BrCl into production, spike 1 mL into a blank and LCS and analyze. If recovery is < 80%, re-prep the BrCl reagent. If it fails again, the reagent lot is not approved for use.

7.17. Nitric acid, concentrated, trace metal grade

7.18. Sulfuric Acid, concentrated, trace metal grade

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Preservation and Holding Time

8.1.1. Holding time from time of collection is extended to 28 days when the sample is preserved with HCl or the oxidation step is performed in the sample bottle used for collection. Preservation/oxidation is verified by the persistence of the yellow color of the BrCl. Up to 2 mL BrCl may be added to digest the sample. Record any additional BrCl used (see Section 11.2.5). Samples to be analyzed for dissolved Hg must be transferred to the filtering apparatus within 48 hours of collection, then preserved as above. Once preserved, holding time is 90 days from sample collection to analysis.

8.1.2. Solid and biological sample holding time for Hg is one year from collection to digestion and preservation. The holding time for digested and preserved solid samples is 90 days from sample preparation.

8.2. Collection and Storage

8.2.1. The clean hands/dirty hands procedure should be followed for collection. Standard sampling kits include environmental sample kit (2 x 40mL vials), MS/MSD kit (4 x 40mL vials), field blank kit (2 empty + 2 DI-filled 40mL vials), and trip blank kit (2 DI-filled 40mL vials). Each kit includes sufficient labels for all vials and one label for the inner bag. Alternative client-specified configurations of sample kits may be provided. Samples are stored in a mercury-clean area in the laboratory. Clients are encouraged to affix their own identification labels to the samples prior to shipment.

8.2.2. Solid samples may be stored in fluoropolymer or borosilicate glass or polyethylene bags.

8.2.3. Tissue samples may be shipped to the laboratory frozen or chilled at 0-4 degrees C, and may be processed and stored in one of the following ways:

8.2.3.1. Tissue that arrives frozen, should be kept frozen until time for homogenization. Thaw, homogenize, and then refreeze the tissue in a glass container. Subsampling can occur immediately after homogenization before the refreeze or at a later date with another

thaw/refreeze cycle. Tissue which is frozen will maintain integrity for 1 year from sample collection.

8.2.3.2. Tissue that arrives cold (0-4 ºC) but not frozen can be homogenized within 24 hours and frozen in a glass jar. Subsampling can occur immediately after homogenization before the freeze or at a later date with another thaw/refreeze cycle.

8.2.3.3. Tissues that arrive cold (0-4 ºC) but not frozen can be frozen upon receipt and kept frozen until time for homogenization. Thaw, homogenize, and refreeze the tissue in a glass container. Subsampling could occur immediately after homogenization before the refreeze or at a later date with another thaw/refreeze cycle

8.2.3.4. Samples that require lab filtration must be filtered within 48 hours of collection in order to meet method suggested holding time requirements for unpreserved samples. Samples must be transferred from the original container to the filtration apparatus. **Note:** All filter apparatus must be precleaned by filtering 100ml of DI water through the filter and discarding it prior to filtering the filtration blank or samples.

9. QUALITY CONTROL

9.1. Carry-Over Determination: The carry-over determination is to be analyzed once on every instrument. The results from the determination must be kept on file.

9.1.1. Analyze system blanks immediately after calibration solutions containing successively higher concentrations of Hg – from this test determine the amount of Hg that will carry >0.5 ng/L of Hg into a succeeding system blank. When a sample with one half or more of this determined amount is analyzed, then a system blank or sample must be demonstrated to be below the reporting limit before a subsequent sample can be reported. Samples with detectable Hg analyzed after the high sample, but before system cleanliness is demonstrated, must be re-analyzed.

9.2. Preparation Batch

9.2.1. A group of up to 20 samples of the same matrix processed together using the same procedures and reagents. The preparation batch must contain a method blank (MB), LCS, and matrix spike/matrix spike duplicate pair (2 MS/MSD pairs if the batch has more than ten samples). In some cases, at client request, it may be appropriate to process a MS and un-spiked sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Method Blank (MB)

9.3.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any mercury at, or above, the reporting limit. If a sample result is less than a minimum of 10 times the MB contamination level, the sample must be re-prepared in a new batch and re-analyzed.

Note: For West Virginia projects, three MBs are required per batch.

9.3.2. If concentrations of mercury are not greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3.3. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exceptions noted above).

9.3.4. If the above criteria are not met and re-analysis is not possible due to limited sample quantity, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.4. Preparation blanks must be prepared for 0.2, 0.4, 0.6, 0.8, and 1 mL volumes of BrCl on each day samples are prepped using these BrCl volumes. The 0.2 mL blank is met by the analysis of the method blank. It is not necessary to prepare a preparation blank with a 2 mL volume of BrCl. See the note in section 11.1.6 for details.

9.4.1. If there is a positive detection in any of these blank samples, this information must be included in an internal narrative of any job containing samples that were spiked with a corresponding level of BrCl. This prep blank does not have any method-specific acceptance criteria. Acceptance is based on the experience and judgment of the analyst

9.5. System / Subtraction Blank

9.5.1. The system (calibration) blank consisting of all reagents used to prepare samples and standards will be used for background subtraction and system cleanliness monitoring. Three system blanks are prepared and analyzed with the initial calibration curve (ICal). The instrument software will apply the average calibration factor from the ICal to the average raw response from these three system blanks. The calculated mercury concentration must be less than the reporting limit. The standard deviation of the three blanks must be < 0.10 ng/L. Subsequent system blanks are analyzed as

ICB and CCB in conjunction with the ICV (identified in Method 1631E as the QCS) and CCV (identified in Method 1631E as the OPR). These IC and CC blanks are used to monitor the cleanliness of the instrument, are calculated in the same manner as samples, and are not used for background subtraction purposes. The absolute value of the calculated mercury concentration in the ICB and CCB must be less than the reporting limit.

9.6. Laboratory Control Sample (LCS).

9.6.1. One aqueous LCS must be processed with each preparation batch. The LCS is a standard used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The method specific acceptance criterion is 77-123% (other analytical programs may have other specific limits that must be used). If the LCS is outside established control limits the system is out of control and corrective action must be performed.

9.6.2. In the instance where the LCS recovery is greater than the maximum and the sample results are < RL, the data may be reported with qualifiers**. Such action must be addressed in the case narrative.**

9.6.3. Corrective action will be re-preparation and re-analysis of the batch unless other corrective action is agreed upon with the client.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.7.1. One MS/MSD pair must be processed for each 10 samples in a preparation batch. An MS is a field sample to which a known concentration of mercury has been added. An MSD is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of un-spiked sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Method 1631 requires that each matrix be spiked at a 10% frequency. Some regulatory agencies interpret each discharge or sampling point as a separate matrix. It is the client's responsibility to determine which sample(s) is to be matrix spiked each time samples are submitted for analysis. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

9.7.2. If mercury recovery or RPD falls outside the acceptance range, corrective action will include:

9.7.2.1. If the MS/MSD fails due to the high background concentration of mercury in the parent sample, spike concentration will be adjusted accordingly, and the parent sample, MS, and MSD will be reanalyzed. Alternately, the parent sample and MS/MSD pair may be diluted and re-analyzed.

9.7.3. MS/MSD results which again fall outside the control limits must be addressed in the case narrative.

9.8. Additional information on QC samples can be found in QA Policy QA-003.

9.9. Control Limits

9.9.1. Control limits are prescribed in method 1631E. Control limits are easily accessible via the LIMS.

9.10. Method Detection Limits (MDLs) and MDL Checks (MDL Verifications or MDLVs)

9.10.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.10.2. MDLs are easily accessible via the LIMS

9.11. Nonconformance and Corrective Action

9.11.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.2, except they do not need a minimum of 12 hours of oxidation time and can be used immediately since the mercury is already in an oxidized state in the standard.

10.2. Calibration is required only when indicated by instrument and preparation QC problems. The instrument calibration date and time must be included in the raw data.

10.3. Set up the instrument with the operating parameters recommended by the manufacturer (Table II). Allow the instrument to become thermally stable before beginning calibration (approximately 1-2 hours of warm-up is required if the lamp has been turned off). The most stable results are obtained if the lamp is left on full time. Refer to the CVAFS instrument manual for detailed setup and operation protocols.

10.4. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of six standards and three calibration blanks. One standard must be at

the TestAmerica Canton reporting limit. Analyze standards in ascending order of concentration, beginning with the blanks. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.5. The calibration factors across the calibration range must have less than 15% RSD or the instrument shall be stopped and recalibrated prior to running samples. Also, the low standard must calculate back against the curve within ±25% of the true value.

10.6. Initial Calibration Verification/Initial Calibration Blank (ICV/ICB)

10.6.1. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately following an Initial Calibration. The ICV result must fall within 20% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within ± the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, and the instrument recalibrated (see Section 11.5.5 for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related, the corrective action will include re-preparation of the ICV, ICB, CCV, and CCB with the calibration curve.

10.7. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB) (

10.7.1. Calibration accuracy is monitored in the analytical sequence through the analysis of a known standard at the end of the analytical sequence or every 12 hours. Additional CCVs may be analyzed as necessary. The CCV concentration must be at 5 ng/L for 1631. The CCV result must fall within 77-123% of the true value for that solution for 1631. A CCB is analyzed immediately following each CCV. (See Section 11.5.5 for required run sequence). The CCB (system blank) must fall within ± the reporting limit (RL) from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid CCV andCCB pairs.

10.7.2. In the instance where the CCV or CCB is greater than the maximum acceptance criteria and the sample results are < RL, the data may be reported. Such action must be addressed in the case narrative.

11. PROCEDURE

11.1. Aqueous Sample Preparation

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) and laboratory QC samples (LCS, MB, MS, MSD) are processed with the same digestion reagents used for the field samples.

11.1.2. Remove about 2.7 mL from each sample vial. This will leave 40 mL in the bottle. Confirm by checking the meniscus and the 40mL calibration point as

determined by verifying vials from each new lot. Set the cap back on the original vial. Repeat this process for all 40 mL vial aliquots of the sample.

11.1.3. The MB consists of 40 mL of DI water with 0.2 mL of BrCl. Mix and store the vial at room temperature for at least 12 hours. Proceed to section 11.5 sample screening and treat the MB the same as the samples for analysis.

Note: The MB also serves as the 0.2 mL BrCl preparation blank.

11.1.4. To prepare the LCS, add 40 mL of DI water to a VOA vial. With a pipette, carefully remove 0.2 mL of the DI water. Spike the LCS with 0.2 mL of the ICV working standard or alternate spiking solution. Add 0.2 mL of BrCl. Mix and store the vial at room temperature for at least 12 hours. Proceed to section 11.5 and treat the LCS the same as the MB and the samples for analysis.

11.1.5. To prepare the samples, lift the cap and add 0.20 mL of BrCl (Section 7.15) to the 40 mL sample vial, reseal and mix. Store the sample vials at room temperature for at least 12 hours.

11.1.6. Starch/iodide paper may be used to detect excess halogens (i.e., BrCl) in colored samples where the yellow color of the BrCl cannot be seen. If the yellow tint from the BrCl disappears and starch/iodide paper does not detect halogens, add additional BrCl to the 40 mL sample vial, reseal, mix and allow to digest for another 12 hours. This process can be repeated by 0.2 mL increments of BrCl up to 1 mL, and then directly to the 2 mL maximum.

Note: If 2 mL of BrCl is used, a 2x dilution must be performed on the sample prior to analysis. Studies have demonstrated that additions of BrCl in excess of 1 mL suppresses mercury recovery.

11.1.7. If starch/iodide paper still does not detect halogens, make a 10x dilution on the aliquot generated from section 11.1.5 and resume the digestion process. Store the sample vials at room temperature for at least 12 hours. Record **the total amount of BrCl added to the sample** in the LIMS.

11.1.8. If 2 mL of BrCl is consumed, a 10x dilution from the original digestion vial is created and digestion is continued with 0.2 mL BrCl additions as above, noting that the equivalent of 0.2 mL BrCl is already present in the 10x dilution.

11.1.9. For aqueous MS/MSDs, two vials will be digested. Equal amounts from each vial will be aliquoted into a 40 mL vial to make the final analytical sample. Three 12.8 mL aliquots will be removed from this vial to create the parent sample and the MS/MSD pair. The MS and MSD aliquots will be spiked with 0.2 mL of the MS/MSD spike solution prior to analysis.

Note: To meet IL EPA requirements NPDES samples must be heated at approximately 50°C for six hours. If the oxidizer has been consumed, add additional BrCl and heat for an additional six hours. Any necessary preparation blanks must have an equivalent amount of BrCl added and also be reheated with the samples..

11.2. Biological Sample Preparation

11.2.1. This procedure is intended for tissue and other primarily organic matrices (excluding coal). It does, however, give quantitative recovery for Hg on finely divided geological matrices such as sediments and soils.

11.2.2. Accurately weigh 1.0 ± 0.05 gram of sample directly into a tared digestion vessel.

Note: The use of too much organic material will consume all of the acid **i**n the digestion, resulting in low recovery.

11.2.3. For the MB, add approximately 1 g of Teflon boiling chips.

11.2.4. For the LCS, add 1.0 mL of the 10 ug/L ICV intermediate mercury standard or alternate spiking solution (Section 7.3) to1g of Teflon boiling chips.

11.2.5. For the MS/MSD, add 0.1 mL of the 1 mg/L mercury standard in addition to the 1g of solid sample.

11.2.6. To each sample, add 3 mLs of H_2SO_4 and 7 mLs of HNO_3. Place the digestion vessel in an acid fume hood and cap. Allow the sample to sit in the acid at room temperature for at least 4 hours before heating in order to insure that potential reaction between the digestion acids and the sample matrix have subsided.

11.2.7. After digesting at room temperature, place the digestion vessel in a hotblock in the hood and slowly bring to temperature over a 1-hour period to 85-95°C. If excessive sample foaming occurs, bring to temperature more slowly. Reflux for 2-3 hours to fully oxidize remaining organic matter. The mineral portion of soil and sediment samples will not dissolve, but will be effectively leached by this digestion.

11.2.8. After the digestion is complete, allow the sample to cool. Add 2mL of BrCl and bring to the calibration mark on the digestion vessel with water. Shake the sample/BrCl solution to homogenize, and allow to sit at least 4 hours prior to proceeding to oxidize remaining dissolved methyl Hg.

11.2.9. Into 38ml of DI water place 2ml of the sample aliquot generated in section 11.2.8. By 0.2ml increments add sufficient BrCl to maintain a visible yellow color. If more than 1ml is required go directly to 2ml. If this volume is

consumed by the sample, generate a 10X dilution on the aliquot by withdrawing 4ml and adding it to 36ml of DI water in a 40ml vial. Noting that an equivalent of 0.2ml of BrCl is present in this dilution, begin adding BrCl by 0.2ml increments as above until a yellow color persists. Allow 12 hours for full digestion prior to analysis.

Note: Because of the digestion reagents added, starch paper is not an adequate indicator of excess BrCl as it will generate a false positive result. Visual confirmation of a persistent yellow color is required to establish affective BrCl oxidation.

11.2.10. Proceed to Section 11.4.1.

11.2.11. For LL Hg digestion for micro volumes of tissues, see work instruction WI-NC-0171.

11.3. Solid Sample Preparation

11.3.1. Solid sample homogenization:

11.3.1.1. The selection of a portion of solid sample for analysis of low level mercury is problematic due to the very small sample size used for the actual preparation and analysis. The application of the method to soil analysis presupposes that the sample will be relatively uniform and composed of fine particles. This is not always the case.

11.3.1.1.1. When large stones or pieces of material are included in the sample vial, but the bulk of the sample is fine-grained material, the fine-grained material will be selected as the sample aliquot for analysis.

11.3.1.1.2. If the sample is almost entirely comprised of one particular kind of material, then that material is the representative sample and a portion of this will be selected. The analyst, with consultation with the client and/or PM, will make the decision of what comprises the most representative aliquot for any given sample and will narrate what portion of the sample was selected when these issues occur.

11.3.1.2. Following the above guidelines, homogenize the sample then weigh 1.0 ± 0.05 g into a 40 mL VOA vial.

11.3.1.2.1. For the MB, add approximately 1g of Teflon boiling chips.

11.3.1.2.2. For the LCS, add 1.0 mL of the 10 ug/L ICV intermediate mercury standard (Section 7.3) or alternate spiking standard to1g of boiling chips.

11.3.1.2.3. For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Section 7.3) to the 1g of solid sample.

11.3.1.3. In a fume hood, add 8 ml of concentrated HCl, swirl, and add 2 mL concentrated HNO_3 to the sample in the 40 mL vial. Cap and allow the sample to digest for at least 4 hours.

11.3.2. Add 2.0 ml of BrCl (Section 7.15) to the digestate, then dilute with reagent water (Section 7.1) to the 40 mL calibration point. Shake, then allow to settle until supernatant is clear. Store the sample vials at room temperature for at least 12 hours. Centrifuge or filter, if necessary to remove particulates.

11.3.3. Into 38ml of DI water place 2ml of the sample aliquot generated in section 11.3.2. By 0.2ml increments add sufficient BrCl to maintain a visible yellow color. If more than 1ml is required go directly to 2ml. If this volume is consumed by the sample, generate a 10X dilution on the aliquot by withdrawing 4ml and adding it to 36ml of DI water in a 40ml vial. Noting that an equivalent of 0.2ml of BrCl is present in this dilution, begin adding BrCl by 0.2ml increments as above until a yellow color persists. Allow 12 hours for full digestion prior to analysis.

Note: Because of the digestion reagents added, starch paper is not an adequate indicator of excess BrCl as it will generate a false positive result. Visual confirmation of a persistent yellow color is required to establish affective BrCl oxidation.

11.3.4. For LL Hg wipe digestion, see work instruction WI-NC-0172.

11.4. Sample Screening

11.4.1. Transfer 1 mL of a preserved sample to a “10X dilution” labeled tube and add 9 mL of reagent water. Reseal the original sample vial caps if it will be greater than three minutes before the next step is performed.

11.4.2. Add 0.05 mL of hydroxylamine solution (Section 7.12) and analyze the 10X screening aliquot of the sample using a single-point calibration (10 ng/L)

11.4.3. If the sample response (note that this is a 10X dilution) exceeds that of the 10 ng/L standard, then the sample concentration is beyond the normal calibration range of Method 1631. Prepare the appropriate dilution.

11.4.4. If the 10X dilution screen response is non-detect at 10 ng/L, then the sample may be analyzed without dilution.

11.5. Sample Analysis

11.5.1. When ready to begin analysis, add 0.10 mL increments of hydroxylamine hydrochloride solution (Section 7.12) per 0.2ml BrCl present in the samples to reduce the excess BrCl (the BrCl has been reduced when no yellow color remains) Cap and shake. **Note**: Spiking of QC samples is done before the addition of the hydroxylamine hydrochloride reagent for aqueous samples. For Solid matrices, the matrix spike has already been added.

11.5.2. With instrument control parameters set to appropriate values (see Table II), load samples into autosampler.

11.5.3. Start autosampler sequence.

11.5.4. All measurements must fall within the defined calibration range to be valid. Dilute and re-analyze all samples for analytes that exceed the highest calibration standard.

11.5.5. The following analytical sequence must be used:

Instrument Calibration
ICV (QCS)
ICB
CCV (OPR)
CCB
Maximum 12 hours
CCV
CCB
Repeat sequence at least every 12 hours between CCV/CCB pairs as required to complete run
CCV
CCB

11.5.6. Refer to Quality Control Section 9 for the appropriate quality control criteria.

Notes: Samples include the MB, LCS, MS, MSD, duplicate, field samples, and sample dilutions.

11.5.7. Instrument calibration need not be performed if the QC parameters for the run indicate that the system is in control.

11.5.8. To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data is reviewed periodically throughout the run.

11.5.9. Five scenarios that may indicate an automatic re-analysis.

11.5.9.1. Laboratory sample duplicates showing poor RPD.

11.5.9.2. Field duplicates showing poor RPD (when these are identified by the client)

11.5.9.3. MS, MSD, and un-spiked samples that don't make sense (sample is higher in concentration than the spiked MS and/or MSD, MS and/or MSD is off by an order of magnitude, etc.) or any failed MS/MSD pairs

11.5.9.4. Field-generated blanks with concentrations of mercury above the reporting limit.

11.5.9.5. Serial dilutions that don't show reasonable agreement with the initial run

11.5.10. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.

11.5.11. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.5.12. Any unauthorized deviations from this procedure must also be documented as a non-conformance with a cause and corrective action described.

11.6. Analytical Documentation

11.6.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.6.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.6.3. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration Factors are calculated according to the equation:

$$CF(x) = \left(\frac{Area(x) - Area(b)}{Conc(x)} \right)$$

Where:

CF(x) = calibration factor of standard (x)
area(x) = area of standard (x)
conc(x) = concentration of standard (x)
area(b) = average area of 3 calibration blanks

12.2. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.3. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.6. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.7 The final concentration for an aqueous sample is calculated as follows:

$$ng/L = C \times D$$

Where:
C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor

12.8 The final concentration for a solid sample is calculated as follows:

$$ug/kg = C \times D \times W \times P$$

Where:
C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor
W = Weight/volume factor = 0.040, when 1 g of sample is digested and diluted to 40 mL
P = Preparation factor = 20, when 2 mL of digestate is diluted to 40 mL

12.9 Appropriate factors must be applied to sample values if dilutions are performed.

13. METHOD PERFORMANCE

13.1. Each laboratory analyst must have initial demonstration of performance capability data on file. Initial Demonstrations of Capability (IDOCs) and Continuing Demonstrations of Capability (CDOCs) are filed and tracked in the analyst's technical training file.

13.2. Method performance is determined by the analysis of method blanks and laboratory control samples. The method blanks must meet the criteria in Section 9.3.

13.3. Training Qualification

The Group/Team Leader has the responsibility to ensure this procedure is performed

by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acid waste-aqueous waste generated by the analysis. Samples vials are collected and taken to the waste storage building. The vials are crushed and the liquid waste and glass are separated. The liquid waste is neutralized and released to the POTW. The glass is disposed of in the trash.

16. REFERENCES

16.1. References

16.1.1. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, U.S. EPA, August 2002

16.1.2. Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, U.S. EPA, January 2001

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Revision History

Historical File:		Revision 1: 04/05/01		Revision 8: 04/28/16
		Revision 2: 08/14/01		
		Revision 3: 09/18/02		
		Revision 4: 12/16/02		
		Revision 5.0: 01/17/05		
		Revision 5.1: 07/28/07		
		Revision 5.2: 03/11/09		
		Revision 5.3: 08/17/10		
		Revision 5.4: 12/09/11		
		Revision 5.5: 02/20/12		
		Revision 6: 09/26/13		
		Revision 7: 01/09/15		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. WI-NC-0171 LL Hg Digestion for Micro Volume Tissues

16.2.4. WI-NC-0172 LL Hg Wipe Digestion

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. Subsampling, NC-IP-001

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from Reference Method

17.1.1. Section 9.1.7 of the reference method requires three method blanks per analytical batch. The section also describes an analytical sequence that includes a CCV (OPR) only at the beginning and end of the sequence, and that includes no CCBs (system blanks) after calibration. This SOP requires only one method blank per preparation batch, but requires additional stability and cleanliness checks through the analysis of a CCV/CCB pair at the beginning, end and after every 12 hours during an analytical run.

17.1.2. Section 9.2.1 of the method recommends that an MDL be determined whenever a new operator begins work. At this laboratory, a new operator receives proper, documented training and must prove competence through an initial demonstration of performance that includes the successful analysis of four LCSs (see Section 9.3.2 of this SOP).

17.1.3. Section 9.4.5.1 of the method recommends that field blank analysis immediately before analyzing samples from the batch. Field blanks are analyzed as normal samples in this laboratory with no particular run order requirement.

17.1.4. Section 9.4.7 of this method recommends that 5% of the bottles in a lot be monitored. Bottle cleanliness in this laboratory is verified by the initial analysis of 5% of the bottles from three boxes of a lot of 40 mL sample vials.

17.1.5. The volume descriptions for the equation in Section 12.3.2 of the method includes subtraction of the volume of reagent used in the standards and the samples. Since the volume of reagents used in samples and standards is typically the same (or differs insignificantly in rare cases), this subtraction is not included in the determination of Hg concentration in this laboratory.

17.1.6. Interpretations and Differences from Method 1631 Appendix A

17.1.7. In the method, after digestion with aqua regia is complete, the digestate is diluted with 0.07 N BrCl for elemental carbon-containing samples. In this SOP, all samples are diluted reagent water to which 1 mL of 0.2 N BrCl has been added. This presents a BrCl concentration in the diluted digestate comparable to the concentration achieved using the method technique. Also, since it is added to all digestates (not only those known to contain elemental carbon), the analyzed digestate will always contain some BrCl, and thereby be more comparable to the calibration standards.

APPENDIX A

TABLE I

MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD, AND SPIKING LEVELS (ng/L)

	1631E			
	Conc ng/L	**µL Std (Sec.7.4)**	**Conc ug/kg Solid**	**µL Std (Sec.7.3) Solid**
Standard Water RL	0.5			
Standard Solid RL			1.0	
Std 1 (in triplicate)	0	0		
Std 2	0.5	20		
Std 3	1	40		
Std 4	2	80		
Std 5	5	200		
Std 6	10	400		
Std 7	25	1000		
Std 8	100	4000		
ICV (QCS)	5	200 (Sec 7.6)		
CCV (OPR)	5	200		
LCS	5	200	10	1000
MS/MSD	5	200	10	1000

The concentrations in this table are subject to change.

TABLE II

RECOMMENDED INSTRUMENT PARAMETERS
(LEEMAN LABS HYDRA AF GOLD PLUS)

Instrument Parameter	1631
Argon flow (L/min)	0.5
Pump flow (mL/min)	10
Rinse (sec)	60
Uptake (sec)	240
Sample volume (mL)	40
Integration (sec)	0.70 (70 sec total)
Method	CVAFS with trap
Furnace 1 temp (□C)	600
Furnace 2 temp (□C)	600
Dry Time (sec)	5
Desorption time (sec)	70
Stabilize time (sec)	10

APPENDIX C

TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Fluorescence or Sensitivity Check Failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won’t Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards Reading Twice or Half Normal Fluorescence or Concentration	Incorrect standard used Incorrect dilution performed Dirty cell

APPENDIX D

CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 hydrochloric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered Gloves must not be used in the mercury laboratory since the powder contains mercury, as well as other metallic analytes. Only powder free gloves should be used in the Metals Laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and discard.

APPENDIX E

PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman Labs Hydra AF Gold Plus) [1]

Daily	Semi-annually	As Needed
Check argon flow	Check Hg lamp intensity	Change Hg lamp
Check pump tubing		Change liquid/gas separator
Check drain		Change Nafion dryer
Check soda lime drying tube		

Title: INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

[Method: EPA Method 200.8, SW846 Methods 6020, 6020A, and 6020B]

Approvals (Signature/Date):

Technology Specialist	10/26/17 Date	Health & Safety Coordinator	10/27/17 Date
Quality Assurance Coordinator	10/26/17 Date	Deputy Technical Director	10/26/17 Date

This SOP was previously identified as SOP No. NC-MT-002, Rev 7, dated 5/31/16

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1. SCOPE AND APPLICATION

1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Methods 6020, 6020A, 6020B, and 200.8. The source method lists the following elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Li, Mg. Mn, Ni, K, Ag, Tl, Se, Na, V, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the method.

1.2. The procedure is applicable to the analysis of waters (groundwaters and surface waters), soils, and wastes. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, biological matrices, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a radio frequency inductively coupled plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas, and by means of a water-cooled differentially-pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution less than, or equal to, 0.9 AMU full width at 10% of the peak height. For analysis by Method 200.8, the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged, to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and the constituents of the sample matrix. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Isobaric Interferences: Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.

4.2. Isobaric Molecular and Doubly Charged Ion Interferences: Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied; and the data flagged to indicate the presence of interferences. Using Collision Cell Technology (CCT) can reduce these interferences. Collision Cell Technology is accomplished by adding an auxiliary gas into the lens chamber. A Hydrogen/Helium (Thermo XSeries 2) or Helium (Agilent 7700) gas mixture is used. This gas mixture is used to knock polyatomic ions out of the path as they collide with the cell gas. The ions are dissociated into their component atoms/ions or converted into non-interfering species. The transmission of analyte ions is minimally affected. This process is called Kinetic Energy Displacement (KED).

4.3. Physical Interferences: Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.3.1. Generally, the mass of the internal standard should be no more than 50 AMU (Atomic Mass Unit) of the mass of the measured analyte.

4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank.

4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards, which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.3.4. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be demonstrated routinely to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014.Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3. The following is a list of the materials used in this method, which have a serious or

significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table.** A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. The RF Generator produces strong radio frequency waves--most of which are unshielded. People with pacemakers must not go near the instrument while in operation.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.6. The ICPMS plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Argon gas: High purity grade (99.99%)

6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution less than, or equal to, 1.0 AMU at 10% peak height from a mass range of at least 6-240 and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.3. A three channel peristaltic pump

6.4. Appropriate water-cooling device

6.5. Calibrated adjustable pipettes

6.6. Autosampler with autosampler tubes

6.7. Hydrogen/helium gas mixture with approximate ratio of 7% hydrogen and 93% helium used for CCT mode on the Thermo X Series II, and helium only on the Agilent.7700

7. REAGENTS AND STANDARDS

7.1. Stock Standards

7.1.1. Stock standards are purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock standard solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017.

7.2. Intermediate / Working Standards

7.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions are stored according to manufacturer's instructions. Intermediate / working standard solutions must be replaced after 6 months or according to the stock standard expiration date if less than 6 months. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem.

7.3. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

7.4. Reagent water - ASTM Type I, or equivalent for the elements of interest, generated using an ion-exchange water polishing system.

7.5. Rinse Solution – 2% HNO3 and 1% HCL in reagent grade water.

7.6. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.7. Concentrated hydrochloric acid (HCl), trace metal grade or better

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Aqueous samples are preserved with nitric acid to a pH of < 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.2. Soil samples do not require preservation, but must be stored at 4° ± 2°C until the time of preparation.

8.3. The analytical holding times for metals are six months from the time of collection to analysis.

8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.

8.5. Samples preserved in the laboratory must be held for 24 hours before digestion.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. Instrument Detection Limit (IDL)

9.1.1.1. The IDL will be determined by calculating the average of the standard deviation of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements each day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse at minimum). The IDL must be performed quarterly (annually for Method 6020B). The IDL is calculated by multiplying by three, the average of the standard deviations obtained on three nonconsecutive days. For Method 6020B, 10 consecutive measurements are analyzed on one day..

9.1.2. Linear Calibration Ranges

9.1.2.1. Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions occurs. In the judgment of the analyst, linear ranges may be lowered based on results obtained during the verification process. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the maximum concentration at which sample results can be reported. The linear range must be verified every six months for Method 6020A and must be within 10% of the true value. For Method 6020B, the upper linear range must be verified daily and must be within 10% of the true value.

9.1.2.2. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The linear range is then set at the concentration of the high standard.

9.1.2.3. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value

9.2. Batch Definition

9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3. Method Blank (MB)

9.3.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB must not contain any analyte of interest at, or above, the reporting limit (exception: common laboratory contaminants see below) or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10x higher than the blank contamination level).

Note: For Ohio VAP samples, all analytes must be less than the reporting limit

unless the sample results are below the requested reporting limit. The exception for 10x blank contamination does NOT apply for OVAP samples.

9.3.2. Corrective Action for MBs

9.3.2.1. If the analyte is a common laboratory contaminant (copper, iron, lead, barium, chromium, manganese, calcium, potassium, magnesium, sodium, or zinc), the data may be reported with qualifiers if the concentration of the analyte in the MB is less than two times the RL. **This is not applicable for Ohio VAP samples.**

9.3.2.2. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.3.2.3. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action must be addressed in the project narrative.

9.3.2.4. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Methods 6020, 6020A, and 6020B have criterion of 80%-120%. For Method 200.8, LCS limits are 85-115%. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and corrective action must take place before the analysis can be reported.

9.4.2. Corrective Action for LCS

9.4.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.4.2.2. The only exception is if the LCS recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest. **This must be addressed in the project narrative.**

9.4.2.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. The spike recovery acceptance limits for each analyte are in the LIMS system. If they are not in control, and all other quality control criteria have been met, then matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the analyst shall determine if the MS/MSD is spiked properly and/or the matrix of the sample is the result of the MS/MSD or RPD failure. If it has been determined that the MS/MSD was not spiked properly and/or the failure is not a result of matrix then the sample along with the MS/MSD will be re-digested and analyzed.

Note: If client program requirements specify to confirm matrix interferences, re-preparation and re-analysis of the MS/MSD may be necessary.

9.5.2.2. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is flagged with a “4” in LIMS.

9.5.2.3. For Method 6020A and 6020B, a post digestion spike will be run on a sample if the MS/MSD for the sample falls outside of the percent recovery criteria. A post digestion spike is a matrix spike on the same sample from which the MS/MSD aliquots were prepared, where the spike is added after the sample preparation is completed. The post digestion spike recovery for Method 6020A should be within 80-120% and for 6020B within 75-125%. If this spike fails, then the dilution test should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. A post digestion spike is not required for Method 200.8 nor Method 6020.

9.6. Sample Duplicate (DU)

9.6.1. A DU is a second aliquot of an environmental sample taken from the same sample container, when possible, that is processed with the first aliquot of that

sample. That is, DUs are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.6.2. DUs may be performed in lieu of, or in addition to, MSDs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are easily accessible via the LIMs.

9.9. General Corrective Action Requirements: The general requirements for evaluation of QC results and corrective action for failures is described in TestAmerica Policy QA-003. Ohio VAP projects must reference this SOP instead of Policy QA-003 for information on QC Samples.

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Startup: Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / Daily Performance / EPA Tune

10.2.1. Tuning the Instrument

10.2.1.1. Tune the Instrument based on manufactures recommendations (See table 4 for recommended values).

10.2.2. Daily Performance / EPA Tune

10.2.2.1. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of five times.

10.2.3. Check mass calibration and resolution daily.

10.2.3.1. Mass Calibration Check

10.2.3.1.1. The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.3.2. Mass Resolution Check

10.2.3.2.1. The resolution must be verified to be less than, or equal to, 0.9 amu full width at 10% peak height.

10.3. Initial Calibration

10.3.1. Calibrate the instrument for the analytes of interest according to manufacturer's instructions. Routine calibration and calibration verification levels are shown in Table 5. The calibration should include a minimum of a blank and one standard. For a linear multi-point calibration curve, the correlation coefficient must be at least 0.995 for Method 200.8, 6020, and 6020B. The correlation coefficient must be at least 0.998 for Method 6020A. Report the average of at least three integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up. Instrument analytical runs may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are met. Calibration standard concentrations and/or vendors are subject to change.

10.4. Initial and Continuing Calibration Verification

10.4.1. ICV/CCV. Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a minimum frequency of 10 samples throughout the analytical run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value... Sample results may only be reported when bracketed by valid CCVs.

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Note: The only exception is if the ICV/CCV recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.5. Low Level CCV (CRI/LLCCV)

10.5.1. The CRI/LLCCV for Method 6020Amust be within the 70 – 130% recovery range and analyzed at the beginning and end of the analytical sequence. In addition a LLCCV can be analyzed on a more frequent basis. For method 6020B the recovery must be within 80-120% and analyzed at the beginning of the analytical sequence. If any analyte is outside the range indicated, the CRI/LLCCV may be re-analyzed once. If the results fall within the required values upon re-analysis, no further corrective action needs to be taken. If still outside the acceptable range, then samples containing the affected analytes at similar concentrations cannot be reported and must be re-analyzed.

Note: The only exception is if the CRI/LLCCV recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.6. RL Verification Standard (CRI) Method 6020

10.6.1. An independent standard is analyzed after the ICB to monitor the lab's ability to produce reliable results at RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value. Individual program requirements may vary.

10.7. ICB/CCB

10.7.1. The ICB/CCB solution is prepared with reagent water (ASTM Type I or equivalent) using the same acid matrix as the calibration standards. The Initial Calibration Blank (ICB) must be analyzed immediately following the ICV. The Continuing Calibration Blank (CCB) must be analyzed at a minimum frequency of 10 samples throughout the analytical run. The ICB/CCB must fall within +/- the reporting limit from zero.

Note: The only exceptions are if the ICB/CCB recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest or at, or above, 10 % of the measured concentration of that analyte in associated samples, (sample result must be a minimum of 10x higher than the ICB/CCB contamination level). **Note:** The exception for 10x ICB/CCB contamination does NOT apply to OVAP.

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This must be addressed in the project narrative.

10.8. Interference Check Solutions (ICSA/ICSAB), ***Methods 6020 and 6020A only***

10.8.1. The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table 2. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" must be monitored for possible interferences.

10.8.1.1. Control limits of spiked analytes in the ICSA/ICSAB solution are ± 50% of true value. Some projects may require control limits of ± 20% of true value. Control limits of non-spiked analytes are +/- the reporting limit when the reporting limit is greater than 10 ug/L, ± two times the reporting limit when the reporting limit is 1 ug/L to 10 ug/L or less than 1 ug/L when the reporting limit is less than 1 ug/L..

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted. The ICSAB is not required for method 6020B.

10.9. Internal Standards

10.9.1. The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 120% of the intensity of the calibration blank for Method 6020, 30-150% for Methods 6020A and 6020B, and between 60% and 125% for Method 200.8. If the sample falls outside of these criteria, perform the following procedures. First, evaluate nearby CCVs and CCBs. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples undiluted. If the internal standard recoveries fall outside acceptance criteria and appear to be due to matrix effects, a five fold dilution is performed on the sample to correct for matrix effects and the sample re-analyzed. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal standard intensities are within acceptance criteria. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported. See Table1 for a list of Internal Standard analytes. See Table 7 for the Internal Standard assignments.

10.9.2. The internal standard for the ICV, ICB, CCV, and CCB should be between 80% to 120% of the intensity of the calibration blank for method 6020 , 50% to 150% for method 6020A, 30% to 150% for method 6020B, and 60% to 125% for method 200.8. If outside these limits, the analyst should check for any instrument anomalies and continue if none are observed.

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Note: The internal standards recoveries should never exceed the upper acceptance criteria. If the internal standard recovery exceeds the upper limit for the ICV, ICB, CCV and CCB the associated samples will need to be re-analyzed.

10.10. Serial Dilution, Methods 6020, 6020A, and 6020B only

10.10.1. One serial five-fold dilution must be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit for 6020 and 6020A and a factor of 10 above the RL for 6020B), the serial dilution must agree within 10% of the original analysis (20% limit for 6020B). If not, an interference effect must be suspected; the result is flagged, and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

10.11. Post-Digestion Spike Addition (PDS), ***Method 6020*** **(*performed when required by client or project)***

10.11.1. If the serial dilution fails to meet the acceptance criteria, a re-analysis of the serial dilution can be performed on a diluted sample provided that the concentration of the original sample after the dilution is above the requested reporting limit. If the serial dilution is still outside acceptance limits then a post digestion spike must be performed. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference is suspected.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

11.3. Sample Preparation

11.3.1. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

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11.4. Sample Analysis

11.4.1. Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

11.4.2. Dilute and re-analyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. The sample should be diluted to the approximate midrange of the linear range unless the dilution is for internal standard recoveries or for sample matrix. To reduce the levels of Total Dissolved Solids (TDS), a two-fold dilution will be performed before analysis on solid digestates including batch QC.

11.4.3. The analytical run sequence must be performed as follows to meet all quality control criteria:

Warm-up
Verify instrument performance
Calibration blank
Calibration standards
ICV
ICB
RL verification standard (CRI/ ICVL)
Linear Range Verification (6020B only) Linear range can be performed at anytime during the sequence.
ICSA (6020, 6020A, and 6020B only)
ICSAB (6020 and 6020A only)
CCV
CCB
10 Samples
CCV
CCB
RL verification standard (CRI/LLCCV) for 6020A if applicable

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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11.5.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

Note: The mean of three exposures is used to derive the sample concentrations used in the calculations in this section.

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{Found\ (ICV)}}{\mathbf{True\ (ICV)}}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{Found\ (CCV)}}{\mathbf{True\ (CCV)}}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{SSR\ -\ SR}}{\mathbf{SA}}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$RPD = \mathbf{100\ x}\left[\frac{\mathbf{(DU1\ -\ DU2)}}{\mathbf{(DU1\ +\ DU2)\ /\ 2}}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{(C \times V1 \times D)}{V2}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result (mg/kg)} = \frac{(C \times V \times D)}{W}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested

12.7. Calculation for Hardness

Total Hardness, mg equivalent $CaCO_3$/L, = 2.497 (Ca, mg/L) + 4.118 (Mg, mg/L)

12.8. Calculation for Trivalent Chromium ($Cr^{=3}$)

Cr^{+3} mg/L = Total Chromium mg/L – Hexavalent Chromium (Cr^{+6}) mg/L

12.9. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file. Each laboratory must have corresponding method detection limit files.

13.2. Refer to Table 5 for the list of analytes that may be analyzed using this SOP for Methods 6020, 6020A, 6020B, and 200.8. Additional analytes may be analyzed if all method-required QC is acceptable.

13.3. Training Qualifications

13.3.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

15.4. Waste Streams Produced by the Method

15.4.1. Acid waste consisting of sample and rinse solution is generated by this method.

15.4.1.1. Any sample waste generated must be collected and disposed of in the acid waste drum located in the Metals Lab.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update III, Method 6020: Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 0, September 1994

16.1.2. Test Methods for Evaluating Solid Waste, EPA SW-846, Method 6020A Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 1, February 2007

16.1.3. Test Methods for Evaluation Solid Waste, SW846, Method 6020B, Inductively Coupled Plasma-Mass Spectrometry, Revision 2, October 2012

16.1.4. Environmental Monitoring Systems Laboratory, EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC version

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File:		Revision 0: 08/01/95		Revision 4.5: 07/30/08
		Revision 1: 06/06/01		Revision 4.6: 02/15/11
		Revision 3: 03/26/02		Revision 4.7-A: 04/27/12
		Revision 4: 03/06/03		Revision 5: 04/24/13
		Revision 4.1: 10/01/03		Revision 6: 04/02/14
		Revision 4.2: 01/08/04		Revision 7: 05/31/17
		Revision 4.3: 07/28/07		
		Revision 4.4: 07/30/08		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Acid Digestion of Soils, SW846 Method 3050B, NC-IP-010

16.2.3. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, NC-IP-011

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Standards and Reagents, NC-QA-017

16.2.8. Selection of Calibration Points, CA-T-P-002

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16.2.9. Calibration Curves (General), CA-Q-S-005

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. Reporting limits for solids and waters are easily accessible via the LIMS.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviations

17.2.1. Deviations from Method 6020

17.2.1.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.1.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.1.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.1.4. Internal standard recoveries may be less than 80% in CCVs and CCBs as long as QC criteria are met and that no anomalies are observed by the analyst.

17.2.1.5. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 1% hydrochloric acid.

17.2.1.6. The method states that the ICV should be prepared near the midpoint of the linear range. The laboratory prepares the standard near the midpoint of the calibration curve.

17.2.1.7. The method states in Section 10.10 that the dilution test sample result must be at least 100 times the concentration in the reagent blank. The laboratory uses 100 times the reporting limit as the criteria.

17.2.1.8. The ICSA/ICSAB solution is prepared at least every six months, or if expired.

17.2.2. Deviations from Method 200.8

17.2.2.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.2.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.2.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.2.4. Resolution criteria of the mass calibration are met if the resolution criteria for Method 6020 are satisfied.

17.2.2.5. The concentration of most analytes in the LCS is 1000 μg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are kept in the laboratory.

17.2.2.6. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 1% hydrochloric acid.

17.2.2.7. The tuning solution and internal standard solution are prepared with 2% nitric acid. The method states 1% nitric acid.

17.2.2.8. The method requires a dilution prior to analysis to adjust the chloride concentration in the sample. Due to newer instrument technology, this dilution is no longer needed.

17.3. Tables and Appendices

Table1: Recommended Internal Standards
Li
Sc
Y
Rh
In

Tb
Ho
Bi
Ge

Table 2: Interference Check Sample Components and Recommended Concentrations

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Ag	0.0	0.1
Al	50	50
As	0.0	0.1
B	0.0	0.1
Ba	0.0	0.1
Be	0.0	0.1
C	100	100
Ca	50	50
Cd	0.0	0.1
Cl	500	500
Co	0.0	0.1
Cr	0.0	0.1
Cu	0.0	0.1
Fe	50	50
K	50	50
Li (Agilent only)	0.0	0.1
Mg	50	50
Mn	0.0	0.1
Mo	1.0	1.1
Na	50	50
Ni	0.0	0.1
P	50	50
Pb	0.0	0.1
S	50	50
Sb	0.0	0.1
Se	0.0	0.1
Sn	0.0	0.1
Sr	0.0	0.1
Ti	1.0	1.1
Tl	0.0	0.1
V	0.0	0.1
W	0.0	0.1
Zn	0.0	0.1

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TABLE 3: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Table 3 A: Thermo XSeries II

Element	Concentration (µg/L)
Mg	10
Rh	10
Pb	10
Li	10
Co	10
In	10
Tl	10

Element	Concentration (µg/L)
Be	10
Mg	10
Co	10
In	10
Pb	10
Ba	10
Ce	10

Table 3 B: Agilent 7700

Element	Concentration (ug/L)
Ce	1
Co	1
Li	1
Mg	1
Tl	1
Y	1

TABLE 4: Suggested Tuning and Response Factor Criteria / Minimum Response from Tuning Solution

Suggested Minimum Response from Tuning Solution (Standard Mode based on a 10 ug/L solution)
With a Peristaltic Pump Speed of 18 RPM on the Thermo XSeries II

Be	> 8,000
In	> 300,000
Pb	> 100,000
Co	> 100,000
Mg	> 10,000

Suggested Minimum Response from Tuning Solution (CCT Mode based on a 10 ug/L solution)
With a Peristaltic Pump Speed of 18 RPM on the Thermo XSeries II

In > 75,000
Se < 20

Suggested Mass Calibration for Thermo XSeries II

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Suggested Response From Tuning Solution (No He Gas based on a 1 ug/L solution) for the Agilent 7700

6 >1000
89 >3000
205 > 2000
156/140 (Oxides) <1.0

Suggested Minimum Response From Tuning Solution (He Gas based on a 1 ug/L solution) for the Agilent 7700

59 >1000 with <5%RSD
51 <200
52 <200
51/59 <10%

TABLE 5: ICP/MS Calibration and Calibration Verification Checklist
Suggested Levels in μg/L

Element	Calibration 1A (Agilent only)	Calibration		ICV	CCV
		1	2		
Aluminum	50	250	500	200	250
Antimony	10	50	100	40	50
Arsenic	10	50	100	40	50
Barium	10	50	100	40	50
Beryllium	10	50	100	40	50
Boron	10	50	100	40	50
Cadmium	10	50	100	40	50
Calcium	5000	25000	50000	20000	25000
Chromium	10	50	100	40	50
Cobalt	10	50	100	40	50
Copper	10	50	100	40	50
Iron	2500	12500	25000	10000	12500
Lead	10	50	100	40	50
Lithium	10	50	100	40	50
Manganese	50	250	500	200	250
Magnesium	5000	25000	50000	20000	25000
Molybdenum	10	50	100	40	50
Nickel	10	50	100	40	50
Potassium	5000	25000	50000	20000	25000
Selenium	10	500	200	40	500
Sodium	5000	25000	50000	20000	25000
Silver	10	50	100	40	50
Strontium	10	50	100	40	50
Thallium	10	50	100	40	50
Tin	10	50	100	40	50
Titanium	10	50	100	40	50
Tungsten	10	50	100	40	50
Vanadium	10	50	100	40	50
Zinc	10	50	100	40	50

This procedure has been developed for additional elements. Additional elements may be included in the calibration solution at the appropriate levels. Levels may be adjusted to meet specific regulatory or client programs.

Table 6 A: Internal Standard Assignments for Thermo XSeries II		
Standard Mode Internal Standards: 6Li and 45Sc		
CCT Mode Internal Standards: 45Sc, 72Ge, 115In, 159Tb*, 165Ho, 209Bi*		
*Not used on a daily basis but may be used as an alternative or additional internal standard		
Mass - Element	**Associated Internal Standards**	**Possible Alternatives**
9Be	45Sc	6Li Standard
10B	45Sc	6Li Standard
23Na	45Sc CCT	72Ge Only
25Mg	45Sc CCT	72Ge Only
27Al	45Sc CCT	72Ge Only
39K	45Sc Standard	6Li
43Ca	45Sc Standard	6Li
47Ti	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
51V	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
52Cr	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
55Mn	45Sc Standard	6Li
56Fe	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
59Co	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
60Ni	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
65Cu	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
66Zn	45Sc CCT and 72Ge	72Ge Only or 45Sc CCT only
75As	72Ge and 115In	72Ge Only or 115In Only
78Se	72Ge and 115In	72Ge Only or 115In Only

88Sr	72Ge and 115In	72Ge Only or 115In Only
95Mo	72Ge and 115In	72Ge Only or 115In Only
107Ag	72Ge and 115In	72Ge Only or 115In Only
111Cd	72Ge and 115In	72Ge Only or 115In Only
118Sn	115In and 165Ho	115In Only, 159Tb Only, or 165Ho only
121Sb	115In and 165Ho	1115In Only, 159Tb Only, or165 Ho only
137Ba	115In and 165Ho	115In Only, 159Tb Only, or 165Ho only
159 Tb		
165Ho		
182W	165Ho	115 In only, 159Tb only, 165Ho only, or 209Bi
205Tl	165Ho	115 In only, 159Tb only, 165Ho only, or 209Bi only
208Pb	165Ho	115 In only, 159Tb only, 165Ho only, or 209Bi
The analyst has the option to associate an alternative Internal Standard with an element if acceptance criteria are not met.		
Generally, the mass of the internal standard should be no more than 50 amu of the mass of the measured analyte, however,		

Table 6-B: Internal Standard Assignments for Agilent 7700		
Mass-Element	**Associated Internal Standards**	**Possible Alternatives**
7Li	45Sc No Gas	
9Be	45Sc	6Li No Gas
11B	45Sc	6Li No Gas
23Na	45Sc He	
25Mg	45Sc He	
27Al	45Sc He	
39K	45Sc He	
44Ca	45Sc He	
47Ti	45Sc He	
51V	45Sc He	
52Cr	45Sc He	
55Mn	45Sc He	103Rh
56Fe	45Sc He	103Rh
59Co	45Sc He	103Rh
60Ni	45Sc He	103Rh
63Cu	45Sc He	103Rh
66Zn	45Sc He	103Rh
75As	115In	103Rh
78Se	115In	103Rh
88Sr	103Rh He	45Sc, 103Rh, 115In
95Mo	103Rh	45Sc He, or 115In
107Ag	103Rh	115In
111Cd	115In	103Rh or 159Tb
118Sn	115In	103Rh, 159Tb, or 165Ho
123Sb	115In	103Rh, 159Tb, or 165Ho
137Ba	115In	103Rh or 159Tb

Table 6-B: Internal Standard Assignments for Agilent 7700		
Mass-Element	**Associated Internal Standards**	**Possible Alternatives**
182W	159Tb	165Ho or 209Bi
205Tl	165Ho	165Ho or 209Bi
208Pb	165Ho	165Ho or 209Bi
i		
The analyst has the option to associate an alternative Internal Standard with an element if acceptance criteria are not met.		
Generally, the mass of the Internal Standard should be no more than 50 amu of the mass of the measured analyte.		

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Title: INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROSCOPY, SPECTROMETRIC METHOD FOR ELEMENT ANALYSES

[Methods: SW846 Methods 6010B, 6010C, 6010D, and EPA Method 200.7]

Approvals (Signature/Date):

Technology Specialist	04/05/18 Date	Health & Safety Coordinator	04/25/18 Date
Quality Assurance Coordinator	04/30/18 Date	Technical Director	04/30/18 Date

This SOP was previously identified as SOP NC-MT-012, Rev 7, dated 10/27/17

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1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of elements including metals in solution by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using SW-846 Methods 6010B, 6010C, 6010D, and EPA Method 200.7. Table 1 of Appendix A lists the elements appropriate for analysis by Methods, 6010B, 6010C, 6010D, and 200.7. Additional elements may be analyzed under these methods provided that the method performance criteria presented in Section 13.0 are met.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity, and optimum concentration ranges of the metals will vary with the matrices and instrumentation used.

1.3. Methods 6010B, 6010C, and 6010D are applicable to the determination of dissolved, suspended, total recoverable, and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, biological, and TCLP and other leachates/extracts. All matrices require digestion prior to analysis. Silver concentrations greater than 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples may be subject to error. Precipitation may occur in samples where silver concentrations exceed these levels, leading to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis. Silver concentrations must be below 0.1 mg/L in aqueous samples for the reasons discussed above.

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multiple elements in solution using simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by radio frequency inductively-coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by a charge injection device (CID). The amplified photocurrents from the charge injection device (CID) are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used for background determination must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences must also be recognized and appropriate actions taken.

2.2. Refer to NC-IP-010, Acid Digestion of Soils by SW846 Method 3050B, and NC-IP-011, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, for details on sample preparation methods.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version for additional definitions. Refer to Appendix B for a cross reference of method definitions.

4. INTERFERENCES

4.1. Physical, chemical, and spectral interference effects may contribute to inaccuracies in the determinations of elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of elements. Background correction is not required in cases where a background correction would actually degrade the analytical result.

4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the

sample emit radiation at wavelengths so close to that of another analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization, and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, dilution of the sample, use of a peristaltic pump or mass flow controller, use of an internal standard, and/or use of a high solids nebulizer can reduce the effect. Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4-ppm STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and

			respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Note: Always add acid to water to prevent violent reactions			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.1. The plasma emits strong UV light and is harmful to vision. **NOTE**: **AVOID looking directly at the plasma**.

5.3.2. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers must not go near the instrument while in operation.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Metals digestates can be processed outside of a fume hood. Solvent and waste containers must be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator

6.3. Argon gas supply, welding grade or equivalent

6.4. Coolflow or appropriate water cooling device

6.5. Peristaltic Pump

6.6. Calibrated pipettes

6.7. Class A volumetric flasks

6.8. Autosampler tubes

7. REAGENTS AND STANDARDS

7.1. Standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the solutions may be used for up to one year from receipt. They must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended, provided that the acceptance criteria described in laboratory-specific SOPs are met. Additional information can be found in SOP NC-QA-017. Standard or spiking concentrations, as well as vendors, are subject to change.

7.2. Working calibration, calibration verification solutions, and internal standard solutions must be prepared in a matrix of 5% hydrochloric and 5% nitric acids. Refer to Tables 2 and 3 (Appendix A) for details regarding the working standard concentrations for interference correction and spiking solutions. Refer to the reagents module in LIMS for details on standard or reagent preparation.

7.3. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.4. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.5. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to digestion.

8.3. Soil samples do not require preservation, but must be stored at 4°C ± 2° until the time of preparation.

8.4. Metals samples that are preserved at the laboratory must be held for 24 hours before digestion.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. Prior to analysis of any analyte using Methods 200.7, 6010B, 6010C, or 6010D the following requirements must be met.

9.1.2. Instrument Detection Limits (IDLs)

9.1.2.1. IDLs are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation; however, it should be understood that the lower limit of quantitation needs to be verified using the criteria in Section 9.9.

9.1.2.2. The IDL for each wavelength used for detection for each analyte must be determined for each instrument. The IDL must be determined annually. Whenever the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be re-determined. The IDL will be determined by multiplying the standard deviation obtained from the analysis of 7 consecutive measurements (, 6010B and 6010C) of a blank solution. 6010D and 200.7 require 10 consecutive replicates. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse at minimum.).

9.1.3. Linear Range Verification (LR):

9.1.3.1. The linear range must be verified every six months for each analyte wavelength used on each instrument. The linear range is the maximum concentration at which sample results can be reported. The standards used to verify the linear range must be analyzed during a routine analytical run, and must read within 10% of the expected value. Method 200.7 requires that any reading above 90% of the established LR must be diluted and re-analyzed. For Method 6010D the upper linear range must be verified during each daily run and must be within 10% of the true value.

9.1.3.2. For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from three different concentration standards across the estimated range. One standard must be near the expected upper limit of the estimated range. The concentration measured at the LDR must be within 10% of the true value.. If an adjustment is performed that may affect the LDRs, new dynamic ranges must be determined. The LDR data must be documented and kept on file.

9.1.4. Lower Limit of Quantitation Check Standard (LLOQ/LLQC) – The LLOQ is the lowest point of quantitation for the laboratory. The LLOQ is a digested standard at or below the reporting limit. The LLOQ verification is analyzed on a quarterly basis for 6010D and on an as needed basis for 6010C to validate quantitation capability at low analyte concentration levels. In most cases the recovery limits for the LLOQ should be ± 35% of the true value and ± 30% for 6010C. The % RSD between successive LLOQ's should be ≤ 20%. If these limits cannot be met, the reporting limit must be reevaluated.

9.1.5. Background Correction Points:

9.1.5.1. To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side, adjacent to the wavelength, and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line inter-element spectral interference, an algorithm is employed by the software for correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Purchased reference standards for individual elements are prepared and used for these determinations. Background correction points must be set prior to determining Inter-element Correction factors. Refer to the ICP instrument manual for specific procedures to be used in setting background correction points.

9.1.6. Inter-element Corrections (IECs):

9.1.6.1. ICP inter-element correction factors must be determined prior to the analysis of samples and every six months thereafter. If an adjustment is performed that may affect the IECs at any other time during the six month period, the IECs must be re-determined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC, then the possibility of contamination must be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., ICP-MS). Published wavelength tables (e.g., MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any inter-element interference which results in a false analyte signal greater than ± the RL. For elements with a reporting limit of 10 µg/L or less, the signal must be ± two times the RL. To determine IECs, run a single element standard at the LDR. To calculate an IEC, divide the observed concentration of the analyte by the actual concentration of the "interfering element." These correction factors are updated in the software and automatically applied.

9.1.7. Rinse Time Determination:

9.1.7.1. Rinse times must be determined upon initial set-up of an ICP instrument. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see Section 9.1.3) must be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes, it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be re-analyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

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9.2. Batch Definition

9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike (MS), and Matrix Spike Duplicate (MSD)) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same process.

9.3. Method Blank (MB)

9.3.1. One MB must be processed with each preparation batch of up to 20 samples. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB must not contain any analyte of interest at, or above, the reporting limit (exception: common laboratory contaminants: see below) or at, or above, 10 % of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10x higher than the MB contamination level). For Ohio VAP projects, all analytes must be less than the reporting limit with the following exceptions: (a) insufficient sample for re-digestion (b) expired holding times, or (c) the elements detected in the MB are < RL for the associated samples. The 10x the concentration rule does not apply for OVAP.

Note: In cases where the analyte is a common laboratory contaminant (copper, iron, lead, or zinc), the data may be reported with qualifiers if the concentration of the analyte in the MB is less than two times the RL. Such action must be addressed in the project narrative.

9.3.1.1. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.3.1.2. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action must be addressed in the project narrative.

9.3.1.3. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

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9.4. Laboratory Control Sample (LCS)

9.4.1. One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table 2 (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.4.1.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur. Unless in-house control limits are established, a control limit of 80 - 120% recovery must be applied for Method 6010B, 6010C, 6010D. For Method 200.7, control limits of 85-115% must be applied.

9.4.1.2. In the instance where the LCS recovery is greater than the upper control limit and the sample results are < RL, the data may be reported with qualifiers. Such action must be addressed in the report narrative.

9.4.1.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. The laboratory may re-analyze an aliquot of the LCS to verify the outlier; however, if the LCS exhibits the same anomaly upon re-analysis, the sample batch must be re-digested and re-analyzed. The exceptions are as follows: (a) insufficient sample for re-digestion (b) expired holding times, or (c) the LCS is biased high and the sample results are < RL for those analytes.

9.5. Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of un-spiked sample duplicates in place of, or in addition to, MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table 2 (Appendix A).

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9.6.1.1. If the analyte recovery or RPD falls outside the acceptance range, the analyst shall determine if the MS/MSD is spiked properly and/or the matrix of the sample is the result of the MS/MSD or RPD failure. If it has been determined that the MS/MSD was not spiked properly and/or the failure is not a result of matrix then the sample along with the MS/MSD will be re-digested and analyzed.

Note: If client program requirements specify to confirm matrix interferences, re-preparation and re-analysis of the MS/MSD may be necessary.

9.6.1.2. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is reported with a “4” flag.

9.6.1.3. For Method 6010C and 6010D samples – If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation batch should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and must be recovered to within 80% to 120% of the known value (75-125% for 6010D). If this spike fails, then the dilution test (serial dilution) must be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed and results are reported with narration.

9.7. Dilution test (Serial Dilution)

9.7.1. A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5X dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample after correction for dilution must agree within 10% (20% for Method 6010D) of the original sample determination when the original sample concentration is greater than 50 times the MDL for 6010B and 6010C, and 25 times the reporting limit for 6010D. If the results are not within acceptance criteria, the possibility of chemical or physical interference exists and the data are flagged.

9.8. Control Limits

9.8.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.8.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMS.

9.9. Method Detection Limits (MDLs) and MDL Checks

9.9.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.9.2. MDLs are easily accessible via the LIMS.

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Deviations are not allowed for Ohio VAP projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.2. Initial Calibration

10.2.1. Optimize and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank after each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to the manufacturer's instruction manuals in the laboratory for calibration procedures. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument standardization date and time must be included in the raw data

10.3. Initial Calibration Verification/Initial Calibration Blank (ICV/ICB)

10.3.1. Calibration accuracy is verified by analyzing an ICV, prepared from a second source standard, immediately after the initial calibration. For analyses conducted under Method 200.7, the ICV must fall within ±5% of the true value for that solution and have an RSD of <3% from the replicate (minimum of three) exposures. For Methods 6010B, 6010C, and 6010D the ICV must fall within ±10% of the true value for that solution. The % RSD must be <5% from the replicate (minimum of three) exposures for Method 6010B.

10.3.2. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB is prepared with reagent water and must contain the same concentrations of the acids used to prepare the standards. The ICB result must fall within ± the RL from zero for each element.

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10.3.3. If either the ICV or ICB fail to meet criteria, the analytical sequence must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified (see Section 11.6 for the required run sequence). Exceptions: If the concentration in the ICB is > RL, sample results < RL can be reported, with an NCM. If the ICV result is outside of criteria high, sample results < RL can be reported, with an NCM.

10.4. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB)

10.4.1. Calibration accuracy is monitored throughout the analytical run through the analysis of a reference standard after every 10 samples and at the end of the analytical sequence. The CCV is prepared from stock standards from the primary supplier (or separate source from that used to prepare the ICV) at the approximate mid-range concentration The CCV for all methods must fall within ±10% of the true value for that solution. For Methods 6010B and 200.7, the RSD from replicate (minimum of three) exposures must be <5%. For Method 6010C and 6010D, there is no criterion for RSD from replicate exposures.

10.4.2. A CCB is analyzed immediately following each CCV (see Sections 11.6 for required run sequence). The CCB is the same solution that is used for the ICB and must contain the same concentrations of the acids used to prepare the standards. The CCB result must fall within ± RL from zero. If the CCB concentration is less than 10-times that of the associated samples, results may be reported if narrated and/or flagged. This is not acceptable for Ohio VAP samples.

10.4.3. If a mid-run CCV or CCB fails, all of the affected samples must be re-analyzed with valid CCV/CCB pairs (refer to Section 11.6 for an illustration of the appropriate rerun sequence). Exceptions: If the concentration in the CCB is > RL, sample results < RL can be reported, with an NCM. If the CCV result is outside of criteria high, sample results < RL can be reported, with an NCM.

10.5. Interference Check Solution Analysis (ICSA/ICSAB)

10.5.1. The validity of the inter-element correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table 3 (Appendix A) for the details of ICSA and ICSAB composition. Custom multi-element ICS solutions must be used. All analytes must be spiked into the ICSAB solution; therefore, if a non-routine analyte is required, then it must be manually spiked into the ICSAB using a certified ultra-high purity single-element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number, then the non-routine elements can be controlled with the ICSA. Aluminum, iron, calcium, and magnesium must always be included in the ICSA/ICSAB pair in every sequence.

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10.5.2. The ICSA and ICSAB solutions must be run at the beginning of the run (see Section 11.6 for required run sequence).

10.5.3. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analytical sequence must be terminated, the problem corrected, the instrument re-calibrated, and the samples rerun.

10.5.4. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within ± 2 times the RL from zero. ICSA results for the non-interfering elements with RLs > 10 µg/L must fall within ± RL from zero. If the ICSA results for the non-interfering elements do not meet the above criteria the field sample data must be evaluated as follows.

10.5.4.1. If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted (vendor contact required if contamination is suspected).

10.5.4.2. If the affected element was not a requested analyte, then the sample data can be accepted.

10.5.4.3. If the analyst determines that interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than ± 2 x the RL from zero, then the field sample data can be accepted.

10.5.4.4. If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2 x the RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than ten times the analyte response in the ICSA.

10.5.4.5. If the data does not meet the above conditions, then the IECs must be re-evaluated and corrected if necessary, and the affected samples re-analyzed, or the sample results must be manually corrected through application of the new IEC to the raw results.

10.6. Low Level ICV/Low Level CCV [ICVL/CCVL]

10.6.1. The ICVL/CCVL for Method 6010C must be within the 70 – 130% recovery range and analyzed at the beginning and end of the analytical sequence. .The ICVL criteria for Method 6010D is within 80-120% and analyzed at the beginning of the analytical sequence. In addition a CCVL can be analyzed on a more frequent basis. If any analyte is outside the range indicated, the CCVL may be re-analyzed once. If the results fall within the required values upon re-analysis, no further corrective action needs to be taken. If still outside the acceptable range, then samples containing the affected

analytes at similar concentrations cannot be reported and the samples must be re-analyzed.

Note: The only exception is if the CCVL recoveries are biased high and the associated sample is below the RL for the parameter(s) of interest. This must be addressed in the project narrative.

10.6.2. RL Verification Standard (ICVL) Method 6010B: An independent standard is analyzed after the ICB to monitor the lab's ability to produce reliable results at or near the RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value. Individual program requirements may vary.

10.7. Laboratory support equipment must be calibrated per SOPs NC-QA-004 and NC-QA-015.

11. PROCEDURE

11.1. A minimum of three exposures readings for each standard, field sample, and QC sample is required. The average of the exposures is reported.

11.2. Prior to calibration and between each sample/standard, the system is rinsed with the calibration blank solution.

11.3. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV, CCV), blanks (ICB, CCB), interference checks (ICSA, ICSAB), and field samples (linear range) to improve the data review process.

11.4. To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data be reviewed periodically throughout the run.

11.5. The following procedural guidelines must be followed when using an internal standard:

11.5.1. Typically used internal standards are Yttrium and Indium. (Note: Any element can be used that is not typically found in environmental samples)

11.5.2. The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing T. Internal standards must be added to blanks, samples, and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.5.3. The concentration of the internal standard must be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.5.4. The internal standard raw intensity counts must be printed on the raw data.

11.5.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte). The instrument automatically adjusts sample results based on comparison of the internal standard intensity in the sample to the internal standard intensity at calibration.

11.5.5.1. If the internal standard counts fall within ±50% of the counts observed in the calibration blank then the data is acceptable.

11.5.5.2. If the internal standard counts in the field samples are more than ± 50% higher than the expected level, a dilution is needed due to matrix interference.

11.6. The following analytical sequence should be used for Methods 6010B, 6010C, 6010D and 200.7:

Instrument Calibration
ICV
ICB
ICVL (6010C/6010D)
ICSA
ICSAB
CCV
CCB
10 samples
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete the run
CCVL (6010C)

11.7. Refer to Quality Control Section 9.0 for Methods 6010B, 6010C, 6010D, and 200.7 quality control criteria.

11.8. Guidelines are provided in Appendix C on procedures to minimize contamination.

11.9. All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range. If an inter-element correction exists for an analyte, which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an over-range analyte may not be required to be reported for a sample, if that analyte is an interferent for any requested analyte in that sample, the sample must be diluted. Acid strength is maintained in the dilution of samples by diluting the sample with the dilution blank solution.

11.10. Nonconformance documentation must be filed in the project file.

11.11. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.12. Analytical Documentation

11.12.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.12.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.12.3. Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs, is available for each data file.

11.12.4. Record all sample results and associated QC into the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates is calculated according to the following equation:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

12.5. The final concentration for a digested aqueous sample is calculated as follows:

$$mg / L = \frac{C \times V1 \times D}{V2}$$

Where:
C = Concentration (mg/L) from instrument readout (mean of two exposures)
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The final concentration determined in digested solid samples is calculated as follows:

$$mg / Kg, dry\ weight = \frac{C \times V \times D}{W}$$

Where:
C = Concentration (mg/L) from instrument readout (mean of two exposures)
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight in Kg of wet sample digested

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result (Instrument reading)
S = Dilution test result (Instrument reading × 5)

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

12.10. Trivalent Chromium

12.10.1. Trivalent chromium (CR^{+3}) is the result obtained by subtracting the hexavalent chromium (CR^{+6}) results for a sample from the total chromium result from that sample. The total chromium result is determined using the procedures in this SOP. The hexavalent chromium result is determined using the procedures in TestAmerica Canton SOP NC-WC-024.

12.10.2. Reporting Limits

12.10.2.1. The TestAmerica Canton water reporting limit for trivalent chromium is 0.02 mg/l.

12.10.2.2. The TestAmerica Canton solid reporting limit for trivalent chromium is 2.0 mg/kg, wet weight.

12.10.2.3. Calculations: Cr^{+3} = total Cr – Cr^{+6}

12.11. Hardness by Calculation (SM2340B)

12.11.1. Total hardness can be determined by a calculation of the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate in mg/L.

12.11.2. Total Hardness mg equivalent $CaCO_3$/L = [2.497 X (Ca concentration in mg/L)] + [4.118 x (Mg concentration in mg/L)]

12.11.3. The reporting limit is 33 mg/L.

12.12. Additional equations and calculations are listed in the following SOP: Calibration Curves (General), CA-Q-P-003.

13. METHOD PERFORMANCE

13.1. Each instrument must have initial demonstration of performance data on file for each analyte of interest as described in Section 13..

13.2. Refer to Table 1 in Appendix A for the list of analytes that may be analyzed using this SOP.

13.3. Training Qualification

13.3.1. The Group/Team Leader or the Supervisor has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the corporate environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by this Method

15.2.1. Acid waste consisting of sample and rinse solution: Any sample waste generated must be collected and disposed of in the acid waste drum located in the Metals Lab.

15.2.2. Standards must be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. References

16.1.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits

16.1.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B

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16.1.3. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Final Update IV, Method 6010C, Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 3, February 2007

16.1.4. Test Methods for Evaluation Solid Waste, Physical/Chemical Methods, SW-846, Final Update V, Method 6010D, Revision 4, October 2012

16.1.5. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7

16.1.6. Inductively Coupled Plasma – Atomic Emission Spectrometric Method for Trace Element Analysis of water and wastes Method 200.7, 40 CFR – Chapter I – Part 136 – Appendix C. Electronic version dated September 30, 2002

16.1.7. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.8. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.9. Corporate Quality Management Plan (CQMP), current version

16.1.10. Revision History

Historical File:		Revision 2.0: 10/27/97		Revision 4: 09/13/13
(formerly CORP-MT-0001NC)		Revision 2.1: 04/19/99		Revision 5: 4/30/15
		Revision 3.1: 10/04/00		Revision 6: 10/13/16
		Revision 3.2: 01/19/01		Revision 7: 10/27/17
		Revision 3.3: 12/05/01		
		Revision 3.4: 01/08/04		
		Revision 0: 01/08/04 (NC-MT-012)		
		Revision 1: 01/07/09		
		Revision 2: 02/22/11		
		Revision 3-A: 04/17/12		

16.2. Associated SOPs and Policies, current version

16.2.1. TestAmerica Canton QC Program, QA-003

16.2.2. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.3. Detection and Quantitation Limits, CA-Q-S-006

16.2.4. Hexavalent Chromium (Colorimetric), NC-WC-024

16.2.5. Acid Digestion of Soils, SW846 Method 3050B, NC-IP-010

16.2.6. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, NC-IP-011

16.2.7. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method

17.1.1. Modifications/interpretations from Methods 6010B and 200.7

17.1.1.1. TestAmerica Canton Laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in-house as recommended by the subject methods.

17.1.1.2. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution must fall within a specific concentration range around the calibration blank. In determining IECs because of lack of definition clarification for “concentration range around the calibration blank,” The laboratory uses the following criteria: +/- RL or +/- 2x RL if RL is 10ug/L or less.

17.1.1.3. Whenever a new or unusual matrix is encountered, a series of tests must be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because TestAmerica Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, TestAmerica Canton may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At TestAmerica Canton, matrix interference is determined by evaluating data for the LCS and MS/MSD. TestAmerica Canton REQUIRES documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a specific client-identified sample.

17.1.2. Modifications from Method 200.7

17.1.2.1. Method 200.7 defines the IDL for an element by determining the standard deviation of ten replicate measurements of the calibration blank signal at the wavelength specific to that

element and multiplying it by three. TestAmerica Canton lab utilizes the IDL definition as defined in Section 9.1 of this SOP.

17.1.2.2. The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix. The former matrix provides improved performance, relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied to samples. The laboratory runs these methods concurrently; therefore, the solution used is used for all analyses.

17.1.2.3. Section 7.12 of Method 200.7 indicates that the quality control sample ICV must be prepared at a concentration greater than or equal to 1 ppm. This SOP specifies ICV concentrations which are appropriate to the mid range of the calibration. The intent of the ICV, verification of the primary calibration standard accuracy, is independent of the ICV concentration used.

17.1.2.4. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 Section 10.4 states that results must fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The laboratory uses the following criteria: +/- RL or +/- 2x RL if RL is 10ug/L or less.

17.1.3. Modifications from Method 6010B

17.1.3.1. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants may be allowed up to two times the reporting limit. This is not acceptable for Ohio VAP projects. For Ohio VAP projects, the MB must be clean down to the RL, unless the sample result is below the RL.

17.1.3.2. Method 6010B Section 8.6.1.3 states that the results of the calibration blank must be within three times the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean. TestAmerica Canton has adopted an absolute control limit of $\pm$ RL from zero for calibration blank criteria. See SOP Section 10.4 for a detailed description of the required corrective action procedures.

APPENDIX A - TABLES

TABLE 1: Methods 200.7, 6010B, 6010C and 6010D Target Analyte List

Element	Symbol	CAS #
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Boron	B	7440-42-8
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Lithium	Li	7439-93-2
Magnesium	Mg	7439-95-4

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Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silicon	Si	7440-21-3
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Strontium	Sr	7440-24-6
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6
Tin	Sn	7440-31-5
Titanium	Ti	7440-32-6

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TABLE 2: Matrix Spike and Aqueous Laboratory Control Sample Levels

Element	Concentration (ug/L)
Aluminum	2000
Antimony	500
Arsenic	2000
Barium	2000
Beryllium	50
Cadmium	50
Calcium	50000
Chromium	200
Cobalt	500
Copper	250
Iron	1000
Lead	500
Lithium	1000
Magnesium	50000
Manganese	500
Molybdenum	1000
Nickel	500
Potassium	50000
Selenium	2000
Silicon	1000
Silver	50
Sodium	50000
Strontium	1000
Thallium	2000
Vanadium	500
Zinc	500
Boron	1000
Tin	2000
Titanium	1000

Note: *Concentration are subject to change.*

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TABLE 3: Interference Check Sample Concentrations

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Lithium		500
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silicon		10000
Silver	-	1000
Sodium	-	10000
Strontium		1500
Thallium	-	1000
Vanadium	-	500
Zinc	-	1000
Tin	-	1000
Boron		1000
Titanium		1000

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APPENDIX B - CROSS REFERENCE OF TERMS COMMONLY USED IN METHODS EPA 200.7, SW 6010B, 6010C, AND 6010D TESTAMERICA CANTON SOP

EPA 200.7	SW 6010B / 6010C / 6010D	TestAmerica Canton SOP
Calibration blank	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory fortified blank (LFB)	Laboratory control sample	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)
Quality control sample (QCS)	Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX C - CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware must be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the Metals Lab. All work areas must be kept clean.

Powdered Gloves must not be used in the Metals Lab since the powder contains silica and zinc as well as other metallic analytes. Glassware must be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY

[Method: MCAWW Method 245.1, SW846 Method 7470A, SW846 7471A, and 7471B]

Approvals (Signature/Date):

Technology Specialist	12/18/17 Date	Health & Safety Coordinator	12/18/17 Date
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This SOP was previously identified as SOP No. NC-MT-014, Rev 6, dated 6/23/16

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW846 Methods 7470A, 7471A, and 7471B, and MCAWW Method 245.1.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants and potassium permanganate has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed; however, Method 7471A is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in surface and saline waters, and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. Methods 7471A and 7471B are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes, biological material, and sludge-type materials. All matrices require sample preparation prior to analysis.

1.6. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric (aqueous samples), or hydrochloric and nitric acids (soil samples). Organic mercury compounds are oxidized with potassium permanganate (aqueous and soil samples) and potassium persulfate (aqueous samples), and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

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3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control (QC) section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.3. Potassium permanganate, which is used to break down organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide (as sodium sulfide) do not interfere with the recovery of inorganic mercury from reagent water.

4.4. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.5. Chlorides can cause a positive interference. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (maximum 25 mL); because during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride

4.6. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.7. Samples containing high concentrations of oxidizable organic materials, as evidenced by high Chemical Oxygen Demand (COD) levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. Reducing the volume of original sample used can eliminate this problem.

4.8. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. Refer to Appendix B for Contamination Control Guidelines.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Mercury (10PPM in Reagent)	Oxidizer Corrosive Poison	0.1 g/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydroxyl-amine Hydro-chloride	Corrosive Poison	None	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Corrosive to the eyes. Irritant and possible sensitizer. May cause burns to the skin.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The Ultra Violet (UV) light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory, and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature-controlled hot block or equivalent

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption cell with quartz end windows perpendicular to the longitudinal axis: Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury-specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.2.3. Peristaltic pump which can deliver 1 L/min air

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min

6.2.5. Recorder or printer

6.2.6. Drying device to prevent condensation in cell

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. Plastic bottles – capable of holding 100 mL

6.4. Nitrogen or argon gas supply, welding grade or equivalent

6.5. Calibrated automatic pipettes

6.6. Class A volumetric flasks

6.7. Top-loading balance, capable of reading up to two decimal places

6.8. Thermometer (capable of accurate readings at 95 °C)

6.9. Disposable cups or tubes

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore Deionized Water (DI) system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm calibration and ICV) mercury standards are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017. Refer to the reagent module in the Laboratory Information Management System (LIMS) for details on standard preparation.

7.3. Working mercury standard (0.1 ppm): Take 2 mL of the 10 ppm stock standard (Section 7.2) and dilute to 200 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (300 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. Refer to the reagent module in LIMS for details on standard preparation.

7.4. Working ICV standard (0.1 ppm): Take 1 mL of the 10 ppm ICV stock standard (Section 7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. Refer to the reagent module in LIMS for details on standard preparation.

7.5. The calibration standards must be prepared fresh daily from the working standard (Section 7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample preparation bottles for solid samples or by transferring 0, 0.1, 0.25, 0.5, 2.5, and 5.0 mL aliquots of the working mercury standard into sample preparation bottles for aqueous samples and proceeding as specified in Section 11.1. The laboratory control sample (LCS) solution is prepared by transferring 5.0 mL (solids) or 2.5 mL (waters) of working standard (Section 7.3) into sample preparation bottles and proceeding as specified in Section 11.1. Refer to the reagent module in LIMS for details on standard preparation.

Note: Alternate approaches to standard preparation may be taken, and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I (Appendix A) are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

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7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table 1 (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better

7.10. Sulfuric acid (H_2SO_4), concentrated, traces metal grade or better

7.11. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.12. Stannous chloride solution: Add 50g ± 0.5g of stannous chloride and 25 mL of concentrated HCl, and bring to a final volume of 500 mL with DI water.

Note: Stannous sulfate may be used in place of stannous chloride. Prepare the stannous sulfate solution according to the recommendations provided by the instrument manufacturer.

7.13. Sodium chloride-hydroxylamine hydrochloride solution: Add 240g ± 0.5g of sodium chloride and 240g ± 0.5g of hydroxylamine hydrochloride to every 2000 mL of reagent water.

7.14. Potassium permanganate, 5% solution (w/v): Dissolve 100g of potassium permanganate for every 2000 mL of reagent water.

7.15. Potassium persulfate, 5% solution (w/v): Dissolve 100 g of potassium persulfate for every 2000 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of sample collection to the time of sample analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples and biological material do not require preservation, but must be collected in wide-mouth glass jars with PFTE-lined lids and stored at 4° C ± 2° C (and/or freezing for tissues) until the time of analysis.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.2.1. Four aliquots of the laboratory check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.3. A Preparation Batch is a group of up to 20 samples, excluding QC Samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike (MS), Matrix Spike Duplicate (MSD)), that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain an MB, an LCS and an MS/MSD. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes. In some cases, at client request, it may be appropriate to process a MS and sample duplicate (DU) in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.4. Method Blank (MB) -

9.4.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB must not contain any analyte of interest at, or above, the reporting or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of ten times higher than the MB contamination level).

Note: For Ohio VAP projects, the result must be below the reporting limit or samples must be re-digested and re-analyzed unless the samples are below the reporting limit.

9.4.2. Re-digestion and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.4.3. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.4.4. If the above criteria are not met and re-analysis is not possible due to limited sample quantity, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.5. Laboratory Control Sample (LCS)

9.5.1. One LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits, the system is out of control and corrective action must occur. See Section 12 for the LCS calculation.

9.5.2. . For Method 245.1, the LCS must be 85% - 115%. For Methods 7470A, 7471A, and 7471B, the laboratory control sample recovery must be 80%-120%.

9.5.3. Corrective action must be re-digestion and re-analysis of the batch unless the LCS recovery is greater than the upper control limit and the sample results are less than the RL. In that situation the results may be reported with proper narration.

9.6. Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.7.1. One MS/MSD pair must be processed for each preparation batch. An MS is a field sample to which known concentrations of target analytes have been added. An MSD is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates (DU) in place of, or in addition to, MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table 1 (Appendix I). See Section 12 for the MS/MSD and Relative Percent Difference (RPD) calculation.

Note: for Method 245.1, an MS/MSD pair is required for every 10 samples.

9.7.2. If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. A control limit of, 70 – 130% for

Method 245.1, and 20% RPD must be applied to the MS/MSD. A control limit of 80-120% for Methods 7470A, 7471A, and 7471B and 20% RPD must be applied to the MS/MSD.

9.7.3. If the analyte recovery or RPD falls outside the acceptance range, the analyst shall determine if the MS/MSD is spiked properly and/or the matrix of the sample is the result of the MS/MSD or RPD failure. If it has been determined that the MS/MSD was not spiked properly and/or the failure is not a result of matrix then the sample along with the MS/MSD will be re-digested and analyzed.

Note: If client program requirements specify to confirm matrix interferences, re-preparation and re-analysis of the MS/MSD may be necessary.

9.7.4. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data are reported with a “4” as a flag. In the event an MS/MSD analysis is not possible, notation in the project narrative is required.

9.8. Control Limits

9.8.1. Control limits are established by the laboratory as described in SOP NC-QA-018

9.8.2. Control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMS

9.9. Method Detection Limits (MDLs) and MDL Checks

9.9.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.9.2. MDLs are easily accessible via the LIMS

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols, separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a calibration blank. One standard must be at, or below, the reporting limit. Analyze standards in ascending order beginning with the calibration blank. Refer to Section 7 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥ 0.995, or the instrument must be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient. NOTE: If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be re-digested.

10.7. Initial Calibration Verification/Initial Calibration Blank (ICV/ICB)

10.7.1. Calibration accuracy is verified by analyzing a second source standard ICV. The ICV result must fall within 5% (for method 245.1) or 10% (for methods 7470A, 7471A, and 7471B) of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within $\pm$ the reporting limit (RL) from zero. See Section 12 for the ICV calculation. If either the ICV or ICB fail to meet criteria, the analysis must be terminated, the problem corrected, and the instrument recalibrated (see Section 11.6.4.1 for required run sequence). The calibration curve standards are reanalyzed to determine if the failure was instrument related. If the cause of the ICV or ICB failure was not directly instrument-related, the corrective action must include re-digestion of the ICV, ICB, CRA, CCV, and CCB with the calibration curve. For Ohio VAP, the sample batch must be re-digested.

Note: If the ICV and/or ICB fail criteria on the high side, samples with results below the reporting limit may be reported with proper narration.

10.8. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB)

10.8.1. Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard from the calibration curve.

10.8.2. The CCV result for Methods 7470A, 7471A, and 7471B must fall within 20% of the true value for that solution. For Method 245.1, the criterion is ± 10%. See Section 12 for the CCV calculation.

10.8.3. A CCB is analyzed immediately following each CCV (see Section 11.7.4 for required run sequence). The CCB result must fall within ± RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. If the CCV/CCB is biased high and the sample results associated with the CCV/CCB are below the requested reporting limit, then the results can be reported. Sample results may be reported when bracketed by valid CCV/CCB pairs. If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be re-digested.

Note: If the CCV and/or CCB fail criteria on the high side, sample results that are below the reporting limit may be reported with proper narration.

10.9. Detection Limit Standard (CRA) - A CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. It is recommended that the recovery be ± 50% of the true value. If the CRA recovery is outside of the recommended criterion, correct any problem and re-analyze. Re-calibration may be required. The CRA is only required when requested.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

11.3. Standard and Sample Preparation- Solids

11.3.1. All calibration and calibration verification standards (ICV, ICB, CCV, and CCB) are processed through the digestion procedure as well as the field samples.

11.3.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (Section 7.3) into a series of sample digestion bottles. The ICB/CCB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. For the ICV, transfer a 5 mL aliquot of the working ICV standard to the digestion bottle. The ICV standard must be from a source other than that used for the calibration standards. For the CCV, transfer a 5.0 mL aliquot of

the working standard into a sample digestion bottle. Add reagent water to each standard bottle for a total volume of 10 mL.

Note: Alternate volumes and concentrations of standard may be prepared as long as the accuracy and final standard concentrations support laboratory or project reporting limits.

11.3.3. To each LCS standard bottle, add 0.6 g of Teflon chips, 5 mL of reagent waterand 5 mL of the working mercury standard (0.1 ppm) (see Section 7.3).

11.3.4. To the MB bottle, add 0.6 g of Teflon chips and 10 mL of reagent water.

11.3.5. For each sample, transfer 0.6g of a well-mixed sample into a clean sample digestion bottle and add 10 mL of reagent water.

11.3.6. Add 5 ml of Aqua Regia to all containers.

11.3.7. Heat for two minutes in a hot block at 90 - 95 □ C.

11.3.8. Add 40 mL of distilled water.

11.3.9. Add 15 mL of potassium permanganate solution. Cover containers with digestion bottle lids.

11.3.10. Heat for 30 minutes in the hot block at 90 - 95 □C.

11.3.11. Record the time on and off of the hotblock in the batch info.

11.3.12. Check the temperature when heating is finished and note in batch information whether temperature requirement was met.

11.3.13. Cool

11.3.14. Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.3.15. Bring each standard, quality control sample, and sample up to a final volume of 100 mL with reagent water.

Note: Digestion bottles are calibrated by vendor lot to ensure the consistency and accuracy of final volumes.

11.3.16. Samples are ready for analysis (section 11.6).

11.4. Sample preparation for incremental sampling method (ISM) solids

11.4.1. ISM samples are prepped and sub-sampled per SOP requirements for ISM. The Metals laboratory will receive a single sample aliquot from the Pre-Prep department containing approximately 3.0g of each sample inside a 500mL plastic container. The acceptable range for HG sample mass is approximately 2.5-3.5g.

11.4.1.1. 3.0g of Teflon boiling chips are weighed into a 500mL bottle for both the MB and LCS. Preparatory method for QC samples will be the same as for the client samples.

11.4.1.2. The laboratory control sample (LCS) is spiked with 25mL of the HG Calibration solution. Matrix spike (MS) and matrix spike duplicate (MSD) are spiked with 5mL of the HG Calibration solution.

11.4.1.3. Add 50mL of deionized water to each sample container except the LCS. Add 25mL of the reagent water into the LCS container for an even volume.

11.4.1.4. To each sample container, including MB and LCS, add 25mL of Aqua Regia.

11.4.1.5. Place each sample into individual sample slots inside the water bath. Heat samples for two minutes at 90-95 degrees Celsius.

11.4.1.6. Add 200mL of deionized water into each sample container.

11.4.1.7. Add 75mL of potassium permanganate solution.

11.4.1.8. Cover 500mL containers with its bottle lids.

11.4.1.9. Digest for 30 minutes inside the water bath at 90-95 degrees Celsius.

11.4.1.10. Add 30 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.4.1.11. Bring each standard, quality control sample, and sample up to a final volume of 500 mL with reagent water.

11.4.1.12. Samples are ready for analysis (section 11.6).

11.5. Standard and Sample Preparation Waters

11.5.1. All calibration and calibration verification standards (ICV, ICB, CCV, and CCB) are processed through the digestion procedure as well as the field samples. Transfer 0, 0.1, 0.25, 0.5, 2.5 and 5.0 mL aliquots of the working standard (Section 7.3) into a series of sample digestion bottles containing 50

mL of reagent water. For the ICV, transfer a 2.5 mL aliquot of the working standard to the digestion bottle containing 50 mL of reagent water. The ICV standard must be from a source other than that used for the calibration standards. For the CCV, transfer a 2.5 mL aliquot of the working standard into a sample digestion bottle containing 50 mL of reagent water.

11.5.2. The Method Blank (MB) consists of 50 mL of reagent water. The LCS consists of 2.5 mL of the HG working standard, and 50 mL of reagent water.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations support laboratory or project reporting limits.

11.5.3. Transfer 50 mL of well-mixed sample or standard to a clean sample digestion bottle. Continue preparation as described under Section 11.6.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

Note: Spiking is done before the addition of acids or reagents.

11.5.4. Add 2.5 mL of concentrated H_2SO_4 and 1.25 mL of concentrated HNO_3.

11.5.5. Add 7.5 mL of potassium permanganate solution. For samples high in organic materials or chlorides, 7.5 mL may be insufficient to fully break down all organic mercury compounds. If the purple color does not persist for at least 15 minutes after the addition of potassium permanganate, the sample must be discarded and re-prepped at a dilution.

11.5.6. Add 4 mL of potassium persulfate solution, cover, and heat for two hours in a hot block at 90 - 95 °C.

11.5.7. Cool samples.

11.5.8. Add 3 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.5.9. Bring each standard, quality control sample and sample up to a final volume of 75mL with reagent water.

Note: The final volume for water samples is 50 mL prior to the addition of digestion reagents. After all prep reagents are added and the samples are digested, reagent water is added to bring each sample to a consistent 75 mL volume. The calibration curve and samples are prepared in the exact same

manner. To avoid result and limit calculation errors, the 50 mL volume is recorded as the final sample volume in the preparation log in LIMS.

Note: Digestion bottles are calibrated by vendor lot to ensure the consistency and accuracy of final volumes.

11.5.10. Samples are ready for analysis (section 11.6).

11.6. Sample Analysis

11.6.1. Automated determination: Refer to the instrument manual for details on instrument setup.

11.6.2. Create a calibration curve by plotting response of calibration standards vs. concentrations of mercury. Determine the mercury concentration in the samples from the linear fit of the calibration curve. The calibration acceptance criteria are listed in Section 10.6. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.6.3. All measurements must fall within the defined calibration range to be valid. Dilute and re-analyze all samples for analytes that exceed the highest calibration standard.

Note: For Method 245.1, the measurement must fall within 90% of the highest standard. Sample measurements that exceed 90% of the highest standard must be diluted and reanalyzed.

11.6.4. The following analytical sequence is consistent with Methods 7470A, 245.1, 7471A and 7471B.

Instrument Calibration
ICV
ICB
CRA if required
CCV
CCB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete the run
CCV
CCB

11.6.5. Refer to Quality Control Section 9.0 for quality control criteria.

Note: Samples include the MB, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.6.6. To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data be reviewed periodically throughout the run.

11.6.7. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.

11.7. Analytical Documentation

11.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.7.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.7.4. Record all sample results and associated QC in LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. Matrix spike (MS) recoveries are calculated according to the following equation:

$$\%\,R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
Matrix Spike (MS) = determined spiked sample concentration
Matrix Spike Duplicate (MSD) = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

mg/kg, dry weight = (C x V x D)/(W x S)

Where:
C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor must be omitted from the above equation.

12.6. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.7. The Laboratory Control Sample (LCS) percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Appropriate factors must be applied to sample values if dilutions are performed.

12.9. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.1.

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State, and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by this Method

15.2.1. The following waste streams are generated by this method.

15.2.1.1. Acid Waste: This waste disposed of in the designated container labeled “Acid Waste”.

15.2.1.2. Acid waste/aqueous waste generated by the analysis: Samples are disposed of in the acid waste drum located in the Metals lab. The contents of the drum are neutralized and released to the POTW.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury)

16.1.2. “Methods for the Chemical Analysis of Water and Wastes”, Rev. 3.0 (1994)

16.1.3. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury)

16.1.4. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Revision 2, February 2007, Method 7471B (Mercury)

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File: (formerly Corp-MT-0007NC, NC-MT-011, and NC-MT-013)				
Revision 1.1: 04/17/97		Revision 2: 03/20/13		
Revision 2.2: 02/06/01		Revision 3: 06/05/13		
Revision 2.3: 05/15/01		Revision 4: 06/06/15		
Revision 2.4: 10/28/02		Revision 5: 06/15/15		
Revision 2.5: 11/24/04		Revision 6: 06/23/16		
Revision 0: 12/12/07 (011)				

Historical File: (formerly Corp-MT-0007NC, NC-MT-011, and NC-MT-013)				
Revision 1: 01/07/09 (011)				
Revision 0: 01/07/09 (013)				
Revision 0: 09/27/10 (014)				
Revision 1-A: 04/17/12				

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Standards and Reagents, NC-QA-017

16.2.6. Calibration Curves (General), CA-Q-S-005

16.2.7. Selection Of Calibration Points, CA-T-P-002

16.2.8. Subsampling, NC-IP-001

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from Reference Method

17.1.1. Modifications from Method 7471A

17.1.1.1. Chapter 1 of SW846 specifies the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2. Modifications from both Methods 7470A and 245.1

17.1.2.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, “Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.”

17.1.3. Modifications from Method 7470A

17.1.3.1. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit if the samples associated with the method blank are equal to or above the reporting limit.

17.1.4. Modifications from Method 245.1

17.1.4.1. Method 245.1 states that standards are not heated. TestAmerica Canton prepares heated standards for this method.

17.1.4.2. Stannous Chloride is prepared in hydrochloric acid, instead of sulfuric acid, per instrument manufacturer recommendations.

17.1.4.3. Section 9.3.4 of the method states that the CCB must be less than the MDL. The laboratory uses the criteria that the CCB result must fall within ± RL from zero.

17.2. Tables and Appendices

APPENDIX A - TABLES

TABLE 1. MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Standard Aqueous RL (mg/L)	0.0002
TCLP RL (mg/L)	0.002
Std 0 (mg/L)	0
Std 1/CRA (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L)	0.010
ICV (mg/L)	0.005
CCV/Laboratory Control Sample (LCS) (mg/L)	0.005
LCS (mg/L)	0.005
Matrix Spike (MS) (mg/L)	0.001
TCLP Matrix Spike (MS)	0.005

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APPENDIX B - CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by Deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas should be kept clean.

Powdered Gloves should not be used in the metals laboratory since the powder contains zinc, as well as other metallic analytes. Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Title: CLEANUP PROCEDURES FOR ORGANIC EXTRACTABLE SAMPLES

[Method: SW846 Method 3660B, 3665A, 3630C, 3610B and 3620C]

Approvals (Signature/Date):

Technology Specialist	02/27/18 Date	Health & Safety Coordinator	02/28/18 Date
Quality Assurance Manager	03/20/18 Date	Technical Director	03/02/18 Date

This SOP was previously identified as SOP NC-OP-025, Rev 7, dated 12/14/15

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1. SCOPE AND APPLICATION

1.1. This SOP describes procedures to be used when performing clean-ups using Sulfuric Acid (3665A), Tetrabutylammonium Sulfite (TBA) (3660B), Silica Gel (3630C), Potassium permanganate (3665A), Florisil (3620C), and Alumina (3610B) for semivolatile organic compound extracts-.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Sulfuric acid cleanup is used to remove certain pesticide compound interferences from organic extracts. Sulfuric acid cleanup may be used for pesticides dependent upon which pesticides are target analytes. The extract to undergo cleanup is mixed with sulfuric acid. The mixture is vortexed and the extract is separated and removed from the acid.

2.2. Tetrabutylammonium sulfite (TBA) cleanup is used to remove chromatographic interference caused by sulfur. The extract to undergo cleanup is mixed with TBA and Isopropyl alcohol. The mixture is vortexed and the extract is removed from the TBA reagent.

2.3. Silica gel cleanup is used to remove chromatographic interferences caused by compounds of different chemical polarity. - The sample extract is eluted through a Resprep ® Silica SPE cartridge (or equivalent), the eluate is further concentrated and the extract is then ready for analysis.

2.4. Potassium Permanganate ($KMNO_4$) cleanup is used to remove interferences from organic extracts. The extract that is to undergo cleanup is mixed with 5% permanganate ($KMNO_4$) solution. The mixture is vortexed, and the extract is separated and removed from the permanganate.

2.5. Florisil® is used for the cleanup of pesticide residues and other chlorinated hydrocarbons to remove steroids, ketones, esters, glycerides, alkaloids, and some carbohydrates from the sample extract. The sample extract is eluted through a Resprep ® Florisil ® SPE cartridge (or equivalent). The eluate is further concentrated and the extract is then ready for analysis.

2.6. Alumina cleanup is used to remove chromatographic interference caused by compounds of different chemical polarity. The sample extract is eluted through a Supelclean ™ LC-Alumina-B SPE cartridge (or equivalent), the eluate is further concentrated and the extract is then ready for analysis.

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3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Nitrile gloves should be used when performing this cleanup procedure. Latex and vinyl gloves provide no significant protection against organic solvents.

5.3. The following is a list of the materials that MAY be used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. The actual materials used during the cleanup will vary, depending on which compounds are to be filtered out of the sample extract. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Isopropyl alcohol	Flammable	400 ppm TWA	Inhalation of vapors irritates the respiratory tract. Exposure to high concentrations has a narcotic effect, producing symptoms of dizziness, drowsiness, headache, staggering, unconsciousness and possibly death.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/ m^3 -TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Florisil®	Irritant	TLV 10mg/ m^3 PEL 5mg/ m^3	May cause irritation if inhaled or adsorbed through the skin.
Potassium Permanganate	Poison Irritant	OSHA PEL 5 mg/m*f* (air)	Irritation to skin, eyes, lungs, mucous membranes, and GI tract. Metal poisoning hazard. Dermatitis.
Tetrabutylammo-nium hydrogen sulfate	Poison, Irritant, Hygroscopic agent	None Listed	Irritation to skin and eyes. Harmful if swallowed (do not induce vomiting). May be harmful if absorbed through skin.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4 The addition of sulfuric acid to the sample extract has the potential to create an exothermic reaction. Both can cause severe burns.

5.5 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.6 Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.7 The preparation of hazardous standards and reagents must be conducted in a fume hood with the sash closed as far as the operation will permit.

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5.8 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the Laboratory Supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Bottles, amber: 250 mL, 1 L

6.2. Autopipettor or volumetric pipettes: 1 and 5 mL capacity

6.3. Disposable pipettes: Pasteur-type

6.4. Culture Tubes: 5 or 10 mL

6.5. Vortex Mixer

6.6. Beakers: Various

6.7. Top loading balance: Capable of accurately weighing ± 0.01 g

6.8. Centrifuge

6.9. Manifold system to hold SPE cartridges

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Hexane: Pesticide grade or equivalent

7.1.2. Methylene Chloride: Ultra-resi analyzed or equivalent

7.1.3. Sodium sulfite, anhydrous: reagent grade

7.1.4. Sulfuric acid (H_2SO_4), concentrated: reagent grade

7.1.5. 5% Potassium permanganate ($KMNO_4$) solution: reagent grade, purchased

7.1.6. Florisil®, activated: pesticide residue grade cartridges such as Resprep® Florisil® SPE cartridges or equivalent

7.1.7. Silica Gel: chromatography grade only cartridges such as Resprep® Silica SPE cartridges or equivalent

7.1.8. Supelclean™ LC-Alumina-B SPE cartridges or equivalent

7.1.9. Acetone: reagent grade

7.1.10. Isopropyl alcohol - Pesticide grade or equivalent

7.1.11. Organic free reagent water

7.1.12. Tetrabutylammonium hydrogen sulfate: reagent grade

7.1.13. Tetrabutylammonium (TBA)-Sulfite Reagent

7.1.13.1. Dissolve 3.39 g of Tetrabutylammonium hydrogen sulfate per 100 mL reagent water and mix well. Extract the100 mL aliquot of deionized water and Tetrabutylammonium hydrogen sulfate solution three times with 20 mL of hexane. Dispose of hexane layer. **Slowly** add 25 g anhydrous sodium sulfite per 100 mLs and shake until dissolved. Store this solution in an amber bottle with PTFE- lined screw cap at room temperature for at least one month

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. See the individual extraction or analytical procedure.

9. QUALITY CONTROL

9.1. The method blank and laboratory control sample associated with any samples subjected to any of the types of cleanups covered in this SOP must also be subjected to the same cleanup procedure(s).

9.2. Refer to the analytical SOPs NC-GC-007, NC-GC-045, NC-GC-042, NC-GC-043 and NC-GC-013 for QC requirements

9.3. Nonconformance and Corrective Action

9.3.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action. Procedural deviations are not allowed for Ohio VAP samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP samples.

11.3. Allow all extracts to reach room temperature if they were in cold storage.

11.4. All PCB extracts will initially go through the sulfuric acid stripping and screening process, followed by further cleanups based on screen results.

11.5. Sample Preparation

11.5.1. Sulfuric acid

11.5.1.1. Add approximately 5 mL of H_2SO_4 to 2 mL of sample extract into a culture tube.

11.5.1.2. Vortex for about one minute.

11.5.1.3. Centrifuge.

11.5.1.4. Remove the extract (top layer) from the acid, and place in a clean culture tube. Examine the extract layer for color and visible emulsions. Repeat as necessary.

11.5.2. Tetrabutylammonium sulfite (TBA)

11.5.2.1. Into a culture tube, add approximately 1-2 mLs of sample extract, 1 mL of TBA solution, and 2 mL of isopropyl alcohol. Shake vigorously or vortex for one minute, after which a precipitate will form.

11.5.2.2. Add 5 mL of reagent water and shake or vortex for one minute. Allow the phases to separate or centrifuge.

11.5.2.3. Remove the sample extract (top layer) from the TBA.

11.5.2.4. Repeat as necessary.

11.5.3. Silica Gel

11.5.3.1. PCB

11.5.3.1.1. A 1 gram silica gel cartridge is utilized: Restek catalog No. 24038 or equivalent.

11.5.3.1.2. Condition the cartridge with 4 mL of hexane. Slowly open the cartridge valve to allow a few drops per

cartridge to pass through the sorbent bed and manifold to remove all of the air bubbles. Close the valve and allow the solvent to soak the entire sorbent bed for 5 minutes.

11.5.3.1.3. Slowly open the cartridge valve to allow the hexane to pass through the cartridge. Close the cartridge valve when there is still approximately 1mm of solvent above the sorbent bed. Do not allow cartridge to become dry.

Note: If the cartridge goes dry repeat the conditioning step.

11.5.3.1.4. Transfer 2 mL of extract to the cartridge. Allow the extract to soak the sorbent bed for 1 minute. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL per minute.

11.5.3.1.5. When the extract has mostly passed through the cartridge, but before the cartridge becomes dry, rinse the extract sample vial with 0.5 mL of hexane, and add this to the cartridge to complete the quantitative transfer.

11.5.3.1.6. Close the cartridge valve when there is still approximately 1mm of hexane above the sorbent bed, ensuring that the cartridge never goes dry.

11.5.3.1.7. Place a new culture tube into the sample rack corresponding to the cartridge position.

11.5.3.1.8. Add 5 mL of hexane to the cartridge. Allow the solvent to soak the sorbent bed for 1 minute. Slowly open the cartridge valve and collect the eluate into the culture tube. Allow the cartridge to completely drain into the culture tube. Close the cartridge valve. Remove the sample tube and concentrate down to 2 mL using an N-Evap. This eluate will contain the PCBs as well as some pesticides.

11.5.3.2. DRO

11.5.3.2.1. A 1 gram silica gel cartridge is utilized: Restek catalog No. 24038 or equivalent.

11.5.3.2.2. Condition the cartridge with 4 mL of methylene chloride. Slowly open the cartridge valve to allow a few drops per cartridge to pass through the sorbent bed and manifold to remove all of the air bubbles. Close the

valve and allow the solvent to soak the entire sorbent bed for 5 minutes.

11.5.3.2.3. Slowly open the cartridge valve to allow the methylene chloride to pass through the cartridge. Close the cartridge valve when there is still approximately 1mm of solvent above the sorbent bed. Do not allow cartridge to become dry.

Note: If the cartridge goes dry repeat the conditioning step.

11.5.3.2.4. Transfer 2 mL of extract to the cartridge. Allow the extract to soak the sorbent bed for 1 minute. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL per minute.

11.5.3.2.5. Close the cartridge valve when there is still approximately 1mm of extract above the sorbent bed, ensuring that the cartridge never goes dry.

11.5.3.2.6. Place a new culture tube into the sample rack corresponding to the cartridge position.

11.5.3.2.7. Add 5 mL of methylene chloride to the cartridge. Allow the solvent to soak the sorbent bed for 1 minute. Slowly open the cartridge valve and collect the eluate into the culture tube

11.5.3.2.8. When the extract has mostly passed through the cartridge, but before the cartridge becomes dry, rinse the extract sample vial with 0.5 mL of methylene chloride, and add this to the cartridge to complete the quantitative transfer.

11.5.3.2.9. Allow the cartridge to completely drain into the culture tube. Close the cartridge valve. Remove the sample tube and concentrate down to 2 mL using an N-Evap. This eluate will contain the Diesel Range Organics.

11.5.4. Potassium Permanganate (KMNO4)

11.5.4.1. Add approximately 5 mLs of 5% $KMNO_4$ solution to approximately 2 mLs of extract.

11.5.4.2. Vortex for about one minute

11.5.4.3. Centrifuge.

11.5.4.4. Remove the extract (top layer) from the $KMNO_4$ solution and place in a clean culture tube. Repeat the cleanup up to three times if necessary.

11.5.5. Florisil

11.5.5.1. A 1 gram Florisil cartridge is utilized: Restek catalog No. 24031 or equivalent

11.5.5.2. Condition the cartridge with 4 mL of hexane. Slowly open the cartridge valve to allow a few drops per cartridge to pass through the sorbent bed and manifold to remove all of the air bubbles. Close the valve and allow the solvent to soak the entire sorbent bed for 5 minutes.

11.5.5.3. Slowly open the cartridge valve to allow the hexane to pass through the cartridge. Close the cartridge valve when there is still approximately 1mm of solvent above the sorbent bed. If the cartridge goes dry, repeat the conditioning step.

11.5.5.4. Transfer 1 mL of sample to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at a drop-wise rate until the hexane level reaches the top of the top frit. Stop the flow.

11.5.5.5. Fill the cartridge with a 90:10 hexane/acetone solution.

11.5.5.6. Place a culture tube into the sample rack corresponding to the cartridge position and restore the drop-wise flow to collect the effluent from the cartridge until 10 ml has been collected. Additional 90:10 hexane/acetone solution will need to be added to collect 10 ml. Stop the flow once 10 mL has been collected.

11.5.5.7. Remove the sample and concentrate down to the final volume of slightly less than 1 ml. Use hexane to bring back up to 1 ml.

Note: If employed in pesticide extracts, a pesticides performance check solution must be recovered at 80 to 110%, the recovery of trichlorophenol is less than 5%, and if no peaks interfering with the target analytes are detected

11.5.5.8. See manufacturer specifications about storage of the cartridges since they are critical for optimum performance.

11.5.6. Alumina

11.5.6.1. A 1 gram Alumina cartridge is utilized: Supelco Part No. 57084 or equivalent

11.5.6.2. Condition the cartridge with 4 mL of hexane. Slowly open the cartridge valve to allow a few drops per cartridge to pass through the sorbent bed and manifold to remove all of the air bubbles. Close the valve and allow the solvent to soak the entire sorbent bed for about 5 minutes.

11.5.6.3. Slowly open the cartridge valve to allow the hexane to pass through the cartridge. Close the cartridge valve when there is still approximately 1mm of solvent above the sorbent bed. Do not allow cartridges to become dry. If the cartridge goes dry, repeat the conditioning step.

11.5.6.4. Transfer 2 mL of the sample extract to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 ml/minute; do not exceed 5 mL/minute.

11.5.6.5. When the extract has mostly passed through the cartridge, but before the cartridge becomes dry, rinse the sample vial with 0.5 mL of hexane and add this to the cartridge to complete the quantitative transfer. Close the cartridge valve when there is approximately 1mm of solvent above the sorbent bed, ensuring that the cartridge never goes dry.

11.5.6.6. Place a new culture tube into the sample rack corresponding to the cartridge position.

11.5.6.7. Add one tube volume of hexane to the cartridge. Allow the solvent to soak the sorbent bed for about 1 minute or less. Slowly open the cartridge valve and collect the eluate into the test tube. Close the cartridge valve. Repeat this step one more time. Remove the sample and concentrate down to the final volume of 2 mL using an N-Evap.

11.6. Sample Analysis

11.6.1. Refer to SOPs NC-GC-045, NC-GC-042, NC-GC-043 and NC-GC-007 for sample analysis.

11.7. Analytical Documentation

11.7.1. All cleanups must be documented.

11.7.2. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.7.3. Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs, is available for each data file.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Training Qualifications

13.1.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

15.3. Waste Streams Produced by the Method

15.3.1. Glassware from extract cleanup / lab trash: Glassware, such as culture tubes, disposable pipettes, etc., is placed in the laboratory trash containers.

15.3.2. Sulfuric acid waste from the cleanup: Sulfuric is collected in a five-gallon container labeled "Sulfuric Acid Waste" located in the fume hood in the GC Prep Room.

15.3.3. Flammable solvent waste collected during silica gel prep and elution. This is collected in a 2.5-gallon waste container labeled "Flammable Waste" located in the GC Prep Room.

15.3.4. Waste hexane: This is collected in a 2.5 gallon waste container labeled

"Flammable Waste" located in the GC Prep Room.

15.3.5. Flammable solvent waste collected during TBA sulfite preparation and Potassium permanganate waste: This is collected in a 2.5-gallon waste container labeled "Flammable Waste" located in the GC Prep Room.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition?, Florisil® Cartridge Cleanup, Method 3620C

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Silica Gel Cleanup, Method 3630C, Revision 3, December 1996

16.1.3. SW-846, Test methods for Evaluating Solid Waste, Third Edition, Sulfuric Acid/Permanganate Cleanup, Method 3665A, Revision 1, December 1996

16.1.4. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Sulfur Cleanup, Method 3660A

16.1.5. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Sulfur Cleanup, Method 3660B, Revision 2, December 1996.

16.1.6. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Alumina Cleanup Method 3610B, Revision 2, December 1996.

16.1.7. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.8. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.9. Corporate Quality Management Plan (CQMP), current version

16.1.10. Revision History

Historical File:		Revision 0: 08/17/06		Revision 5; 08/05/13
		Revision 1: 04/30/08		Revision 6: 09/30/14
		Revision 2: 01/07/09		Revision 7: 12/14/15
		Revision 3: 02/02/10		
		Revision 4: 03/04/11		

16.2. Associated SOPs and Policies, current version

16.2.1. Gas Chromatographic Analysis Based on Methods 8082 and 8082A, SOP NC-

GC-045

16.2.2. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, SOP NC-GC-042

16.2.3. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, SOP NC-GC-043

16.2.4. Analysis of Pesticides and PCBs, SOP NC-GC-007

16.2.5. Glassware Washing, NC-QA-014

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Troubleshooting Guide

17.1.1. Sulfuric Acid

17.1.1.1. If the acid and extract will not separate, try diluting the extract before acid cleanup.

Title: TOXICITY CHARACTERISTIC LEACHING PROCEDURE AND SYNTHETIC PRECIPITATION LEACHING PROCEDURE

[Method: SW846 Methods 1311 and 1312]

Approvals (Signature/Date):

Technology Specialist	11/02/17 Date	Health & Safety Coordinator	11/03/17 Date
Quality Assurance Manager	11/02/17 Date	Technical Director	11/29/17 Date

This SOP was previously identified as SOP NC-OP-033, Rev 6, dated 2/17/17

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1. SCOPE AND APPLICATION

1.1. This SOP describes the application of the Toxicity Characteristic Leaching Procedure (TCLP), SW846 Method 1311. The Toxicity Characteristic (TC) of a waste material is established by determining the levels of 8 metals and 31 organic chemicals in the aqueous leachate of a waste. The TC is one of four criteria in 40 CFR Part 261 to determine whether a solid waste is classified as a hazardous waste. The other three are corrosivity, reactivity, and ignitability. The TC Rule utilizes the TCLP method to generate the leachate under controlled conditions that were designed to simulate leaching through a landfill. EPA's "worst case" waste disposal model assumes mismanaged wastes will be exposed to leaching by the acidic fluids generated in municipal landfills. The EPA model also assumes the acid/base characteristics of the waste will be dominated by the landfill fluids. The TCLP procedure directs the testing laboratory to use a more acidic leaching fluid if the sample is an alkaline waste, again in keeping with the model's assumption that the acid fluids will dominate leaching chemistry over time.

1.2. The specific list of TC analytes and regulatory limits may be found in Appendix A. Other regulatory programs or client specific projects may identify alternative action limits and/or additional constituents of concern.

1.3. This SOP also describes the application of the Synthetic Precipitation Leaching Procedure (SPLP) which was designed to simulate the leaching that would occur if a waste was disposed in a landfill and exposed only to percolating rain water. The procedure is based on SW846 Method 1312. The list of analytes for SPLP may extend beyond the toxicity characteristic compounds shown in Appendix A. With the exception of the use of a modified extraction fluid, the SPLP and TCLP protocols are essentially equivalent. Where slight differences may exist between the SPLP and TCLP, they are distinguished within this SOP.

1.4. The procedure is applicable to liquid, solid, and multiphase wastes.

1.5. The results obtained are highly dependent on the pH of the extracting solution, the length of time that the sample is exposed to the extracting solution, the temperature during extraction, and the particle size/surface area of the sample. These parameters must be carefully controlled.

1.6. The reporting limits are based on the individual samples as well as the individual analysis techniques. However, the sample is determined to be hazardous if it contains any analyte at levels greater than or equal to the regulatory limits.

1.7. If a total analysis of the waste demonstrates that individual analytes are not present in the waste or they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the procedure need not be run. If the total analysis results indicate that TCLP is not required, the decision to cease TCLP analysis should be remanded to the client.

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1.8. Volatile organic analysis of the leachate obtained using a bottle extraction, normally used for extractable organics and metals, can be used to demonstrate that a waste is hazardous, but only the ZHE option can be used to demonstrate that the concentration of volatile organic compounds is below regulatory limits due to potential analyte loss into the headspace during the bottle extraction.

2. SUMMARY OF METHOD

2.1. For liquid wastes that contain less than 0.5% dry solid material, the waste, after filtration through 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP leachate.

2.2. For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solids and stored for later analysis or recombination with the leachate. The particle size of the remaining solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. For TCLP, the extraction fluid employed for extraction of non-volatile analytes is a function of the alkalinity of the solid phase of the waste. For SPLP, the extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater the extraction fluid employed is a pH 4.2 solution. Two leachates may be generated: a) one for analysis of non-volatile constituents (semi-volatile organics, pesticides, herbicides and metals, and/or, b) one from a Zero Headspace Extractor (ZHE) for analysis of volatile organic constituents. Following extraction, the liquid leachate is separated from the solid phase by filtration through a 0.6 to 0.8 μm fiber filter.

2.3. If compatible (i.e., multiple phases will not form on combination), the initial liquid filtrate of the waste is added to the liquid leachate and these are prepared and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3. DEFINITIONS

3.1. “Leachate” is used to refer to the solutions generated from these procedures (TCLP, SPLP, deionized water leach).

3.2. “Wet Solids” is that fraction of a waste sample from which no liquid may be forced out by pressure filtration.

3.3. Other definitions of terms used in this SOP may be found in the glossary of the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Oily wastes may present unusual filtration and drying problems. If requested by the client and as recommended by EPA (see Figure 3), oily wastes can be assumed to be 100% liquid and analysis for total concentrations of contaminants will be performed. This applies specifically to samples containing viscous non-aqueous liquids that would be difficult to

filter. Alternately, the oil may be subjected to pressure filtration. The portion that passes through the filter will be prepared and analyzed separately as an organic waste. The "wet solid" portion that remains behind on the filter will be subjected to leaching. After preparation and analysis, the results will then be mathematically combined.

4.2. Wastes containing organic liquids (e.g., oil, paint thinner, fuel) may require dilution following the TCLP procedure, during preparation and/or analysis to address the matrix interferences. This often results in reporting limits elevated above the TCLP regulatory limits.

4.3. Solvents, reagents, glassware, and other sample processing hardware may contribute artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks as described in Section 9 and the individual determinative SOPs.

4.4. Glassware and equipment contamination may result in analyte degradation. Soap residue on glassware and equipment may contribute to this. All glassware and equipment should be rinsed very carefully to avoid this problem.

4.5. Phthalates may be eliminated by proper glassware cleanup and by avoiding plastics. Only borosilicate glass, PTFE, or Type 316 stainless steel tumblers may be used for leachates to be analyzed for organics. Plastic tumblers may be used for leachates to be analyzed for the metals.

4.6. Overexposure of the sample to the environment will result in the loss of volatile components.

4.7. Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Gas pressurized equipment is employed in this procedure. Be sure all valves and gauges are operating properly and that none of the equipment, especially tubing, is over-pressurized. CAUTION: Do not open equipment that has been pressurized until it has returned to ambient pressure.

5.3. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Glacial Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and

discarded; other gloves will be cleaned immediately.

5.5. A rotary agitation apparatus is used in this procedure. Certain samples may break the glass jars used in the procedure. For these samples, extra caution, including plastic or polyethylene overwraps of the glass jar, may be necessary. Turning the jar or bottle sideways rather than tumbling end over end may also reduce the chance of breakage. If sideways tumbling is used, note this change in the logbook "Comment" section. Guards must be placed in front of any rotating equipment.

5.6. Secure the tumbler and extraction apparatus before starting rotary agitation apparatus.

5.7. During sample rotation, pressure may build up inside the bottle. Periodic venting of the bottle will relieve pressure.

5.8. Any sample requiring cyanide or sulfide analysis should be prepped as a DI leach (leachate solution #3). When exposed to acidic conditions, the release of hydrogen cyanide gas or hydrogen sulfide gas is possible. SPLP Fluid #3 reagent water must be used for these samples. **NOTE: Do not use an acidic SPLP fluid due to the potential release of hydrogen cyanide gas or hydrogen sulfide gas.**

5.9. Exposure to hazardous chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.10. The preparation of hazardous standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.11. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and Laboratory Supervisor.

5.12. Due to the potential for ignition, flammability or production of noxious fumes, do not attempt to dry non-aqueous liquid samples in an oven. Use extended drying in a ventilation hood.

6. EQUIPMENT AND SUPPLIES

6.1. Extraction vessels

6.1.1. For volatile analytes - zero-headspace extraction (ZHE) vessel, gas-pressure actuated, Associated Design 3745 ZHE or equivalent (see Figure 2)

6.1.2. For metals - either borosilicate glass jars (2.5 L, with Teflon lid inserts) or 2.5 L HDPE (Nalgene or equivalent) bottles may be used

6.1.3. For semi- or non-volatile organics - only borosilicate glass may be used

6.2. Vacuum filtration apparatus and stainless steel pressure filtration apparatus (142 mm diameter), capable of 0 - 50 psi

6.3. Borosilicate glass fiber filters, 0.6 - 0.8 μm (Whatman GF/F 14.2 cm, 9.0 cm, 4.7 cm, 0.7 μm or equivalent): When analyzing for metals, wash the filters with 1 N nitric acid and de-ionized water prior to use, or purchase pre-washed filters. Glass fiber filters are fragile and should be handled with care.

6.4. Rotary agitation apparatus, multiple-vessel, Associated Design and Manufacturing Company 3740-6 or equivalent (see Figure 1): The apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm.

6.5. ZHE Extract Collection Device: Gas-tight syringes, 50 or 100 mL capacity, Hamilton 0158330 or equivalent

6.6. Top loading balance, capable of 0 - 4000 ± 0.01g (all measurements are to be within ± 0.1 grams)

6.7. pH meter and probe capable of reading to the nearest 0.01 unit, and with automatic temperature compensation

6.8. Magnetic stirrer/hotplate and stirring bars

6.9. VOA vials, 40 mL, with caps and septa

6.10. Glass bottles, 1 liter, with Teflon lid-inserts

6.11. Nalgene plastic bottles or equivalent, 1 liter

6.12. Miscellaneous laboratory glassware and equipment

7. REAGENTS AND STANDARDS

7.1. Reagent water for non-volatile constituents must be produced by a Millipore DI system or equivalent. For volatile constituents, water must be passed through an activated carbon filter bed (Milli-Q or tap water passed through activated carbon). Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Hydrochloric acid, 1 N: Carefully add 83 mL concentrated reagent grade HCl to approximately 800 mL reagent water. Cool and dilute to one liter with reagent water. Cap and shake to mix well.

7.3. Sodium hydroxide, 1 N: Carefully add 80g reagent grade NaOH pellets to approximately 1.5 liters of reagent water and stir until dissolved. Cool and dilute to two liters with reagent water.

CAUTION: Heat is generated during this process.

7.4. Sodium hydroxide, 5 N: Carefully add 600g reagent grade NaOH pellets to approximately 2500mL of reagent water and stir until dissolved. Cool and dilute to three liters with reagent water.

CAUTION: Heat is generated during this process.

7.5. Acetic acid, glacial: concentrated, reagent grade liquid (HOAc)

7.6. pH calibration solutions: buffered to a pH of 4, 7, and 2. Commercially available.

7.7. TCLP Leaching Fluids

7.7.1. General Comments

7.7.1.1. The pH probes are to be calibrated prior to use.

7.7.1.2. The leaching fluids MUST be prepared correctly. If the desired pH range is not achieved and maintained, the TCLP may yield erroneous results due to improper leaching. If the pH is not within the specifications, the fluid must be discarded and fresh extraction fluid prepared. The pH of TCLP fluids #1 and #2 may not be adjusted by the addition of acid or base.

7.7.1.3. Additional volumes of extraction fluids listed below may be prepared by multiplying the amounts of acetic acid and NaOH by the number of liters of extraction fluid required.

7.7.1.4. At the end of the day, remaining buffer solution will be discarded or stored in a properly sealed container (lid or stopper, depending on the bottle used). The pH of the buffer must be confirmed each day of use before proceeding. If the buffer's pH is not within range, the buffer will be discarded and new fresh extraction fluid prepared.

7.7.2. TCLP Fluid #1: Carefully add 5.7 mL glacial acetic acid and 64.3 mL of 1 N NaOH to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid and 514.4 mL 1N NaOH, dilute to 8 L with reagent water. For 48L of fluid, use 273.6 mL of glacial acetic acid and 617.28 mL of 5N NaOH. When correctly prepared, the pH of this solution is 4.93 ± 0.05. The density of TCLP fluid #1 is 0.997 g/mL. If a pH within this range is not achieved, the fluid must be discarded and fresh fluid prepared. The pH may not be adjusted by the addition of additional acid or base.

Note: Reagent volumes may need to be determined gravimetrically. 1N NaOH has a density of approximately 1.040 g/mL at 23ºC and 514.4 mL of 1 N NaOH has a

mass of 534.97 g at 23ºC. 5M NaOH has a density of approximately 1.21742 g/mL at 23ºC and 617.28 mL of 5M NaOH has a mass of 751.49 g at 23ºC.

7.7.3. TCLP Fluid #2: Carefully add 5.7 mL glacial acetic acid to 500 mL reagent water in a 1 liter volumetric flask. Dilute to a final volume of 1 L with reagent water, cap and shake to mix well. For 8 L of fluid use 45.6 mL glacial acetic acid, dilute to 8 L with reagent water. When correctly prepared, the pH of this solution is 2.88 ± 0.05. The density of TCLP fluid #2 is 0.997 g/mL. If a pH within this range is not achieved, the fluid must be discarded and fresh fluid prepared. The pH may not be adjusted by the addition of additional acid or base.

7.8. Nitric acid, 50% solution: Slowly and carefully add 500 mL concentrated HNO_3 to 500 mL reagent water. Cap and shake to mix well. Acid should always be added to water when diluting. Do not add water to acid

7.9. Sulfuric acid / nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3: Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

7.10. SPLP Leaching fluids

7.10.1. SPLP solutions are unbuffered and exact pH may not be attained. The pH of TCLP and SPLP fluids should be checked prior to use. If not within specifications, the fluid should be discarded and fresh fluid prepared. SPLP fluid pH may be adjusted by the addition of the sulfuric and nitric acids mixture, but may not be adjusted by the addition of base.

7.10.2. SPLP fluid #1: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 4.20 ± 0.05 This fluid is used for soils from a site that is east of the Mississippi River and for wastes and waste waters. The 60/40 weight percent mixture sulfuric and nitric acids mixture may be diluted by adding several drops of the acid mixture (less than .5mL) to approximately 40mL of reagent water in a vial prior to use in this fluid.

Note: Acid should always be added to water when diluting. Do not add water to acid.

7.10.3. SPLP fluid #2: Add 60/40 weight percent mixture of sulfuric and nitric acids to reagent water until the pH is 5.00 ± 0.05. This fluid is used for soils from a site that is west of the Mississippi River. The 60/40 weight percent mixture sulfuric and nitric acids mixture may be diluted by adding several drops of the acid mixture (less than .5mL) to approximately 40mL of reagent water in a vial prior to use in this fluid.

Note: Acid should always be added to water when diluting. Do not add water to acid.

7.10.4. SPLP fluid #3: This fluid is reagent water and is used for leaching of volatiles. Additionally, any cyanide-containing waste or soil is leached with fluid #3

because leaching of cyanide containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.11. Methanol and methylene chloride - used to aid in cleaning oil contaminated equipment.

Note: All equipment must be thoroughly washed and rinsed following methylene chloride exposure to eliminate contamination of the ZHE vessels and VOC samples. Only methanol should be stored in the leachate room; any cleaning in which methylene chloride or other solvents is used should be carried out in the Organic Prep room. Equipment that is cleaned with methylene chloride or solvents other than methanol should be washed with soap and water before leaving the Organic Prep room, and again upon its return to the leachate room. This is to prevent solvent contamination of the ZHE process and vessels.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples being analyzed for semi- and non-volatile organic compounds should be collected and stored in glass containers with Teflon lid liners. Chemical preservatives shall NOT be added **UNTIL AFTER** leachate generation. Glass containers should be placed in the recycling bin in the Extractions department after use.

8.2. Samples being analyzed for metals only can be collected in either borosilicate glass or polyethylene containers.

8.3. When the waste is to be evaluated for volatile analytes, care should be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon lined septum capped vials with minimal headspace and stored at 4 ± 2°C). Samples should be opened only immediately prior to extraction.

8.4. Samples should be refrigerated to 4 ± 2°C unless refrigeration results in irreversible physical changes to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

8.5. The minimum TCLP sample collection size is determined by the physical state or states of the waste and the analytes of concern. The amount of waste required varies with the percent solids. The lower the percent solids, the more waste will be required for preliminary and final testing. For aqueous samples containing between 0.5 and 10% solids, several kilograms of sample are required to complete the analyses. The general minimal requirements when the samples are 100% solids include: 1 - 32 oz jar for semi-volatile organic analysis and metals, and 1 - 4 oz jar for volatile organic analysis. Low-density sample materials, such as rags or vegetation, will require larger volumes of sample. For liquid samples (less than 50% solids), the minimum requirements are 2 x 32 oz. jars for semi-volatile organic analysis and metals, and 2 x 8 oz. jars for volatile organic analysis. If volatile organic analysis is the only requested parameter, 2 separate jars are required. If matrix spike or duplicate control samples are requested, additional sample volume is required. If sufficient sample volumes were not received, analyses cannot be started and the client must be notified as soon as possible.

8.6. TCLP leachates should be prepared for analysis as soon as possible. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. If precipitation occurs upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate shall not be acidified and the leachate shall be analyzed as soon as possible. All other leachates should be stored under refrigeration (4 ± 2°C) until analyzed. ZHE leachates must be stored in VOA vials filled to eliminate all headspace.

8.7. Samples are subject to appropriate treatment within the following time periods.

Table 1
Holding Times (Days)

Parameter	From: Field collection To: TCLP Extraction	From: TCLP Extraction To: Preparative Extraction	From: Preparative Extraction To: Determinative Analysis	Total Elapsed Time
Volatiles	14	N/A	14	28
Semi-volatiles	14	7	40	61
Mercury	28	N/A	28	56
Other Metals	180	N/A	180	360

NOTE: The initial holding time is measured from date of collection to date TCLP extraction started. (This should be the TCLP extraction date in LIMS.) Semi-volatile method prep holding time is measured from the day tumbling is complete to the start of method extraction. Subsequent analysis holding times are measured from the date extraction (TCLP or method prep) starts**.** If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding holding times is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory limit. The Total Elapsed Time is to be used as guidance. If preps are initiated at the last possible moment of a holding time, the elapsed times may be exceeded.

9. QUALITY CONTROL

9.1. Quality Control Batch (QC Batch)

9.1.1. The batch is a set of up to 20 client samples and appropriate QC that are of the same matrix and are processed together using the same procedures and reagents. A minimum of one TCLP extraction blank (Method Blank), one Laboratory Control Sample (LCS), and one Matrix Spike (MS) will be prepared with each TCLP leachate batch. See the facility QA Policy QA-003 for further information.

9.2. TCLP Extraction Blanks

9.2.1. A minimum of one blank (using the same extraction fluid as used for the samples) must be prepared and analyzed for every batch of samples extracted in a particular vessel type. The blanks are generated in the same way as the samples (i.e., blanks will be tumbled and filtered with the samples). If particle size reduction was performed on any sample in the batch, an equipment blank may be generated by passing blank fluid through the particle reduction apparatus. ZHE Extraction vessels will be uniquely numbered. Consult the TestAmerica QC Program and the individual analysis SOPs for blank acceptance criteria.

9.3. Laboratory Control Sample (LCS)

9.3.1. A LCS is required with each batch of 20 or fewer samples. The LCS shall be generated after a batch of TCLP leachates have been generated (i.e., at the time of the preparative digestion or extraction) by spiking an aliquot of the appropriate extraction fluid used for that batch or reagent water. Consult the individual analysis SOPs for additional LCS guidance (i.e., spike amounts, spike levels, recovery criteria, etc.).

9.4. Matrix Spike (MS)

9.4.1. Matrix spikes are used to monitor the performance of the analytical methods on the matrix and to assess the presence of interferences. An MS is required with each batch of 20 or fewer samples.

9.4.2. Matrix spikes are to be added after filtration of the TCLP leachate. Spikes are not to be added prior to the TCLP leaching. For metals, matrix spikes are to be added before preservation with nitric acid.

9.4.3. Consult the individual analysis SOPs for additional guidance on spike compounds and levels.

9.5. Corrective Actions

9.5.1. Consult the TestAmerica QC Program and individual analysis SOPs for corrective action for blanks and LCS.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to appropriate analysis SOPs.

10.1.1. The calibration of bottle top dispensers and non-Class A beakers is required. Per DoD requirements, a check is performed on these quarterly and the records are maintained electronically.

10.2. Calibrate the pH meter on each day of use in accordance with the electrometric pH SOP NC-WC-010, using fresh buffer solutions. Record the pH meter calibration in the TCLP pH meter calibration electronic logbook.

11. PROCEDURE

11.1. General Comments

11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented on a Nonconformance Memo.

11.1.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.1.3. All sample masses should be recorded to the nearest 0.1 g.

11.2. Preliminary Sample Evaluations (Refer to Flow Chart #1, Appendix D)

11.2.1. Determine the total volume of TCLP leachate (solid phase leachate plus liquid filtrate) that will need to be generated for all of the required analyses according to the following table:

Table 2
Minimum Recommended TCLP Leachate Volume

Analysis	Minimum TCLP Required Volume (mL)	Minimum SPLP Required Volume (mL)
Volatiles	2 x 40	2 x 40
Semi-volatiles	250	1000
Pesticides	250	250
Herbicides	100	1000
PCBs	250	250
Metals (Hg and ICP)	100	100
Metals (ICP only)	50	50
Metals (Hg only)	50	50

11.2.1.1. It is suggested that additional volume for each test be provided as the above values are the minimum required volumes, for a single, undiluted analysis.

11.2.1.2. For TCLP and SPLP samples used for matrix spike analysis, at least two times the listed volumes is required. For TCLP and SPLP samples used for both the matrix spike and matrix spike duplicate analysis, at least three times the listed volumes is required.

11.2.2. Sample Description (determine sample matrix)

11.2.2.1. Solid - If the waste will obviously yield no free liquid when subjected to pressure filtration, then proceed to Section 0 or 11.4 (Bottle Extraction Procedure or ZHE Procedure).

11.2.2.2. Liquid - If the sample is a monophasic liquid, proceed to Section 11.2.3 (Percent Solid Determination).

11.2.2.3. Multiphasic – The sample has discernible layers (liquid/liquid or liquid/solid). If more than one container of multiphasic materials is received from the field, each container might show different amounts of each phase. Consult client to determine sample selection alternatives (composite all sample containers, select one, resample, etc.) if this occurs. Multiphasic liquids are also subject to Section 11.2.3 (Percent Solid Determination) if expected to contain less than .5% dry solids.

11.2.3. Solids Determination

11.2.3.1. Determine Type of Filtration Apparatus and Process

11.2.3.1.1. Percent Solids and ZHE Extractions - The ZHE filtration apparatus cannot accurately determine?? percent solids less than 5%. If an extraction is to be performed solely for volatile organic compounds and the percent solids concentration is obviously greater than 5% upon visual observation, proceed to Section 11.4 (ZHE Extraction Procedure, Volatile Constituents). Otherwise, continue with Section 11.2.3.2. The aliquot of sample used here for the solids determination cannot be used again for the ZHE extraction.

11.2.3.1.2. If the sample is mostly a non-viscous liquid (water or non-viscous organic liquid) of low solids content (expected to be < 0.5%), vacuum filtration should be used initially. Proceed to determination of percent dry solids (Section 11.2.3.2).

11.2.3.1.3. If the sample is viscous (sludge, extremely viscous oil, or is expected to have solids content > 0.5%), use pressure filtration. Proceed to determination of wet solids (Section 11.2.3.3).

11.2.3.2. Determination of Percent Dry Solids

11.2.3.2.1. Measure and record the weight of the filter. Load the filter into the filter holder and assemble vacuum filter apparatus.

11.2.3.2.2. Homogenize the waste; then transfer a subsample of at least 100 g into a clean beaker or snap-top vial. Record the sample weight in the percent dry solids section of the logbook.

11.2.3.2.3. Turn on the vacuum source. Transfer the sample to the vacuum filtration device, spreading the waste sample as evenly as possible over the surface of the filter. Be sure to transfer all significant particulates from the beaker to the filter. Use a reagent water rinse if necessary.

11.2.3.2.4. Once all liquid has been pulled though the filter, remove the filter with the wet solids from the vacuum filtration apparatus.

11.2.3.2.5. Dry the filter and solid phase at 100 ± 20°C for approximately 15 minutes.

Note: To avoid potential flash hazards, if the liquid phase is organic (contains solvents and/or oil), the oven should not be used. Prolonged periods of air-drying may be an appropriate replacement for oven-drying potentially flammable solids.

11.2.3.2.6. Remove the filter from the oven, and allow to cool.

11.2.3.2.7. Weigh and record the dry weight of filter + particulates.

11.2.3.2.8. The percent dry solids will be calculated by the electronic logbook and appear in the column labeled “% Dry Solids”.

11.2.3.2.9. If the percent dry solids is ≥ 0.5%, repeat the drying step. Weigh and record the second filter + particulates dry weight. If the two weighings do not agree within 1%, perform additional drying and weighing until successive weighings agree within 1%.

11.2.3.2.10. If the dry solids result is ≥ 0.5%, proceed to Section 11.2.3.3 using a fresh wet portion of the multiphase waste.

11.2.3.2.11. If the percent solids result is less than 0.5%, discard the solid phase. No leaching will be necessary. Filter sufficient sample with either the pressure filtration system or ZHE system as described in Sections 11.3 and 11.4. The filtrate is the TCLP leachate.

11.2.3.3. Determination of Wet Solids

11.2.3.3.1. Assemble the pressure filtration apparatus (use blunt forceps to handle the 0.6 to 0.8 μm filter membrane).

11.2.3.3.2. Homogenize the waste; transfer a minimum of a 100g subsample to the glass beaker. Measure and record the gross weight in the electronic logbook column labeled “Weight of Container + Sample (g)”.

11.2.3.3.3. Measure and record the tare weight of the filtrate collection bottle in the electronic logbook column labeled “Weight of Filtrate Bottle (g)”.

11.2.3.3.4. Transfer the sample to the filtration device spreading the waste sample as evenly as possible over the surface of the filter. Measure and record the tare weight of the empty glass beaker and any residual sample in the electronic logbook column labeled “Weight of Container + Residue (g)”.

11.2.3.3.5. The electronic logbook will calculate the net weight of sample used for testing and it will appear in the column labeled “Difference (A - B) Sample Weight (g)”.

11.2.3.3.6. Slowly apply gentle pressure of 10 psi to the filtration apparatus. Allow the sample to filter into the pre-weighed filtrate collection bottle until no **SIGNIFICANT** additional liquid has passed through the filter during a two-minute period.

11.2.3.3.7. If necessary, repeat the previous step while increasing the pressure in 10 psi increments until a maximum of 50 psi is reached. Stop the filtration when no additional filtrate is generated within a two-minute period.

Note: Some samples will contain liquid material that does not filter (e.g., oil). Do not attempt to filter the sample again by exchanging filters. Viscous oils, or any wastes that do not pass through the filter, are classified by the method as a solid.

11.2.3.3.8. Remove the filtrate collection bottle, weigh and record the gross weight in the electronic logbook column labeled “Weight of the Filtrate bottle + Filtrate (g)”.

11.2.3.3.9. The electronic logbook will calculate the net weight of sample aliquot added to the filtration apparatus. This weight will appear in the column labeled “Difference (E - D) Filtrate Weight (g)”. This result is used in the calculation of wet solids, which is calculated by the electronic logbook and appears in the column labeled “Difference (C – F) Wet Solids Weight (g)”.

11.2.3.3.10. To determine the amount of filtrate, place a container of the same size and type as the filtrate container next to the filtrate. Add water to the empty container to the same exact level as that of the filtrate container. Transfer the water to a graduated cylinder and record the volume. This step will reduce the amount of contamination, which may exist from transferring the filtrate to a graduated cylinder.

11.2.3.3.11. Retain the filtrate for possible recombination with the leachate in Section 11.3.7. Retain the filter and wet solids for the leaching in Section 11.3.

11.2.3.3.12. For multiphase sample preparations, the electronic spreadsheet will calculate the total weight of wet solids. This weight will appear in the column labeled “Difference (C-F) Wet Solids Weight (g)”.

11.2.3.3.13. The weight of wet solids that is tumbled should generate enough leachate for the tests requested. If this is not feasible, due to limited solids content, matrix. or limited available sample volume, the project manager must be contacted.

11.2.4. Particle-size Reduction for Fluid Selection

11.2.4.1. The subsample used for fluid selection must consist of particles less than approximately 1 mm in diameter (versus the less than 1 cm requirement for the material used for the actual TCLP/SPLP extraction). The method requires a smaller particle size to partially compensate for the shorter duration of contact time with the leachate solution, as compared to the full extraction. Inappropriate use of coarser materials could result in the selection of the wrong fluid type.

11.2.4.2. Surface area exclusion - size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram.

11.2.4.3. If the sample contains particles greater than approximately 1 mm in diameter, crush, cut, or grind the solids to the required size.

11.2.4.4. Consult a supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick, etc.).

Note: Equipment used for particle size reduction should be used by trained personnel only. See SOP NC-OP-044 Soil Processing.

11.2.5. Determination of Appropriate Extraction Fluid

11.2.5.1. If the solid content is greater than or equal to 0.5%, and if the sample is being analyzed for metals or nonvolatile organic compounds, the type of leaching solution must be determined.

11.2.5.2. Follow times, temperature, and particle size specified in this section as closely as possible. If reaction time between the acid solution and solid waste is too short or too long, the procedure may produce false pH readings.

11.2.5.3. 11.2.5.3. For SPLP, refer to Section 7.10 for fluid selection. Record the fluid type in the logbook.

11.2.5.4. 11.2.5.4. The TCLP leaching fluid for all volatiles is TCLP Fluid #1.

11.2.5.5. 11.2.5.5. TCLP leach fluid determination for non-volatile analytes

11.2.5.5.1. Weigh out a 5.0 ± 0.1 g subsample (less than 1 mm particle size) of the solid phase into a plastic snap-top vial and record in the logbook. Also weigh 5.0 ± 0.1 g of reagent-free sand into a snap-top vial and record this weight in the logbook. This will serve as a temperature blank during heating.

Note: If sample quantity is limited, consult supervisor or project manager.

Note: Many multiphase samples have limited solids content. In these instances, use a 5g aliquot of the whole sample. Document this difference in the logbook comment section.

11.2.5.5.2. Add 96.5 ± 1.0 mL of reagent water to each vial, add magnetic stir bar, close lid to the snap-top vial, and stir for 5 minutes.

11.2.5.5.3. Measure and record the pre-test sample pH in the logbook. It is not necessary to record the pH of the temperature blank.

Note: To avoid damaging a glass pH probe when organic liquid is present, use narrow range pH indicator paper or an ISFET pH meter.

11.2.5.5.4. If the pH is less than or equal to 5, use TCLP Fluid #1.

11.2.5.5.5. If the pH is greater than 5, add 3.5 mL 1 N HCl. Slurry the sample briefly. Insert a thermometer into the temperature blank vial. One temperature blank must be used for each group of samples heated. All samples and the temperature blank in the group must be heated at the same time in order for the temperature of the blank to represent the others. Heat to 50 ± 2°C and maintain for ten minutes.

Note: The heating cycle is a critical step. If the solid waste does not remain in contact with the acidic solution under specified time and temperature conditions, an erroneous pH may be measured.

11.2.5.5.6. Cool to 23 ± 2°C.

11.2.5.5.7. Measure and record the pH immediately after the sample has reached 23 ± 2°C.

11.2.5.5.7.1. If the pH is less than or equal to 5, use TCLP Fluid #1. Record the buffer in the logbook.

11.2.5.5.7.2. If the pH is greater than 5, use TCLP Fluid #2. Record the buffer in the logbook.

11.2.5.5.7.3. If the pH is between 4 and 6, as read on the pH paper, use of the pH meter is required. Record the pH to the proper significant figures as given by the pH meter, if used.

11.2.6. For samples requiring analysis for semi-volatile organics, pesticides, herbicides or metals proceed to Section 11.3.

11.2.7. For samples requiring analysis for volatile organics (ZHE), proceed to Section 11.4.

11.3. Bottle Extraction Procedure: Non-Volatile Constituents: Semi-Volatiles, Pesticides, Herbicides, Metals (Refer to Flow Chart 2, Appendix D).

11.3.1. Evaluate the solid portion of the waste for particle size. If it contains particles greater than 1 cm in size, prepare the solid portion of the waste for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size (i.e., capable of passing through a 9.5 mm, 0.375 inch, standard sieve). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. If particle size reduction was required, record this in comments column in logbook.

11.3.1.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick, etc.). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Determination of particle size reduction tools should take into account the requested analytes (e.g., avoid chromium steel tools when TCLP metals have been requested). Bricks, rocks, or other solids amenable to grinding may be subcontracted out for particle size reduction (contact PA or PM). Note that size reduction to fine powder is not appropriate, and could invalidate results. If necessary, consult client for guidance. See particle size reduction SOP NC-OP-044 for additional details.

11.3.2. Determine the minimum total volume of solid phase leachate that needs to be generated. Refer to Section 11.2.1.

11.3.3. Use 100 g of solid unless sample quantity is limited. If limited sample, divide the total volume of solid phase leachate required by 20 to determine the minimum mass of solid phase required for leaching. Round this mass **up** to the nearest 5 g. Client must be notified, and a nonconformance memo issued if less than 100 g of solid material is used. The client may choose to send additional sample volume if insufficient volume is available to meet method requirements of 100g. If additional sample volume will be provided, the TCLP preparation should be stopped until the additional sample arrives, or the project manager gives additional direction.

Note: Solid phase material is often in limited quantity from multiphase samples. Generally all the *solid* phase material and the filter from Section 11.2.3.3.11 are transferred to the leaching bottle. The mass of the solid of a multiphase sample is calculated by the electronic logbook column labeled “Difference (C-F) Wet Solids Weight (g)”.

11.3.4. All non-ZHE extraction vessels should be labeled with the sample name on both lid and bottle during weighing and tumbling. Before each tumbling, a new label is to be placed prominently on each reusable glass vessel for each use. After three uses, (once the bottle has three labels) the bottle is to be discarded. If the vessel cracks, breaks, becomes scratched, or is used for an oily sample, it must be discarded immediately after use.

11.3.5. Weigh the required mass of solid phase into an appropriate extraction vessel (plastic for metals only, borosilicate glass for all others), and **slowly** add 20 times its mass of appropriate leaching fluid (e.g., 100 g of sample would require 2000 mL of leaching fluid). Record the weight of the sample aliquoted for the extraction. Record the volume of extraction fluid added in the logbook, if other than 2000 mL. This volume is calculated by the electronic logbook for multiphase samples; the result can be found in the column labeled “G x 20 Buffer Amount (mL)”.

11.3.6. Ensure any effervescence has stopped before capping the bottle tightly. Secure in a rotary agitator and rotate end-over-end at 28-32 rpm for 16-20 hours. The temperature of the room should be 23 ± 2°C. The temperature of the room is recorded using a continuous temperature monitor. Record the rotary agitator I.D. and the date and time extraction is started and completed in the logbook. Record the RPM of the agitator(s) in the LIMS batch in the “Batch Information” window.

Note: As agitation continues, pressure may build up within the bottle for some types of wastes. To relieve excessive pressure, the bottle may be removed and opened periodically in a properly vented hood to relieve any built-up pressure.

11.3.7. After tumbling in the rotary agitator is completed, remove the bottle and allow the solids to settle. Record the date and time the extraction is completed in the logbook. If sample was multiphase with an initial filtrate, drop a few drops of the filtrate (with a disposable glass pipette) into the extraction bottle and observe whether the filtrate is insoluble (floats on top or sinks to the bottom) or forms a precipitate with the leachate. If so, then the filtrate is not compatible with the

leachate and must be bottled and analyzed separately. The results are normally mathematically recombined (Section 12.1.2). If the filtrate is compatible with the leachate (i.e., completely soluble), retain the filtrate to be physically combined with the leachate after filtration. Proceed with the leachate filtration step in the next section.

11.3.8. Filter the sample using pressure or gravity filtration by filtering through a new glass fiber filter. Gravity filtration through the pressure filtration vessel or a plastic funnel may also be used if the sample is amenable. Plastic funnels should not be used when organic compounds are of interest. All samples in a batch, including QC samples, will be filtered through the same type of equipment (i.e. funnel or filtration device). For this final filtration of the TCLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration if the original filter becomes over-loaded with particulate matter. Filters must be acid washed if metals are to be determined (see Section 6.3). The entire sample need not be filtered; however, sufficient volume should be generated to support the required analyses. For samples with retained compatible filtrates from the multiphase preparation, proceed to the multiphase worksheet to calculate how much of the compatible filtrate should be added to the filtered leachate.

11.3.9. Measure the pH of the TCLP leachate and record in the logbook. A small aliquot (approximately 10 to 15 mL) of the filtered leachate in a separate container should be used to measure the pH of the leachate. The pH probe or paper should not be placed directly into bottles of samples that will be used for further prep or analysis.

11.3.9.1. In general, the use of pH paper is appropriate for determining the final pH of the leachate. The pH meter may be used if it is not possible to determine the pH with pH paper (e.g. there is color interference when using pH paper).

11.3.10. Prepare sufficient volume for MS/MSD quality control testing, as necessary. Refer to the appropriate determinative SOPs for further guidance on the spike components, levels and action criteria.

11.3.11. Immediately preserve the leachate as follows:

Metals	pH < 2 w/ HNO_3 for aqueous filtrates and leachates (do not acidify oils and other non-aqueous liquids)
All others	Refrigerate to 4 ± 2 ^{o}C

Note: Refer to Section 8.5 if precipitation occurs upon preservation.

Note: Preservation of Metals samples is generally performed by Metals personnel. The MS/MSD volume must be spiked prior to preservation.

11.3.12. Label each sample with the appropriate information and submit to the appropriate analytical groups for prep and analysis. For multiphase samples requiring mathematical recombination, the electronic logbooks are available to the sample

preparation and analysis groups and are attached to the LIMS batches. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the Project Manager to ensure the proper sample login is completed.

11.4. ZHE Extraction Procedure: Volatile Constituents (Refer to Flow Chart #3, Appendix D)

11.4.1. Use the ZHE device to obtain a TCLP leachate for analysis of volatile compounds only. Leachate resulting from the use of the ZHE shall NOT be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, herbicides and semi-volatile organics).

11.4.2. Due to some shortcomings of the method, losses of volatile compounds may occur. Extra care should be observed during the ZHE procedure to ensure that such losses are minimized. Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere any longer than necessary.

11.4.3. Install new O-rings and adjust the ZHE piston in the ZHE body to the appropriate height (slightly moisten the O-rings with leaching fluid if necessary).

11.4.4. If the preliminary evaluations indicated the need for particle size reduction, homogenize the waste, weigh out a subsample of sufficient size and prepare for leaching by crushing, cutting, or grinding such that all particles are less than 1 cm in size as measured with a ruler (Do NOT sieve the sample). Size reduction is not required if the sample surface area is greater than or equal to 3.1 cm^2 per gram. If particle size reduction was required, record this in the “Comments” column of the logbook.

Note: To minimize loss of volatiles, samples for volatiles that require particle size reduction should be kept in sample storage (at 4ºC) until immediately before size reduction. Aggressive reduction, which would generate heat, should be avoided; and exposure of the waste to the atmosphere should be avoided to the extent possible. Size reduction to a fine powder is not appropriate. Also see Section 11.2.

11.4.4.1. Consult your supervisor or manager when dealing with unusual sample matrices (e.g., wood, cloth, metal, brick). Scissors or shears may be used to cut cloth, plastic or sheet metal. Saws may be used for wood or solid metal. Bricks, rocks, or other solids amenable to grinding may be subcontracted out for particle size reduction or processed in-house. Contact the project manager for specific guidance.

11.4.5. Homogenize and transfer an appropriately sized subsample of the waste into the ZHE and record the mass in the logbook.

11.4.5.1. For wastes that are solid, a 25g sample is used, unless sample volume is limited. Smaller weights may also be used if the sample is of an unusual matrix that may damage the ZHE vessel.

11.4.5.2. For wastes containing < 0.5% solids, the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Filter enough of the sample to support all of the volatile analyses required.

11.4.5.3. If the sample has ≥ 0.5% solids and has non-volatile TCLP/SPLP requested, the appropriate sample size should be estimated based on the wet solids content determined in Section 11.2.3.3. If ZHE only is requested, use visual wet solids estimate to sample sub-aliquot. Record the weight of the waste and the beaker in the electronic logbook column labeled "Weight of Container + Sample (g)". After adding the sample to the ZHE extraction vessel, record the weight of the empty container and any residue in the electronic logbook column labeled "Weight of Container + Residue (g)". The electronic logbook will calculate the sample weight and the result will appear in the column labeled "Difference (A – B) Sample Weight (g)".

11.4.5.4. The weight of wet solids that tumbles in the ZHE does not need to be 25g. Sufficient leachate should be generated to perform the analysis, however. If there is insufficient leachate volume available after performing the multiphase procedure (including all compatible filtrate that will be returned to the vessel after leaching), the entire process must be started over and all sample volumes generated from the failed procedure must be discarded. **Note:** For wastes containing greater than 0.5% wet or dry solids, the "solids" value from the ZHE filtration process is used to determine the volume of fluid to load into the ZHE. This value is calculated by the electronic spreadsheet and the volume of fluid appears in the column labeled "G x 20 Buffer Amount (mL) Leachate Vol".

11.4.6. Carefully place the glass fiber filter between the support screens and secure to the ZHE. Tighten all of the fittings.

11.4.7. Place the ZHE in a vertical position; open both the gas **AND** liquid inlet/outlet valves; and attach a gas line to the gas inlet/outlet valve.

11.4.8. If the waste is solid, slowly increase the pressure to a maximum of 50 psi to force out as much headspace as possible and proceed to Section 11.3.13.

11.4.9. If this is a multiphase sample, carefully apply gentle pressure of 10 psi (or more, if necessary) to force all headspace slowly out of the ZHE. At the **FIRST** appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue gas pressure.

11.4.10. Assemble a syringe and push the plunger in all the way. Attach the pre-weighed syringe to the liquid inlet/outlet valve and open the valve. Record the tare weight of the collection syringe in the electronic logbook column labeled "Weight of Syringe (or vials) (g)". If the volume of the filtrate is expected to exceed the volume of the syringe (e.g., more than 50mL), then record the tare weight of an appropriate number of vials, instead of the syringe.

11.4.11. Carefully apply gas pressure of no more than 10 psi to force out the liquid phase. Allow the sample to filter until no **SIGNIFICANT** additional filtrate has passed in a two-minute period.

Note: If the capacity of the syringe is reached, close the liquid inlet/outlet valve, discontinue gas pressure, remove the syringe, dispense the volume into the pre-weighed vials, record weight in Column E and filtrate volume in the logbook.

11.4.12. Repeat previous steps increasing the pressure in 10 psi increments until 50 psi is reached and no significant liquid has passed in a two-minute period. Close the valve and discontinue gas pressure. Remove the collection device and record the total weight of the collection device with filtrate in the electronic logbook column labeled Weight of the Syringe (or vials) + Filtrate (g). Record the filtrate volume in the electronic logbook column labeled "Volume of Filtrate* (mL)." Transfer the filtrate to VOA vials and label appropriately. The weight of the filtrate is calculated by the logbook and appears in the column labeled "Difference (E – D) Filtrate Weight (g)".

Note: If the original waste contained less than 0.5% solids (Section11.2.3.2), this filtrate is defined as the TCLP leachate and you may proceed to Section 11.3.22. Otherwise, save the vials by storing at 4ºC under minimal headspace conditions, for recombination as in Section 11.3.21.

11.4.13. The material remaining in the ZHE is defined as the "solid" phase. The weight of the solid phase is calculated by the logbook and appears in the column labeled "Difference (C – F) Wet Solids Weight (g)".

11.4.14. Determine the amount of buffer to use. Solid samples of 25g use 500 mL of leach fluid (20 X 25 g). For multiphase samples or other samples using weights of other than 25g, the volume of buffer will be equal to 20 times the weight of the sample. The multiphase sheet of the electronic logbook calculates the volume of fluid required for multiphase samples and this value appears in the column labeled "G x 20 Buffer Amount (mL) Leachate Volume".

Note: The TCLP ZHE prep uses only TCLP fluid #1; the SPLP ZHE prep uses only SPLP fluid #3 reagent water.

11.4.15. Load the fluid transfer reservoir with an excess of Fluid #1, and preflush the transfer line to eliminate air pockets. Be sure the required volume remains.

11.4.16. Attach the transfer line to the liquid inlet/outlet valve and open the valve. Carefully pump the required volume into the ZHE and close the valve. Disconnect the transfer line.

11.4.17. Check the ZHE to make sure all of the valves are closed, and manually rotate the ZHE (end-over-end) two or three times. Reposition the ZHE in the vertical position.

11.4.18. Pressurize the ZHE to 5-10 psi. If the ZHE appears to be leaking, follow the corrective action protocols recommended by the manufacturer and repeat the procedure.

11.4.19. Slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced during the introduction of the Fluid. Upon the first sign of liquid from the valve, close the valve.

11.4.20. Re-pressurize the ZHE to 5-10 psi and place in the rotary agitator. Rotate at 28-32 rpm for 16-20 hours. Record the rpm of the agitator and the date and time of the start and stop of agitation in the appropriate logbooks. Room temperature should be 23 ± 2 °C. The room temperature is recorded using a continuous temperature monitor.

11.4.21. Confirm that the pressure of 5-10 psi was maintained throughout the leaching. If it was **NOT** maintained, return to Section 11.3, and repeat the leaching with a new aliquot of sample.

11.4.22. If there is an initial liquid filtrate (Section 11.3.12) determine if it is compatible with the leachate if the filtrate has not been previously tested (Section 11.3.7).

11.4.22.1. Remove the plunger from the syringe and attach the barrel to the ZHE vessel. Open the outlet valve and pressurize as necessary to transfer about 1 mL of leachate into the syringe. Close the outlet valve.

11.4.22.2. With a glass pipette transfer a few drops of initial filtrate into the open syringe barrel. Formation of separate layers or a precipitate indicates the filtrate and leachate are not compatible. Bottle the filtrate for separate preparation and analysis. The results are normally mathematically recombined.

11.4.22.3. If the filtrate is compatible, gently pour the remainder of the filtrate into the syringe barrel. Install the plunger. Bleed any pressure in the ZHE piston. Open the inlet/outlet valve and depress the syringe plunger to inject the filtrate into the ZHE vessel. Do not inject the air bubble (if present) from the syringe.

11.4.22.4. Close the valve and rotate a few times to mix. Proceed with leachate filtration as described in the next section.

11.4.23. Attach an empty syringe to the outlet valve. Open the valve and pressurize the piston to expel the leachate from the ZHE vessel. Following collection, store the TCLP leachate in two or three 40-mL VOA vials with minimal headspace at 4 ± 2 ^{o}C and prepare for analysis as soon as possible, using the appropriate organic analysis procedure (see Section 16.1).

11.4.24. If the individual phases are analyzed separately, combine the results mathematically by using the recombination calculation in Section 12.1.2. Electronic copies of the TCLP preparation logbook sheets are available to the

sample preparation and analysis groups. Most mathematically recombined samples will require data entry for the filtrate and leachate portions as well as for the mathematically recombined results. Contact the Project Manager to ensure the proper sample login is completed.

11.4.25. ZHE Vessel Cleaning

11.4.25.1. Disassemble the vessel.

11.4.25.2. Clean all parts (vessel, lid, bottom, piston, and metal filters) with soapy water.

11.4.25.3. Rinse all parts with tap water followed by DI water.

11.4.25.4. Discard all used gaskets.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Calculation of weight of extraction fluid to use:

Volume of extraction fluid = 20 X weight of wet solids to be extracted

12.1.2. Mathematical recombination of analytical results:

$$Final\ Analyte\ Concentration = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2}$$

Where,
V_1 = total volume of the initial filtrate phase (L).
C_1 = analyte concentration in initial filtrate phase (mg/L).
V_2 = volume of the theoretical solid phase leachate (L).
C_2 = analyte concentration in solid phase leachate (mg/L).

12.2. Reporting Requirements

12.2.1. Follow these reporting conventions for multi-phase samples.

12.2.1.1. If both phases have positive results, use the values from each phase to calculate the recombined result. Use the reporting limit for each phase to calculate the recombined reporting limit.

12.2.1.2. If both phases are “ND” (not detected) the recombined result is “ND,” and the reporting limit is calculated from the reporting limit for each phase.

12.2.1.3. If one phase is “ND” and the other phase has a positive result, use zero for the “ND” phase and the positive value for the other phase to calculate the combined result. This will produce a minimum known concentration. Alternatively, at client request, the maximum possible concentration can be calculated by using the reporting limit for the “ND” phase, rather than zero. The combined reporting limit is based on the reporting limit for both phases calculated with a weighted sum similar to the process used to calculate the final result.

12.2.2. Units - regardless of the nature of the sample, all TCLP and SPLP results are reported in units of mg/L.

12.2.3. For limits and significant figures, consult the appropriate analytical methods (Section 16.1).

12.2.4. Anomalies - all anomalies observed during the leach procedure must be noted on the worksheet or an NCM form. Some examples of such anomalies are:

12.2.4.1. Sample was monolithic - particle size reduction not possible due to nature of matrix.

12.2.4.2. Insufficient sample - less than the required 100g minimum was available.

12.3. Review Requirements

12.3.1. Review all applicable holding times. If a holding time was exceeded, confirm that a holding time violation was properly documented in an NCM.

12.3.2. If Total analysis results are available, those results may be compared with the TCLP analysis results according to the following:

$$Total \geq 20 \times TCLP$$

Note: Assumes the sample is 100% Solids.

12.3.3. Total constituent analysis results can be used to demonstrate the TCLP protocol is unnecessary. In performing a TCLP analysis, there is a 20:1 dilution of the original sample with the leaching solution. Thus, if the “total constituent” result is less than 20 times the TC level, it is impossible for the leachate to “fail” and the TCLP does not need to be performed. For example, the TC level for lead is 5.0 mg/L (ppm). Therefore, if a sample of lead-contaminated soil contains less than 100 ppm total lead, a TCLP test need not be run to demonstrate that lead is less than the TCLP limit.

13. METHOD PERFORMANCE

13.1. Refer to individual analysis SOPs.

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Acidic waste from sample extract: This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.2. Buffer solutions: This waste can be poured down the drain with copious amounts of water.

15.2.3. Solid waste from sample extract, solid sample waste and used filter paper from the sample filtration step: This waste is disposed of in a designated container identified as "Solid Waste".

15.2.4. Flammable solvent waste and remaining TCLP extracts: This waste is disposed of in a flammable liquid solvent container identified as "Mixed Flammable Solvent Waste".

15.2.5. Glassware contaminated with acidic sample residue: Broken or unusable glassware is disposed of in a designated container identified as "Solid Waste". Glassware used in this test method is washed per the Glassware Washing SOP.

16. REFERENCES

16.1. References

16.1.1. Method 1311, Toxicity Characteristic Leaching Procedure, Revision 0, July 1992, SW-846 Final Update I

16.1.2. Method 1312, Synthetic Precipitation Leaching Procedure, Revision 0, November 1994, SW-846 Update II

16.1.3. Toxicity Characteristic: Corrections to Final Rule. Method 1311, Federal Register, Vol. 55, No. 126, Friday, June 29, 1990

16.1.4. Toxicity Characteristic: Final Rule. Method 1311, Federal Register, Vol. 55, No. 61, Thursday, March 29, 1990

16.1.5. Technical Background Document and Response to Comments, Method 1311, Toxicity Characteristic Leaching Procedure, USEPA/OSW, April 1989

16.1.6. Corporate Quality Management Plan (CQMP), current version

16.1.7. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.8. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.9. Revision History

Historical File:		Revision 1.0: 02/01/00		Revision 3: 08/22/12
		Revision 1.1: 10/10/00		Revision 4: 10/31/13
		Revision 1.2: 11/11/04		Revision 4: 11/17/14
		Revision 0: 03/31/08		
		Revision 1: 07/15/10		
		Revision 2: 6/16/11		

16.2. Associated SOPs and Policies, current version

16.2.1. TestAmerica Canton Quality Control Program, QA-003

16.2.2. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, NC-IP-011

16.2.3. Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis, Method 6010B and Method 200.7, NC-MT-012

16.2.4. Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1, NC-MT-013

16.2.5. Determination of Volatile Organics by GC/MS based on Methods 8260B, NC-MS-019

16.2.6. SGC/MS Analysis Based on Method 8270C, NC-MS-018

16.2.7. Gas Chromatographic Analysis Based on Methods 8000B, 8021B, 8081A, 8082, 8151A, and 8015B, NC-GC-038

16.2.8. Extraction Procedure for Chlorinated Acid Herbicides Based on Method 8151A, NC-OP-031

16.2.9. Continuous Liquid / Liquid Extraction of Organic Compounds from Waters Based on Method SW846 3520C NC-OP-037

16.2.10. Separatory Funnel Extraction of Organic Compounds from Waters Based on Method SW846 3510C and 600 Series NC-OP-038

16.2.11. pH Electrometric Method, NC-WC-010

16.2.12. Standards and Reagents, NC-QA-017

16.2.13. Glassware Washing, NC-QA-014

16.2.14. Subsampling, NC-OP-046

16.2.15. Soil Processing, NC-OP-044

17. MISCELLANEOUS

17.1. Modifications/Interpretations from Reference Methods

17.1.1. Section11.2: Preliminary Evaluations. Section 7.1 of the source Method 1311 states that the sample aliquot used for the preliminary evaluation "...may not actually undergo TCLP extraction." Section 7.1.5 of the source method indicates that the portion used for the preliminary evaluation may be used for either the ZHE or non-volatile extraction if the sample was 100% solid. Section 7.1.5 of the source method further indicates that if the sample was subjected to filtration (i.e., < 100% solid) that this aliquot may be used for the non-volatile extraction procedure only as long as sufficient sample is available (minimum 100 g). Samples that have been subjected to the oven-drying step may not be used for TCLP extraction because solid phase degradation may result upon heating.

17.1.2. Sections 11.3.7and11.4.22: Determination of Filtrate/Extraction Fluid Compatibility. Section 7.2.13 of the source method provides no guidance as to how to make this determination. As a result, the procedure herein was developed.

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17.1.3. Section 9.2: TCLP Extraction Blanks. Section 8.1 of the source method states that a minimum of one blank for every 20 extractions "…that have been conducted in an extraction vessel." TestAmerica has interpreted this to mean one blank per twenty samples leached per TYPE of leaching vessel (i.e., Bottle or ZHE) per leach fluid used. In practice, a minimum of 1 "daily blank" per 20 extractions of each vessel (bottle or ZHE) is performed AS WELL AS a minimum of 1 per 20 ZHE extractions from each identified ZHE vessel are performed.

17.1.4. Section11.2.5.5.7: Determination of Appropriate Extraction Fluid. Method 1311 does not address the appropriate approach to take if the pH equals 5.0. This SOP requires that Fluid #1 must be used if the pH is less than or equal to 5.0.

17.1.5. Section9.4: QA/QC - Matrix Spike: Section 8.2 of the source method states "A matrix spike shall be performed for each waste type..." and "A minimum of one matrix spike must be analyzed for each analytical batch". Further, Section 8.2.3 of the source method also states "The purpose of the matrix spike is to monitor the performance of the analytical methods used and to determine whether matrix interferences exist". The standard TestAmerica QAM is designed to address the performance monitoring of analytical methodology through the LCS program. A minimum of one MS will be prepared for each TCLP leachate batch. The MS results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS results have immediate bearing only on the specific sample spiked and not all samples in the batch.

17.1.6. Section 8.2.2 of the source method states that "In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level". The method also states "If the analyte concentration is less than one half the regulatory level the spike concentration may be as low as one half of the analyte concentration but may not be less than five times the method detection limit". For several analytes, spiking at the regulatory level is inappropriate to the range of analysis afforded by the determinative methods. Due to the wide range in these levels, TestAmerica spikes at the levels specified in the determinative SOPs.

APPENDIX A: Tables

Table 3 - Toxicity Characteristic Analytes and Regulatory Levels (Final Rule)	
Contaminant	**mg/L**
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresols	200.0
m-Cresols	200.0
p-Cresols	200.0
Total Cresols (used if isomers not resolved)	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
2,4-Dinitrotoluene	0.13
1,1-Dichloroethylene	0.7
Endrin	0.02
Heptachlor (& epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

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APPENDIX B: Figures

Figures 1 and 2 - Rotary Agitation Apparatus and Zero Headspace Extraction Vessel (ZHE)

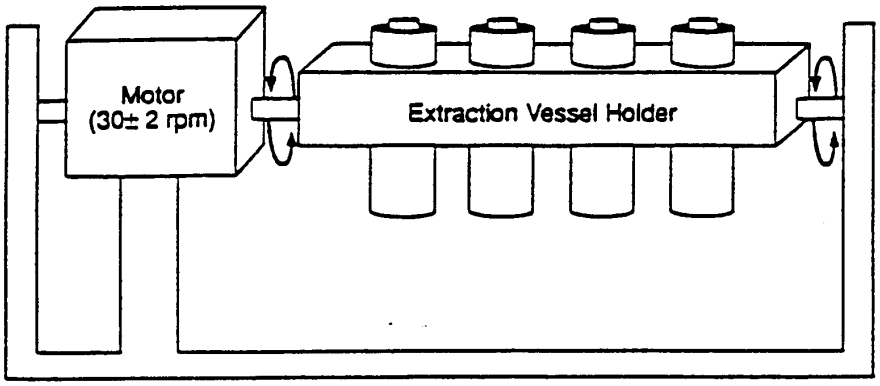

Figure 1. Rotary Agitation Apparatus

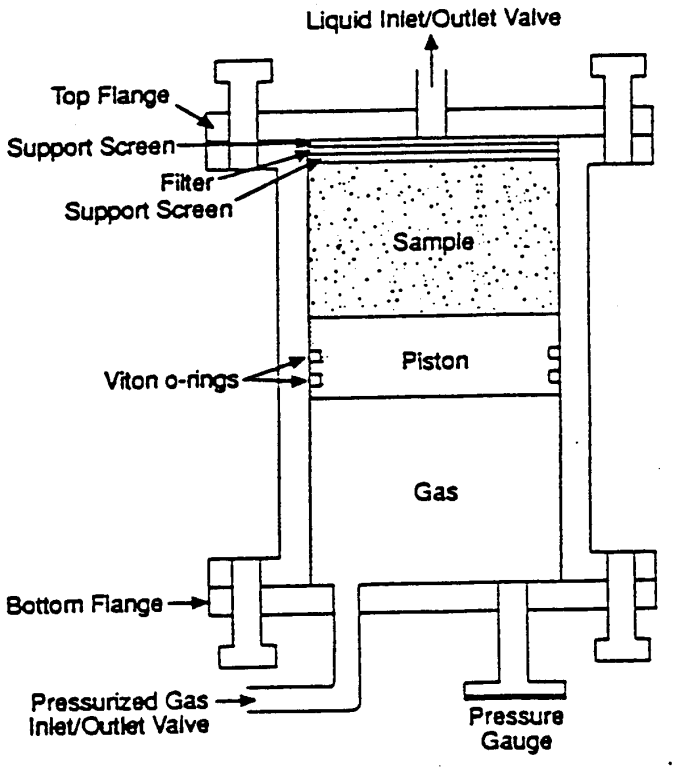

Figure 2 – Cross Section of Zero Headspace Extraction Vessel (ZHE)

Figure 3 - US Environmental Protection Agency Memorandum #35, Page 1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
SOLID WASTE AND EMERGENCY RESPONSE

MEMORANDUM # 35

DATE: June 12, 1992

SUBJECT: Notes on RCRA Methods and QA Activities

From: Gail Hansen, Chief
Methods Section (OS-331)

This memo addresses the following topics:

- o 1992 Symposium on Waste Testing and Quality Assurance
- o SW-846 Update
  - Final Rule for January 23, 1989 Proposed Rule
  - Notice, Proposed Rulemaking for the Second Update to the Third Edition
- o Chlorofluorocarbon 113 (CFC-113) Solvent Replacement Update
- o Environmental Monitoring Methods Index (EMMI)
- o Sampling Work Group Formation
- o MICE Update
- o Oily Waste Analysis
- o Electronic SW-846 Availability.

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Figure 3 - US Environmental Protection Agency Memorandum #35, Page 10 (cont'd)

Oily Waste Analysis

One of the most frequently asked questions on the MICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

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APPENDIX C : Logbook Sheets

TESTAMERICA NORTH CANTON ZHE LOGBOOK

Batch #	Sample ID	Ext. Vessel ID	Matrix	Sample Wt (g)	Ext. Buffer ID	Date On	Time On	Initials On	Date Off	Time Off	Initials Off	Tumbler ID	Tumbler Speed 30±2 RPM	Ext. Fluid ID	Initial ZHE Pressure	Final ZHE Pressure	Comments

TESTAMERICA NORTH CANTON ZHE LOGBOOK - MULTIPHASE

	A	B	C	D	E	F			G	H				
Sample Number	**Weight of Container + Sample (g)**	**Weight of Container + Residue (g)**	**Difference (A – B) Sample Weight (g)**	**Weight of the Syringe (or vials) (g)**	**Weight of the Syringe (or vials) + Filtrate (g)**	**Difference (E – D) Filtrate Weight (g)**	**Volume of Incompatible Filtrate (mL) (ie, oil)**	**Volume of Compatible Filtrate (mL) (ie, water filtrate)**	**Difference (C – F) Wet Solids Weight (g)**	**G x 20 Buffer Amount (mL) Leachate Vol.**	**Vessel ID**	**Initials**	Total Water-Soluble Volume in L (TCLP)	Incompatible Volume in L **(Waste Dilution)**

TESTAMERICA NORTH CANTON TCLP LOGBOOK

				Pre-Test			% Dry Solids				Leach Start						Leach Finish					
Batch #	Sample ID	Parameters	Matrix	Wt (g) Sample	pH after water	pH after heating	Wt (g) Sample	Wt (g) Filter	Filter + Particulates Wt (g)	% Dry Solids	Wt (g) Sample	Buffer #	Date On	Buffer ID	Time On	Initials On	Date Off	Time Off	pH Off	Initials Off	Tumbler ID	Comments

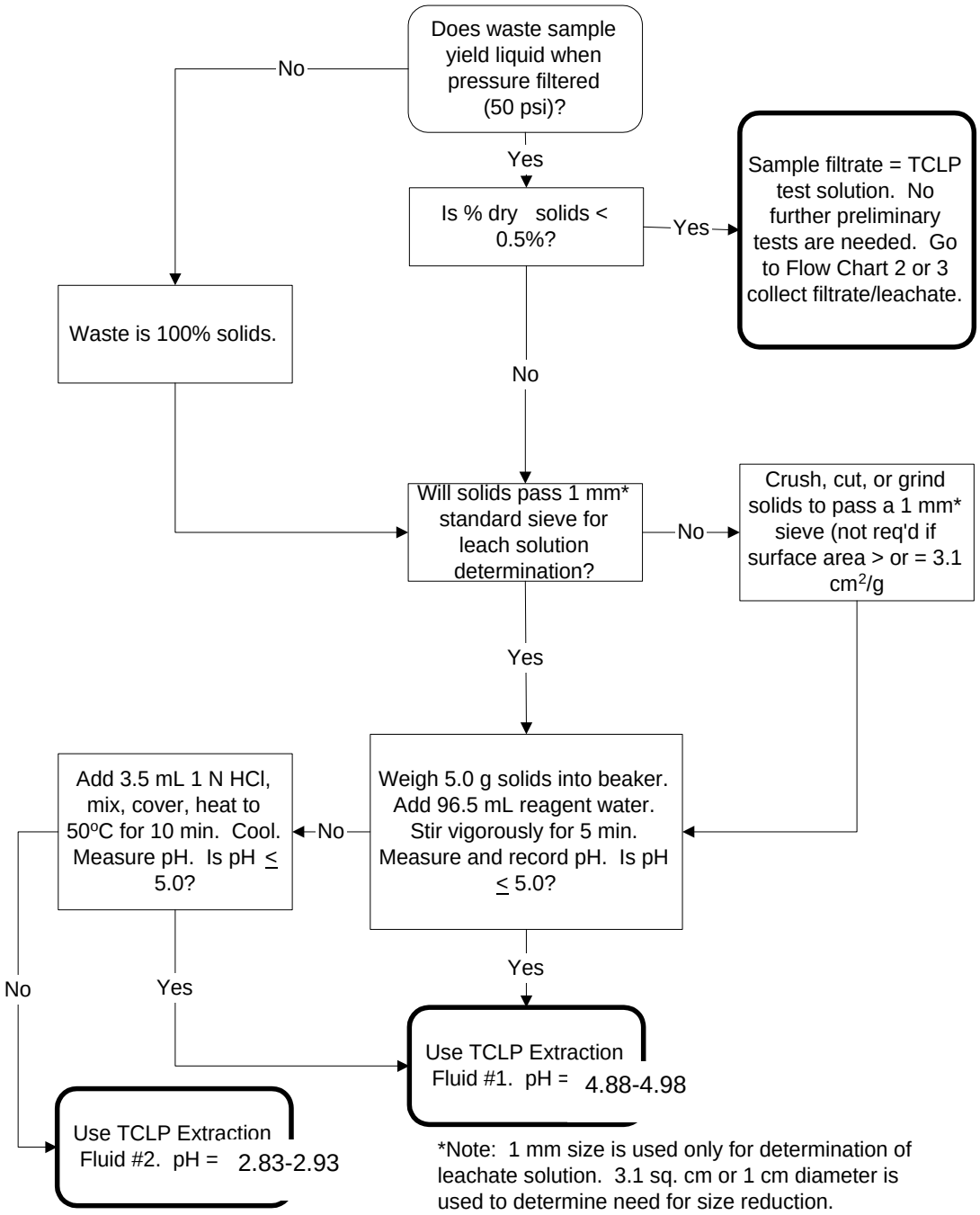
TESTAMERICA NORTH CANTON TCLP LOGBOOK – MULTIPHASE

	A	B	C	D	E	F			G	H				
Sample Number	Weight of Container + Sample (g)	Weight of Container + Residue (g)	Difference (A – B) Sample Weight (g)	Weight of the Syringe (or vials) (g)	Weight of the Syringe (or vials) + Filtrate (g)	Difference (E-D) Filtrate Weight (g)	Volume of Incompatible Filtrate (mL) (ie, oil)	Volume of Compatible Filtrate (mL) (ie, water filtrate)	Difference (C-F) Wet Solids Weight (g)	G x 20 Buffer Amount (mL) Leachate Vol.	Vessel ID	Initials	Total Water-Soluble Volume in L (TCLP)	Incompatible Volume in L (Waste Dilution)

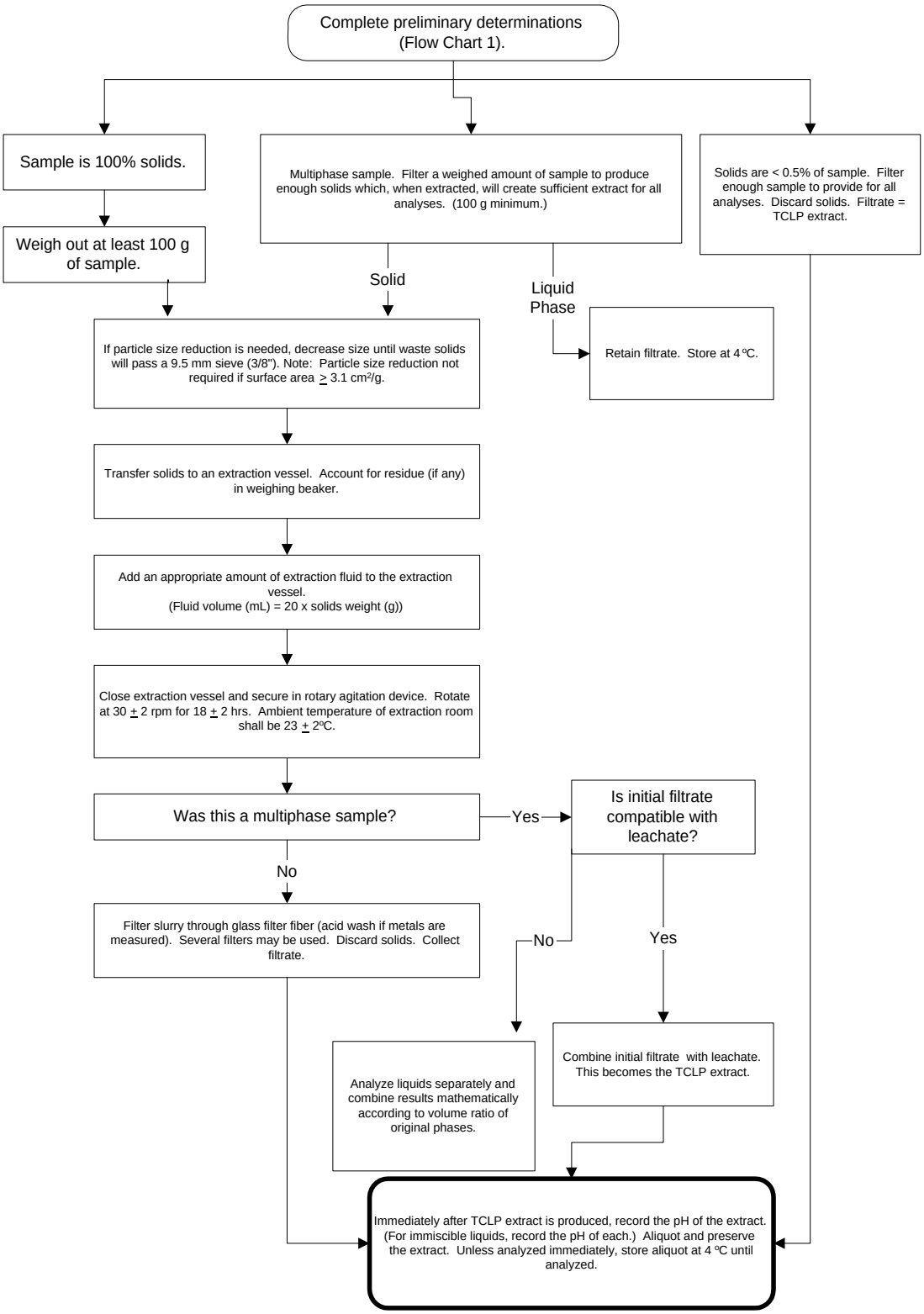
APPENDIX D

FLOW CHARTS

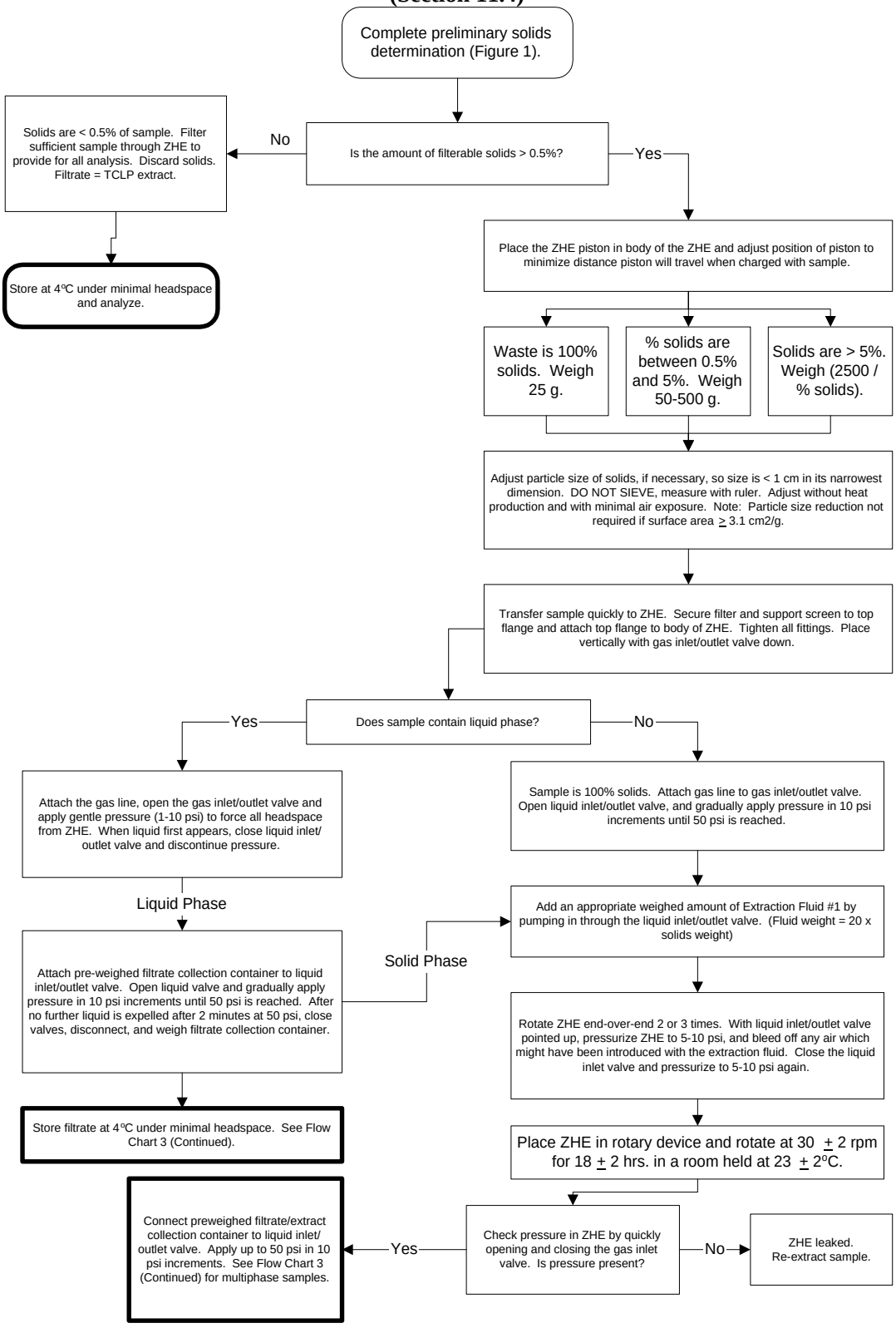
Flow Chart 1. Preliminary Sample Evaluation (Section 11.2)



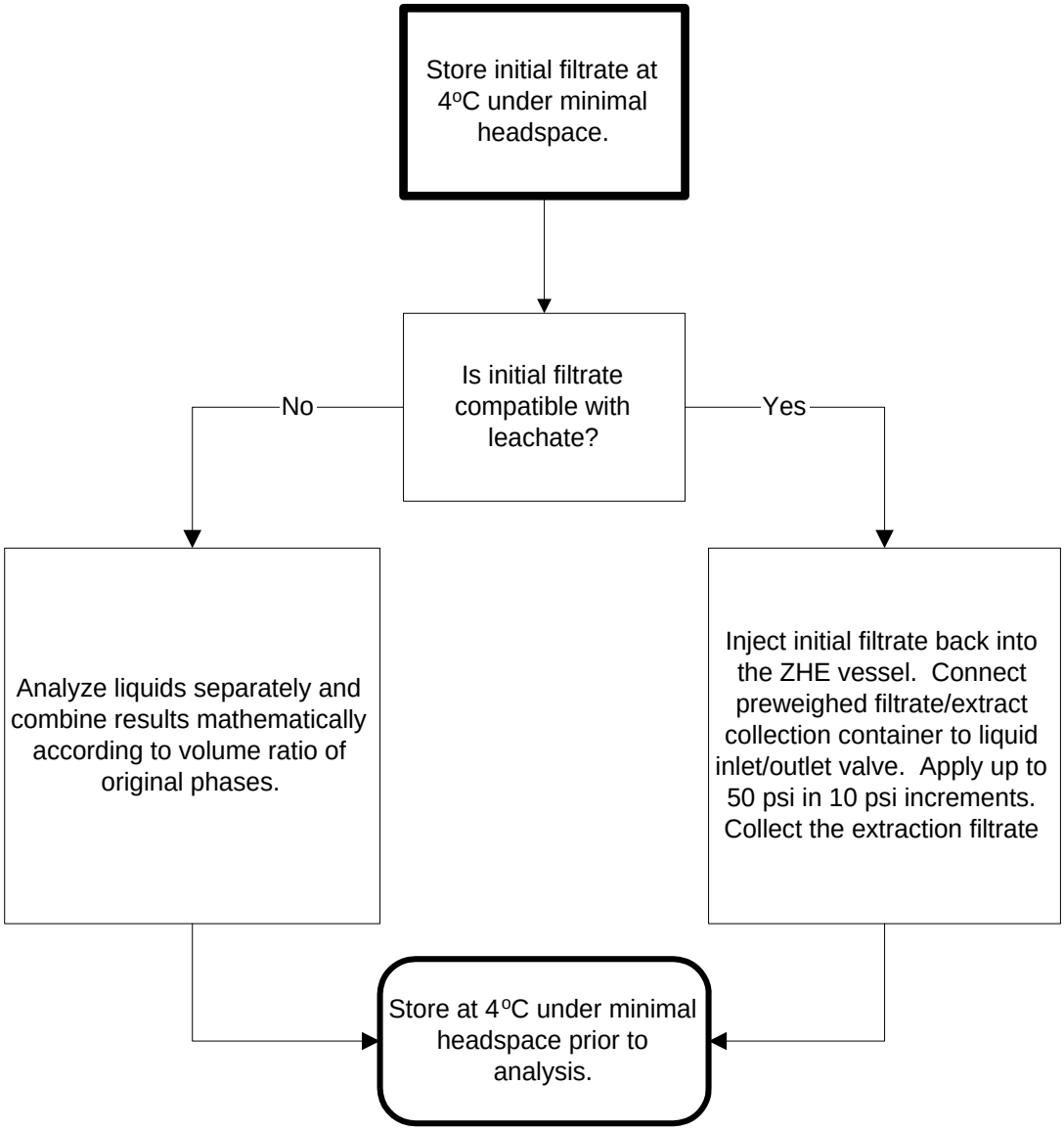
Flow Chart 2. Bottle Extraction, Non-Volatile Constituents (Section 11.3)



Flow Chart 3. ZHE Extraction, Volatile Constituents (Section 11.4)



Flow Chart 3. ZHE Extraction
(Continued)



Title: CONTINUOUS LIQUID / LIQUID EXTRACTION OF ORGANIC COMPOUNDS FROM WATERS BASED ON METHOD SW846 3520C AND 600 SERIES

[Methods: SW846 3520C and 600 Series]

Approvals (Signature/Date):

Caitlin L Scott	09/19/17		09/20/17
Technology Specialist	Date	Health & Safety Coordinator	Date
	09/25/17		11/07/17
Quality Assurance Manager	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-OP-037, Rev 5, dated 11/9/15

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1. SCOPE AND APPLICATION

1.1. This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in aqueous, and TCLP leachate, matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS) using Continuous Liquid/Liquid Extraction. The procedures are based on SW846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8270C, 8270D, 8015B, 8015C, 8015D, 608, and 625.

1.1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

2. SUMMARY OF METHOD

2.1. Continuous Liquid/Liquid Extraction

2.1.1 A measured volume of sample (typically 1 liter, or 250 mL for reduced volume extraction requiring large volume injection) is placed into a continuous liquid/liquid extractor, adjusted if necessary, to a specific pH, and extracted with the appropriate solvent for 18-24 hours.

2.2. Concentration

2.2.1 Procedures are presented for drying and concentration of the extract to final volume for analysis.

3. DEFINITIONS

3.1. Definitions of terms and acronyms used in this SOP may be found in the glossary of the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded, other gloves must be cleaned immediately.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds must be prepared in the hood.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

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Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 mg/m^3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid (1)	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain, and severe tissue burns. Can cause blindness.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride must be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints, which can become stuck. Technicians must use Kevlar or

other cut/puncture-resistant gloves when separating stuck joints.

5.9. 3520 Extraction Continuous Liquid/Liquid

5.9.1. All personnel are to ensure liquid-liquid area is clear of unnecessary items. Heating mantles used with liquid-liquid extractions generate temperatures that could ignite some materials that come in contact with the heating mantles.

5.9.2. Ensure all solvents are away from liquid-liquid extractor. Increased temperatures near solvents can cause the pressure in the containers to increase.

5.9.3. Ensure all boiling flasks have cooled to room temperature before disconnecting liquid-liquid bodies from boiling flasks to prevent any burns.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware must be cleaned per Glassware Washing, SOP NC-QA-014.

6.2. Equipment and supplies for extraction procedures:

EQUIPMENT AND SUPPLIES	CLLE	Conc
pH Indicator paper, ranges: 0-14, 7.5-14, 0-6	√	
Graduated cylinder: Class A 1 liter. (other sizes may be used as needed)	√	√
Methylene chloride collection tank for waste disposal	√	
Initial volume template	√	
Chlorine Test Strips	√	
Solvent dispenser pump or 100 mL Class A graduated cylinder		√
Continuous liquid / liquid extractor	√	
Round or flat bottom flask: 250	√	
Boiling chips: contaminant-free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent)	√	√
Cooling condensers	√	
Heating mantle: rheostat controlled	√	
Auto-timer for heating mantle	√	
Beakers: 250 & 400 mL, graduated	√	√
Kuderna-Danish (K-D) apparatus: 500 mL		√
Concentrator tube: 10 mL, attached to K-D with clips		√
Snyder column: three-ball macro		√
Water bath: heated, with concentric ring cover, capable of temperature control 90-98°C. The bath must be used in a hood or with a solvent recovery system.		√
Vials: glass, 2 / 2.5/ 40 mL capacity with Teflon®-lined screw-cap		√
Nitrogen blowdown apparatus		√
Nitrogen: reagent grade.		√

EQUIPMENT AND SUPPLIES	CLLE	Conc
Culture tubes: 10 mL, 16 mmx100 mm		√
Microliter pipette, syringe 1 mL	√	
Funnel: 75 X 75 mm	√	√
Disposable pipettes, 5 ¾ in, and 9in.	√	√
Aluminum foil	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents For Extraction Procedures

7.1.1. All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	CLLE	Conc
Sodium hydroxide (NaOH), pellets: reagent grade	√	
Sodium hydroxide solution, 10 N: dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	
Sulfuric acid (H_2SO_4), concentrated: reagent grade	√	
Sulfuric acid (1:1): carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	
Organic-free reagent water	√	
Sodium thiosulfate ($Na_2S_2O_3$): granular		
Sodium sulfate (Na_2SO_4), granular, anhydrous: purify by heating at 800°C a minimum of two hours	√	√
Extraction / exchange solvents: methylene chloride, hexane, acetone, pesticide quality or equivalent	√	√
Acetone, methylene chloride: used for cleaning	√	√
TCLP Fluid #1 : Made fresh daily in the Leachates department, or see SOP NC-OP-033 TCLP-SPLP	√	√

7.2. Standards

7.2.1. Stock Standards

7.2.1.1 Stock standards are purchased as certified solutions. Standards shall be stored according to manufacturer's instructions. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is opened if purchased). Standards must be allowed to come to room temperature before use.

7.2.2. Surrogate Spiking Standards

7.2.2.1 Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light or

stored according to manufacturer's instructions. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.3. Matrix Spiking and Laboratory Control Spiking Standards

7.2.3.1 The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards.

7.2.3.2 Spiking solutions must be refrigerated and protected from light or stored according to manufacturer's instructions. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.4 See SOP NC-QA-017 for additional information on Standards and Reagents.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. The holding time for aqueous samples is seven days from sampling to extraction. If permitted by the state or responsible party, PCB samples have a 1 year holding time.

8.3.2. For TCLP leachates, the holding time is 14 days from sampling to the leach process. The extraction holding time seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step, to the extraction step. If the filtration step requires extended times, this time counts as part of the seven-day holding time.

8.3.3. Analysis of the extracts is completed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS, and a matrix spike / matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS / MSD). If

clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD. See Policy QA-003 for further definition of the batch.

9.2. Sample Count

9.2.1. Laboratory-generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.3. Method Blank (MB)

9.3.1. A MB consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the MB at the same level as the samples. See Table 3 for the appropriate amount of surrogate to use for each analytical method. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.3.2. Aqueous MBs use 1000 mL (or 250 mL for reduced volume extraction) of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure.

9.3.3. TCLP MBs use 250 mL of leachate fluid spiked with the surrogates. SPLP MBs use 1000 mL of leachate fluid spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The MB goes through the entire analytical procedure.

9.4. Laboratory Control Sample (LCS)

9.4.1. LCSs are well-characterized laboratory-generated samples used to monitor the laboratory day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure.

9.4.2. The LCS is made up in the same way as the method blank (see Sections 9.3.1 through 9.3.3), but spiked with the LCS standard and the surrogates. See Tables 3 and 4 for the appropriate amount of spike to use for each analytical method.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Each applicable sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. See Table 3 for the appropriate amount of surrogate spike to use for each analytical method.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. A MS is an environmental sample to which known concentrations of target analytes have been added. A MSD is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and MS. See Tables 3 and 4 for the appropriate amount of spike to use for each analytical method.

9.7. QC requirements can be found in the various associated analytical SOPs.

9.8. Initial Demonstration of Capability

9.8.1. The initial demonstration and method detection limit studies described in Section 13 must be acceptable before analysis of samples may begin.

9.9. Control Limits

9.9.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.10. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs

9.11. Method Detection Limits (MDLs) and MDL Checks

9.11.1. MDLs and MDL Checks are established by the laboratory as described in SOPs

9.11.2. MDLs are accessible via the LIMs.

9.12. Nonconformance and Corrective Action

9.12.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volumes of solvents into the appropriate sized glass culture tubes gravimetrically. The “standard” glass culture tubes are sealed, and the meniscus is noted by marking a line on the bottles. The glass culture tubes containing the sample extracts are then compared against the

"standard" glass culture tubes of the appropriate volume and solvent to ensure the volumes are consistent. The bottle top dispenser is calibrated quarterly and must be within ±5% of the target volume with an RSD ≤ 1%.

10.2. Calibration verification of the initial volume template is required annually. Bottle top dispensers are verified quarterly. See SOP NC-QA-004, current revision for details on volumetric equipment calibration.

11. PROCEDURE

11.1. Procedural Variations

11.1.1. Procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance memo. Procedural variations are not allowed for Ohio VAP projects.

11.2. Continuous Liquid/Liquid Extraction from Water Samples

11.2.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to return to room temperature.

11.2.2. Assemble the apparatus. Add approximately 250 mL of methylene chloride (or approximately 100 mL for reduced volume extractor bodies) to the extractor body. Add three to five boiling chips to the round-bottom distilling flask. Label the flask with a LIMS ID label.

11.2.3. Measure the initial sample pH with wide-range pH by inserting a disposable pipette into the sample, and placing a drop of sample onto the wide range pH paper. Record the pH on the extraction benchsheet. pH will be entered manually into the LIMS during level I review.

11.2.4. For 600 series tests, check for the presence of chlorine by inserting a disposable pipette into the sample and placing a drop of sample onto a chlorine test strip. If no chlorine is present, proceed to section 11.2.5. If chlorine is present in any amount, add 80 mg to 100 mg of sodium thiosulfate. Test the sample again. If chlorine is still present, add another 80 to 100 mg of sodium thiosulfate. Repeat sodium thiosulfate additions and testing until the chlorine is gone. Note the presence of chlorine in the appropriate column in the worksheet in the LIMS.

11.2.5. Measure the initial volume using the volume template. Place the template next to the sample bottle and read the volume marking from the template. Record this volume on the benchsheet. Volumes will be entered manually into the LIMS during level I review. Prepare a MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP. See Tables 3 and 4 for

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the appropriate amount of spike to use for each analytical method. Use 1 L of reagent water for method blanks and LCS. If the sample cannot be prepared using continuous liquid/liquid extraction due to matrix, a waste dilution may be required. Refer to SOP NC-OP-043 for the waste dilution procedure.

Note: bottles that do not fit the volume template must be measured using a Class A graduated cylinder.

11.2.6. For pesticide and PCB samples (method series 8000 and method series 600), add 20 mL of TCLP Buffer Fluid #1.

11.2.7. Use 250mL of leachate for TCLP semivolatiles and TCLP pesticides. Use 1000 mL of leachate for SPLP semivolatiles and SPLP pesticides. Dilute to about 1 liter with reagent water.

11.2.8. For a TCLP method blank and LCS, measure 250 mL of the buffer solution in a beaker and transfer to the continuous liquid/liquid extractor. Dilute to about 1 liter with reagent water. For an SPLP method blank and LCS, measure 1000 mL of the buffer solution using the volume template and transfer to the continuous liquid/liquid extractor. No dilution with reagent water is required.

11.2.9. Less than one liter of sample may be used for highly contaminated samples, or if the reporting limit can be achieved with less than one liter of sample. In this event, dilute the sample to about 1 liter with reagent water. This must be documented with a Non-Conformance Memo.

11.2.10. Add reagent water to the extractor body until approximately 150 mL (approximately 50mL for reduced volume preps) of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Prime the extractor using reagent water.

11.2.11. The MB and samples are spiked with the surrogates, the LCS and matrix spikes with the surrogates, and matrix spiking solutions. All samples are spiked in the original sample bottle.

11.2.12. Pour the sample into the extraction vessel. Use 15 mL of Methylene Chloride to rinse the bottle and pour it directly into the extraction vessel. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH, as necessary. Recheck the sample with pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible. Attach cold condenser (about 10^{o}C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours (24 hours required for 600 series).

Note: for BNA analyte Acrylamide there is **no** pH adjustment. Separate batch QC (without pH adjustment) must be prepared for Acrylamide.

11.2.13. If extraction at a secondary pH is required (see Table 1), turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure by inserting a disposable pipette into the sample, and placing a drop of sample on the pH paper. Record the adjusted pH on the benchsheet. Re-attach the condenser, and turn on the heating mantle. Extract for 18-24 hours.

11.2.14. Turn off the heating mantle and allow the extractor to cool.

11.2.15. Cover with aluminum foil and refrigerate if the extract is not concentrated immediately. Refer to Section 11.4 for concentration.

11.3. Concentration

11.3.1. According to the type of sample, different solvents and final volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.3.2. Kuderna-Danish (KD) Method

11.3.2.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL K-D flask. Label the CT and K-D. Transfer the sample to the labeled K-D flask, filtering Continuous Liquid/Liquid and Soxhlet samples through funnels filled with sodium sulfate. Rinse the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

11.3.2.2. Add one or two clean boiling chips to the KD flask and attach a three-ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column. (This is important to ensure that the balls are not stuck, and the column will work properly). Attach to the KD flask.

11.3.2.3. Place the KD apparatus on a water bath (90-98^{o}C) so the tip of the concentrator tube is submerged. The water level must not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter; but the chambers should not flood.

11.3.2.4. Concentrate to 15-20 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent to the top of the Snyder Column, and then continue the water bath concentration back down to 5-8 mL. Refer to Table 2 for details of

exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.3.2.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.4. Nitrogen Evaporation to Final Concentration

11.4.1. Transfer the CT to the evaporation apparatus.

11.4.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but must not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.4.3. Refer to Table 1 to determine the final volume needed for a specific test method. Evaporate to slightly less than the required final volume.

11.4.4. Quantitatively transfer the extract to the appropriate final container and dilute to the appropriate final volume using the “standard” glass vial noted in Section 10.1. Cap the sample and affix the appropriate label. The sample is now ready for analysis.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Record all sample and associated QC information in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must have initial and continuing demonstrations of capability data on file and the laboratory must maintain corresponding method detection limit files.

13.1.2. See SOP NC-QA-028, current revision, for details on demonstrations of capability. See SOP NC-QA-021, current revision, for details on MDLs.

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

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15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Extracted aqueous samples contaminated with methylene chloride are disposed of in the Methylene chloride collection tank. This tank is then periodically rolled to the Tank Room, the pH is verified, contents are neutralized with sodium bicarbonate, pH re-verified, and Dichloromethane waste drained into a waste drum located outside the building. The wastewater is discharged to the POTW.

15.2.2. Used sodium sulfate and filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.3. **Assorted flammable solvent waste from various rinses**: These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.4. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.5. **Hexane- Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.6. **Waste Hexane in vials:** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Waste Methylene Chloride sample vials**: These vials are placed in the vial waste located in the GC prep laboratory.

15.2.8. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCBs must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB, and PCB vial waste.

15.2.9. Solvent Recovery System Waste. Methylene Chloride waste from the Solvent Recovery System is collected and disposed of in the liquid-liquid separation unit. Acetone/Methylene Chloride waste from this system is disposed of in the flammable waste containers located in the laboratory.

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16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3520C, and 3580A

16.1.2. Federal Register - Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

16.1.3. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

16.1.4. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Corporate Quality Management Plan (CQMP), current version

16.1.7. Revision History

Historical File:		Revision 3.4: 10/16/98		Revision 0: 03/12/08 (NC-OP-032)
(formerly CORP-OP-0001NC)		Revision 3.5: 04/22/99		Revision 1: 01/07/09 (NC-OP-032)
		Revision 3.6: 05/13/99		Revision 0: 03/03/11 (NC-OP-037)
		Revision 3.7: 03/20/01		Revision 1: 04/24/12
		Revision 3.8: 05/23/01		Revision 2: 02/05/13
		Revision 3.9: 04/22/02		Revision 3: 04/05/13
		Revision 4.0: 02/04/03		Revision 4: 06/04/14
		Revision 4.1: 10/07/03		Revision 5: 11/09/15
		Revision 4.2: 01/30/06		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. GC/MS Analysis based on Method 8270C and 8270D, NC-MS-018

16.2.6. Analysis of Pesticides and PCBs by EPA Method 608, NC-GC-007

16.2.7. GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Method 625, NC-MS-003

16.2.8. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.9. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.10. Gas Chromatographic Analysis of PCBs Based on Methods 8082 and 8082A, NC-GC-045

16.2.11. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.3. Sodium Sulfate is heated for 1 hour at 800°C to purify. The reference method lists a minimum of 4 hours at 400°C.

17.1.4. The SW-846 method recommends that the water bath temperature for the concentration step be set at 10-20 °C above the solvent boiling point. The laboratory maintains the water bath temperatures at 90 – 98 °C.

17.2. Tables

TABLE 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA	Acid ext; 1-2 or Base ext; 11-12	Acid ext; 1-2 or Base ext; 11-12
BNA Acrylamide only[2]	NA	NA
Pesticide/PCB	5-9	None
TPH	1-2	None

[1] If the laboratory has validated acid only 8270 extraction for the target compound list required then the base extraction step may be omitted. The required validation consists of a four-replicate initial demonstration of capability and a method detection limit study (see Section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

[2] If the laboratory is analyzing for Acrylamide, the pH of the sample is not adjusted.

TABLE 2
Final Volumes and Exchange Solvents

Type	Exchange Solvent for Analysis	Final Volume for Analysis in mL
BNA	N/A	2.0 mL
PCB	Approximately 18 mL hexane – water	5.0 for SPLP / TCLP 2.0 for regular aqueous and LVI*
Pesticides	Approximately 18 mL hexane	5.0 for SPLP2.0 for regular aqueous*
Pesticides/TCLP	Approximately 18 mL hexane	3.0 mL
BNA – SIM	N/A	2.0 mL 5.0 mL for reduced volume preps
TPH	N/A	5 mL

* Michigan work requires a final volume of 2 mL.

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

TABLE 3 Surrogate Spiking Solutions		
Analyte Group	**Surrogate Spike Solution ID**	**Volume (mL)**
BNA	20 ppm BNA Surrogate Spike	1.0 mL
PEST	0.2 ppm DCB/TCX	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
TPH	40 ng/uL o-Terphenyl	1.0 mL
PCB	0.2 ppm DCB/TCX	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
BNA – SIM	20 ppm BNA Surrogate Spike	0.1 mL

* Note: surrogate spiking levels are adjusted for reduced volume preps which utilize large volume injection.

TABLE 4 Matrix Spike and LCS Solutions		
Analyte Group	**Matrix Spike Solution ID**	**Volume (mL)**
PEST	1.0 ppm Pest NPDES Spike	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
TPH	2500 ppm Diesel Spike	1.0 mL
PCB	10 ppm PCB Spike	0.25 mL for 2 mL final, 0.5 mL for 5 mL final
BNA – SIM	20 ppm BNA List 1	0.1 mL
BNA	20 ppm BNA All-Analyte Spike	1.0 mL

* Note: surrogate spiking levels are adjusted for reduced volume preps which utilize large volume injection.

TABLE 5

Surrogate Spike Components

Analyte Group	Compounds	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	20
	Nitrobenzene-d_5	20
	2-Fluorophenol	20
	Phenol-d_5	20
	2,4,6-Tribromophenol	20
	Terphenyl-d_{14}	20
Pesticides PCB	Decachlorobiphenyl	0.2
	Tetrachloro-m-xylene	0.2
TPH	o-Terphenyl	40.0

TABLE 6
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
BNA	1,1'Biphenyl	20
	1,2,4,5-Tetrachlorobenzene	20
	1,2,4-Trichlorobenzene	20
	1,2-Dichlorobenzene	20
	1,2-Diphenylhydrazine	20
	1,3-Dichlorobenzene	20
	1,3-Dinitrobenzene	20
	1,4-Dichlorobenzene	20
	1,4-Dioxane	20
	1-Methylnaphthalene	20
	2,2'-oxybis[1-chloropropane]	20
	2,3,4,6-Tetrachlorophenol	20
	2,4,5-Trichlorophenol	20
	2,4,6-Trichlorophenol	20
	2,4-Dichlorophenol	20
	2,4-Dimethylphenol	20
	2,4-Dinitrophenol	40
	2,4-Dinitrotoluene	20
	2,6-Dichlorophenol	20
	2,6-Dinitrotoluene	20
	2-Chloronaphthalene	20
	2-Chlorophenol	20
	2-Methylnaphthalene	20
	2-Methylphenol	20
	2-Nitroanaline	20
	2-Nitrophenol	20
	3&4-Methylphenol	20
	3,3'-Dichlorobenzidine	40
	3-Methylphenol	10
	3-Nitroanaline	20
	4,6-Dinitro-2-methylphenol	40
	4-Bromophenyl phenyl ether	20
	4-Chloro-3-methylphenol	20
	4-Chloroanaline	20
	4-Chlorophenyl phenyl ether	20
	4-Methylphenol	10
	4-Nitroanaline	20
	4-Nitrophenol	40

TABLE 6
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
BNA	Acenaphthene	20
	Acenaphthylene	20
	Acetophenone	20
	Aniline	20
	Anthracene	20
	Atrazine	40
	Azobenzene	20
	Benzaldehyde	40
	Benzidine	40
	Benzo[a]anthracene	20
	Benzo[a]pyrene	20
	Benzo[b]fluoranthene	20
	Benzo[g,h,i]perylene	20
	Benzo[k]fluoranthene	20
	Benzoic acid	40
	Benzyl alcohol	20
	Bis(2-chloroethoxy)methane	20
	Bis(2-chloroethyl)ether	20
	Bis(2-ethylhexyl)phthalate	20
	Butyl benzyl phthalate	20
	Caprolactam	40
	Carbazole	20
	Chrysene	20
	Dibenz(a,h)anthracene	20
	Dibenzofuran	20
	Diethyl phthalate	20
	Dimethyl phthalate	20
	Di-n-butyl phthalate	20
	Di-n-octyl phthalate	20
	Fluoranthene	20
	Fluorene	20
	Hexachlorobenzene	20
	Hexachlorobutadiene	20
	Hexachlorocyclopentadiene	20
	Hexachloroethane	20
	hexadecane	20
	Indene	40
	ideno[1,2,3-cd]pyrene	20
	isophorone	20
	Methyl phenols, Total	40
	Naphthalene	20
	n-Decane	20

TABLE 6
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
	Nitrobenzene	20
	N-Nitrosodimethylamine	20
	N-Nitrosodi-n-propylamine	20
	N-Nitrosodiphenylamine	40
	n-Octadecane	20
	Pentachlorophenol	40
	Phenanthrene	20
	Phenol	20
	Pyrene	20
	Pyridine	20
Pesticides TCLP	Heptachlor	0.5
	Heptachlor epoxide	0.5
	Lindane	0.5
	Endrin	0.5
	Methoxychlor	1.0
Pesticides NPDES	Aldrin	1.0
	Alpha-BHC	1.0
	beta-BHC	1.0
	delta-BHC	1.0
	gamma-BHC (Lindane)	1.0
	4,4'-DDD	1.0
	4,4'-DDE	1.0
	4,4'-DDT	1.0
	Dieldrin	1.0
	alpha-Endosulfan	1.0
	beta-Endosulfan	1.0
	Endosulfan Sulfate	1.0
	Endrin	1.0
	Heptachlor	1.0
	Heptachlor Epoxide	1.0
TPH	Diesel Fuel	2500 **µg/mL**

Note: *Other analytes may be added per program requirements. For OVAP, only analytes listed in the reference methods are certified.*

Title: SEPARATORY FUNNEL EXTRACTION OF ORGANIC COMPOUNDS FROM WATERS BASED ON METHOD SW846 3510C AND 600 SERIES

[Methods: SW846 3510C and 600 Series]

Approvals (Signature/Date):

Technology Specialist	02/22/18 Date	Health & Safety Coordinator	02/26/18 Date
Quality Assurance Manager	03/19/18 Date	Technical Director	03/01/18 Date

This SOP was previously identified as SOP No. NC-OP-038, Rev 6, dated 2/17/17

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1. SCOPE AND APPLICATION

1.1. This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in aqueous and TCLP leachate matrices for analysis by Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS) using Separatory (Sep) Funnel Extraction. The procedures are based on SW846 and 600 series methodologies and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8270C, 8270D, 8015B, 8015C, 8015D, 608, 608.3, 625.1, and 625.

1.1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

2. SUMMARY OF METHOD

2.1. Separatory Funnel Extraction

2.1.1. A measured volume of sample, (typically one liter, or 250 mL for low volume initiative/ [LVI]) is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2. Concentration

2.2.1. Procedures are presented for drying and concentration of the extract to final volume for analysis.

3. DEFINITIONS

3.1. Definitions of terms and acronyms used in this SOP may be found in the glossary of the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

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5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds must be prepared in the hood.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 mg/m^3 - Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.

Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.6. The preparation of hazardous standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride must be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints that can become stuck. Technicians must use Kevlar or other cut/puncture-resistant gloves when separating stuck joints.

5.9. 3510 Separatory Funnel

5.9.1. The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. Initial venting must be done immediately after the sample container has been sealed and inverted. Periodic venting may be necessary during the extraction. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity. The use of a face shield over safety glasses or goggles is recommended. Keep the sash on the fume hood as low as reasonably possible.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware must be cleaned per Glassware Washing, SOP NC-QA-014.

6.2. Equipment and supplies for extraction procedures:

EQUIPMENT AND SUPPLIES	Sep Fun.	Conc
Separatory funnel: 2 L	√	
Separatory funnel rack	√	
pH indicator paper, ranges: 0-14, 7.5-14, 0-6	√	
Chlorine test strips: 0-10 ppm		
Class A Graduated cylinder: 1 liter. (other sizes may be used as needed)	√	√
Centrifuge	√	
Methylene chloride collection tank	√	√
Initial volume template	√	
Solvent dispenser pump or 100 mL Class A graduated cylinder		√
Boiling chips: contaminant-free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent)		√
Beakers: 250 & 400 mL, graduated 450mL wide-mouth glass jars	√ √	√ √
Kuderna-Danish (K-D) apparatus: 500 mL		√
Concentrator tube: 10 mL, attached to K-D with clips		√
Snyder column: three-ball macro		√
Water Bath: heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.		√
Vials: glass, 2 mL, 2.5mL, and 40 mL capacity with Teflon®-lined screw-cap		√
Nitrogen blowdown apparatus		√
Nitrogen: reagent grade.		√
Culture tubes: 10 mL, 16 mmx100 mm		√
Microliter pipette, syringe 1 mL	√	
Glass wool	√	
Glass funnel: 75 X 75 mm	√	√
Disposable pipettes, 5 ¾ in, and 9in.	√	√
Aluminum foil	√	√
Paper towels	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

7.1.1. All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep Fun.	Conc
Sodium hydroxide (NaOH), pellets: reagent grade	√	
Sodium hydroxide solution, 10 N: dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	
Sulfuric acid (H_2SO_4), concentrated: reagent grade	√	
Sulfuric acid (1:1): carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	
Hydrochloric acid (HCl)	√	
Sodium Thiosulfate: reagent grade	√	
Organic free reagent water	√	
Sodium Chloride (NaCl) crystals	√	
Sodium Chloride Solution: add NaCl crystals to DI water until the DI water is saturated.	√	
Sodium sulfate (Na_2SO_4), granular anhydrous: purify by heating at 800°C a minimum of one hour.	√	√
Extraction/exchange solvents: methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√
Acetone, methylene chloride: used for cleaning	√	√
TCLP Fluid #1: Made fresh daily in the Leachates department, or see SOP NC-OP-033 TCLP-SPLP	√	

7.2. Standards

7.2.1. Stock Standards

7.2.1.1. Stock standards are purchased as certified solutions. Semivolatile stock standards for all of the applicable methods are stored according to manufacturer's instructions. All stock standards must be protected from light. Stock standard solutions must be replaced after one year from the time of preparation, if prepared in house, or from the time the ampoule is opened, if purchased. Standards must be allowed to come to room temperature before use.

7.2.2. Surrogate Spiking Standards

7.2.2.1. Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced at least every six months, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.3. Matrix Spiking and Laboratory Control Spiking Standards

7.2.3.1. The same spiking solution is used for the matrix spike (MS) and the Laboratory Control Sample (LCS). Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced at least every six months, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.4. See SOP NC-QA-017 for additional information on Standards and Reagents.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. The holding time for aqueous samples is seven days from sampling to extraction.

8.3.2. For TCLP leachates, the holding time is 14 days from sampling to the leach process. The extraction holding time is seven days from when the TCLP Leach tumbling has been completed, excluding the filtration step, to the extraction step. If the filtration step requires extended times, this time counts as part of the seven-day holding time.

8.3.3. Analysis of the extracts is completed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix which are processed together, using the same procedures and reagents. The batch must contain a method blank (MB), an LCS, and a matrix spike/matrix spike (MS/MSD) duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and un-spiked sample duplicate in place of the MS/MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. See Policy QA-003 for further definition of the batch.

9.2. Sample Count

9.2.1. Laboratory-generated QC samples (MB, LCS, MS, and MSD) are not included in the sample count. Field samples are included.

9.3. Method Blank

9.3.1. A MB consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the MB at the same concentration as the samples. See Table 3 for the appropriate amount of surrogate to use for each analytical method. The MB is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated compound concentrations or false positive results.

9.3.2. Aqueous MBs use 1000 mL of reagent water (250 mL for LVI) spiked with the surrogates. The MB goes through the entire preparation procedure.

9.3.3. TCLP MBs use 250 mL of leachate fluid spiked with the surrogates. SPLP MBs use 1000 mL of leachate fluid spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The MB goes through the entire preparation procedure.

9.4. Laboratory Control Sample (LCS)

9.4.1. LCSs are well-characterized laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the preparative and analytical processes, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire preparative and analytical procedure.

9.4.2. The LCS is made up in the same way as the MB (see Sections 9.3.1 through 9.3.3), but spiked with the LCS standard and the surrogates. See Tables 3 and 4 for the appropriate amount of spike to use for each analytical method.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Each applicable sample, MB, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the applicable recovery limits. See Table 3 for the appropriate amount of surrogate spike to use for each analytical method.

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9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. A MS is an environmental sample to which known concentrations of target analytes have been added. A MSD is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and matrix spike. See Tables 3 and 4 for the appropriate amount of spike to use for each analytical method. An MS/MSD is required for every 20 samples, otherwise a nonconformance memo must be included with associated samples.

9.7. QC requirements can be found in the various associated analytical SOPs.

9.8. Control Limits

9.8.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.8.2. Laboratory control limits are internally generated and updated periodically, unless method specified. Control limits are easily accessible via the LIMs.

9.9. Method Detection Limits (MDLs) and MDL Checks

9.9.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.9.2. MDLs are accessible via the LIMs.

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volumes of solvents into the appropriately sized glass culture tubes, gravimetrically. The “standard” glass culture tubes are sealed, and the meniscus is noted. The glass culture tubes containing the sample extracts are then compared against the “standard” glass culture tubes of the appropriate volume and solvent to ensure the volumes are consistent. See Table 2 for final volumes.

11. PROCEDURE

11.1. Procedural variations are allowed only if deemed necessary in the professional judgment of QA, Operations Supervisor, or designee, to accommodate variation in sample matrix, chemistry, sample size, or other conditions. Any variation in procedure must be completely documented using a Nonconformance memo, and approved by a supervisor. Procedural variations are not allowed for Ohio VAP

projects.

11.2. Separatory Funnel Liquid/Liquid Extraction of Water Samples

11.2.1. Remove surrogate and matrix spiking solutions from the refrigerator and allow to warm to room temperature.

11.2.2. Measure the initial sample pH by inserting a disposable pipette into the sample, and placing a drop of sample on the wide-range pH paper. Record the pH value in LIMS.

11.2.3. For 600 series tests, check for the presence of Chlorine by inserting a disposable pipette into the sample and placing a drop of sample onto a Chlorine test strip. If no Chlorine is present, proceed to section 11.2.4. If chlorine is present in any amount, add 80g to 100g of sodium thiosulfate. Test the sample again. If chlorine is still present, add another 80 to 100 g of sodium thiosulfate. Repeat sodium thiosulfate additions and testing until the chlorine is gone. Note the presence of chlorine in the appropriate column in the worksheet in the LIMS.

11.2.4. Measure the initial volume using the bottle volume template. Place the template next to the sample bottle and read the volume marking from the template. Record this volume on the benchsheet. The normal sample volume is 1 liter (or 250 mL for LVI) Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for highly contaminated samples. If the sample cannot be prepared using a separatory funnel due to matrix issues, a waste dilution may be required. Refer to Section 11.3 for the waste dilution procedure.

11.2.5. Prepare a MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP. Use 1 L of reagent water for MBs and LCS. Use 1000 mL of sample for the MS/MSD. The LCS and MS/MSD are spiked with the surrogate and matrix spike solutions, the MB only with the surrogates. See Tables 3 and 4 for the appropriate amount of spike solution to use for each analytical method.

11.2.6. Use 250 mL of leachate for TCLP pesticides and TCLP semivolatiles, measured in a beaker. Use 1000 mL of leachate for SPLP semivolatiles and SPLP pesticides measured in a beaker.

11.2.7. For a TCLP method blank and LCS, measure 250 mL of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add approximately 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction, if needed, due to matrix. For an SPLP MB and LCS, measure 1000 mL of the buffer solution using the volume template and transfer to the separatory funnel.

11.2.8. Spike the samples with the appropriate surrogate and/or spike solutions. All samples are spiked in the original sample bottle with the exception of TCLP.

11.2.9. Pour the sample into a separatory funnel. Rinse the sample bottle with approximately 60 mL methylene chloride. Add the rinsate to the separatory funnel. Use approximately 60 mL of methylene chloride per sample (40mL for LVI).

11.2.10. Place a labeled collection jar under each separatory funnel. Place a small amount of glass wool into a funnel and fill with anhydrous sodium sulfate. Place one of these prepared funnels on each collection jar.

11.2.11. Adjust sample pH as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH, as necessary. Recheck the sample by inserting a disposable pipette into the sample, and placing a drop of sample onto the pH paper. Record adjusted pH, spiking volumes, and LIMS standard ID numbers on the benchsheet. Return spiking solutions that require cold storage to the refrigerator as soon as possible.

11.2.12. For PCBs, add approximately 10 mL of TCLP buffer solution number 1 to each sample and associated QC.

11.2.13. Seal and shake or rotate the separatory funnel vigorously for two minutes with periodic venting to release excess pressure. An autoshaker may be used to shake and rotate the separatory funnel.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting must be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

11.2.14. Allow the organic layer to separate from the water phase until complete visible separation has been achieved. A minimum of 10 minutes is required for the organic layer to separate from the water phase for the first serial extraction. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in the continuous liquid-liquid extraction SOP NC-OP-037 (If this is done, the sample must be extracted as part of a valid CLLE batch).

*__Note__: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes must recover at least 50 mL of solvent.

11.2.15. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water, replace the existing sodium sulfate with fresh sodium sulfate. For 8270 acid fraction analysis, rinse the funnel immediately with a fresh aliquot (approximately 50 mL) of DCM.

11.2.16. Repeat the extraction process two more times using fresh approximately 60 mL portions of solvent, combining the three solvent extracts in the collection container.

11.2.17. If extraction at a secondary pH is required, replace the filtration funnel and adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure by inserting a disposable pipette into the sample, and placing a drop of sample onto the pH paper. Record the adjusted pH on the benchsheet. Serially extract with three approximately 60 mL portions of methylene chloride (40 mL for reduced volume preps), as outlined in Steps 11.2.7 to 11.2.10. Collect these three extracts in the same container used for the previous fraction.

11.2.18. Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

11.2.19. Dispose of solvent and water remaining in the extractor into the appropriate waste container.

11.2.20. Cover with aluminum foil and refrigerate, if the extract is not going to be concentrated immediately. Refer to Section 11.3 for concentration.

11.3. Concentration

11.3.1. According to the type of sample, different solvents and final volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

11.3.2. Kuderna-Danish (KD) Method

11.3.2.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube (CT) to the 500 mL KD flask. Label the CT and KD with the sample ID. Transfer the sample to the labeled K-D flask, rinse the collection vessel with 20-30 mL DCM and transfer to the KD to complete the quantitative transfer.

11.3.2.2. Add one or two clean boiling chips to the KD flask and attach a three-ball Snyder Column. Add approximately 1 mL of clean

methylene chloride to the top of the Snyder column. (This is important to ensure that the balls are not stuck, and the column will work properly).

11.3.2.3. Place the KD apparatus on a water bath (90-98°C) so the tip of the concentrator tube is submerged. The water level must not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter; but the chambers should not flood.

11.3.2.4. Concentrate to 15-20 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent to the top of the Snyder Column, and then continue the water bath concentration back down to 5-8 mL. Refer to Table 2 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.3.2.5. Remove the KD apparatus from the water bath and allow to cool and drain for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.3.3. Nitrogen Evaporation to Final Concentration

11.3.3.1. Transfer the CT to the evaporation apparatus.

11.3.3.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but must not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.3.3.3. Refer to Table 2 to determine the final volume needed for a specific test method. Evaporate to slightly less than the required final volume.

11.3.3.4. Quantitatively transfer the extract to the appropriate final container and dilute to the appropriate final volume using the “standard” glass tube noted in Section 10.1.

11.3.3.5. Cap the sample and affix the appropriate label. The sample is now ready for analysis.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.4. Analytical Documentation

11.4.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.4.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

Note: When making new standards, it is required that all information entered into TALS is reviewed by another analyst.

11.4.3. Record all sample and associated QC information directly into LIMS. Level I and Level II review is performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which must contain all the analytes of interest. The spiking level must be equivalent to a mid-level calibration. (For certain tests, more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.1.2. Four aliquots of the QC check sample are prepared and analyzed using the same procedures used for the samples.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. See SOPs NC-GC-038, NC-MS-018, NC-MS-003, and NC-GC-007 for detailed information on the determinative methods.

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13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method the policies in Section 13 of the Corporate Environmental Health and Safety Manual
(CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Extracted aqueous samples contaminated with methylene chloride. This tank is then periodically rolled to the tank room, the pH is verified, the contents are neutralized with sodium bicarbonate, the pH re-verified and the Dichloromethane waste drained into a waste drum located outside the building. The wastewater is discharged to the POTW.

15.2.2. Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.3. **Assorted flammable solvent waste from various rinses**. These wastes are put into the halogenated/non-halogenated 25-gallon solvent waste container located under the fume hood in extractions.

15.2.4. Methylene chloride waste from various rinses: These wastes are disposed of in the liquid-liquid separation unit.

15.2.5. Hexane-Hexane waste: These samples are to be disposed in the flammable waste.

15.2.6. Waste Hexane in vials. These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. Waste Methylene Chloride sample vials. These vials are placed in the vial waste located in the GC prep laboratory.

15.2.8. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCBs must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB, and PCB vial waste.

15.2.9. Solvent Recovery System Waste. Methylene Chloride waste from the Solvent Recovery System is collected and disposed of in the liquid-liquid separation unit. Acetone/Methylene Chloride waste from this system is disposed of in the flammable waste containers located in the laboratory.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B and 3510C

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. The appropriate release of the Federal Register - Environmental Protection Agency, 40 CFR, Part 136, Appendix A to part 136 – Methods for Organic Chemical Analysis of Municipal and Industrial Waste Water. Specific Methods are kept on file.

16.1.6. Revision History

Historical File:		Revision 3.4: 10/16/98		Revision 0: 03/12/08 (NC-OP-032)
(formerly CORP-OP-0001NC)		Revision 3.5: 04/22/99		Revision 1: 01/07/09 (NC-OP-032)
		Revision 3.6: 05/13/99		Revision 0: 03/03/11 (NC-OP-038)

		Revision 3.7: 03/20/01		Revision 1A: 04/24/12
		Revision 3.8: 05/23/01		Revision 2: 02/05/13
		Revision 3.9: 04/22/02		Revision 3: 05/15/13
		Revision 4.0: 02/04/03		Revision 4: 08/20/14
		Revision 4.1: 10/07/03		Revision 5: 11/25/15
		Revision 4.2: 01/30/06		Revision 6: 02/17/17

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.6. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.7. Gas Chromatographic Analysis of PCBs Based on Methods 8082 and 8082A, NC-GC-045

16.2.8. GC/MS Analysis based on Method 8270C and 8270D, NC-MS-018

16.2.9. Analysis of Pesticides and PCBs by EPA Method 608 and 608.3, NC-GC-007

16.2.10. GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Method 625, NC-MS-003

16.2.11. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Spiking levels for method 608 and 608.3 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.1.3. Sodium sulfate is heated for 1 hour at 800°C to purify. The reference method lists a minimum of 4 hours at 400°C.

17.2. Tables

TABLE 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH	Secondary Ext. pH
BNA	Acid ext; 1-2 or Base ext; 11-12	Acid ext; 1-2 or Base ext; 11-12
Pesticide/PCB	5-9	None
TPH	As received	None

Note: If the laboratory has validated acid only 8270 extraction for the target compound list required, then the base extraction step may be omitted. The required validation consists of a four-replicate initial demonstration of capability and a method detection limit study (see Section 13). Additionally, either of the base or acid fractions of Method 8270 can be run first.

TABLE 2
Final Volumes and Exchange Solvents

Type	Exchange Solvent for Analysis	Final Volume for Analysis in mL
PCB	Approximately 18 mL Hexane	2.0 or 5.0
Pesticides	Approximately 18 mL Hexane	2.0 or 5.0
BNA –	N/A	2.0 mL 5.0 mL for reduced volume preps
TPH	N/A	5.0 mL
BNA-SIM	NA	2.0 mL

* Michigan work requires a final volume of 2 mL.

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

Table 3

Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Non-LVI Spike Volume	LVI Spike Volume
BNA	20 ppm BNA Surrogate Spike	1.0 mL	400 uL
PEST	0.2 ppm DCB/TCX	1 mL for 2 mL final, 1 mL for 5 mL final	NA
TPH	40 ng/uL o-Terphenyl	1.0 mL	200 uL
PCB	0.2 ppm DCB/TCX	1 mL for 2 mL final, 1 mL for 5 mL final	1 mL
BNA – SIM	20 ppm BNA Surrogate Spike	0.1 mL	0.4 mL (1,4-Dioxane)

* Note surrogate spiking levels adjusted for reduced volume preps which utilize large volume injection

Table 4

LCS and Matrix Spiking Solutions

Analyte Group	LCS Spike Solution ID	Non-LVI Spike Volume	LVI Spike Volume
BNA	20 ppm BNA Spike	1.0 mL	400 uL
PEST	1.0 ppm Pest NPDES Spike	0.25 mL for 2 mL final, 0.5 mL for 5 mL final	NA
TPH	2500 ppm Diesel Spike	1.0 mL	200 uL
PCB	10 ppm PCB Spike	0.25 mL for 2 mL final, 0.5 mL for 5 mL final	0.25 mL
BNA – SIM	20 ppm BNA Spike	0.1 mL	0.4 mL (1,4-Dioxane)

* Note surrogate spiking levels adjusted for reduced volume preps which utilize large volume injection

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TABLE 5 Surrogate Spike Components		
Analyte Group	**Compounds**	**Conc. (µg/mL)**
BNA	2-Fluorobiphenyl	20
	Nitrobenzene-d_5	20
	p-Terphenyl-d_{14}	20
	2-Fluorophenol	20
	Phenol-d_6	20
	2,4,6-Tribromophenol	20
	1,2-Dichlorobenzene-d_4	20
	2-Chlorophenol-d_4	20
Pesticides PCB	Decachlorobiphenyl	0.2
	Tetrachloro-m-xylene	0.2
TPH	Nonane (C9)	40.0

TABLE 6 LCS and Matrix Spike Components		
Type	**Compounds**	**Conc. (µg/mL)**
BNA	1,1'Biphenyl	20
	1,2,4,5-Tetrachlorobenzene	20
	1,2,4-Trichlorobenzene	20
	1,2-Dichlorobenzene	20
	1,2-Diphenylhydrazine	20
	1,3-Dichlorobenzene	20
	1,3-Dinitrobenzene	20
	1,4-Dichlorobenzene	20
	1,4-Dioxane	20
	1-Methylnaphthalene	20
	2,2'-oxybis[1-chloropropane]	20
	2,3,4,6-Tetrachlorophenol	20
	2,4,5-Trichlorophenol	20
	2,4,6-Trichlorophenol	20
	2,4-Dichlorophenol	20
	2,4-Dimethylphenol	20
	2,4-Dinitrophenol	40
	2,4-Dinitrotoluene	20
	2,6-Dichlorophenol	20
	2,6-Dinitrotoluene	20
	2-Chloronaphthalene	20
	2-Chlorophenol	20

TABLE 6
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
BNA	2-Methylnaphthalene	20
	2-Methylphenol	20
	2-Nitroanaline	20
	2-Nitrophenol	20
	3&4-Methylphenol	20
	3,3'-Dichlorobenzidine	40
	3-Methylphenol	10
	3-Nitroanaline	20
	4,6-Dinitro-2-methylphenol	40
	4-Bromophenyl phenyl ether	20
	4-Chloro-3-methylphenol	20
	4-Chloroanaline	20
	4-Chlorophenyl phenyl ether	20
	4-Methylphenol	10
	4-Nitroanaline	20
	4-Nitrophenol	40
	Acenaphthene	20
	Acenaphthylene	20
	Acetophenone	20
	Aniline	20
	Anthracene	20
	Azobenzene	20
	Benzidine	40
	Benzo[a]anthracene	20
	Benzo[a]pyrene	20
	Benzo[b]fluoranthene	20
	Benzo[g,h,i]perylene	20
	Benzo[k]fluoranthene	20
	Benzoic acid	40
	Benzyl alcohol	20
	Bis(2-chloroethoxy)methane	20
	Bis(2-chloroethyl)ether	20
	Bis(2-ethylhexyl)phthalate	20
	Butyl benzyl phthalate	20
	Carbazole	20
	Chrysene	20
	Dibenz(a,h)anthracene	20
	Dibenzofuran	20
	Diethyl phthalate	20
	Dimethyl phthalate	20
	Di-n-butyl phthalate	20
	Di-n-octyl phthalate	20

TABLE 6
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
	Fluoranthene	20
	Fluorene	20
	Hexachlorobenzene	20
	Hexachlorobutadiene	20
	Hexachlorocyclopentadiene	20
	Hexachloroethane	20
	hexadecane	20
	Indene	40
	ideno[1,2,3-cd]pyrene	20
	isophorone	20
	Naphthalene	20
	n-Decane	20
	Nitrobenzene	20
	N-Nitrosodimethylamine	20
	N-Nitrosodi-n-propylamine	20
	N-Nitrosodiphenylamine	40
	n-Octadecane	20
	Pentachlorophenol	40
	Phenanthrene	20
	Phenol	20
	Pyrene	20
	Pyridine	20
Pesticides TCLP	Heptachlor	0.5
	Heptachlor epoxide	0.5
	Lindane	0.5
	Endrin	0.5
	Methoxychlor	1.0
Pesticides NPDES	Aldrin	1.0
	Alpha-BHC	1.0
	beta-BHC	1.0
	delta-BHC	1.0
	gamma-BHC (Lindane)	1.0
	4,4'-DDD	1.0
	4,4'-DDE	1.0
	4,4'-DDT	1.0
	Dieldrin	1.0
	alpha-Endosulfan	1.0
	beta-Endosulfan	1.0
	Endosulfan Sulfate	1.0

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TABLE 6 LCS and Matrix Spike Components		
Type	**Compounds**	**Conc. (µg/mL)**
	Endrin	1.0
	Heptachlor	1.0
	Heptachlor Epoxide	1.0
TPH	Diesel Fuel	2500 **µg/mL**

Title: SONICATION EXTRACTION OF ORGANIC COMPOUNDS FROM SOILS BASED ON METHOD SW846 3550C

[Methods: SW846 3550C]

Approvals (Signature/Date):

Technology Specialist — 07/20/17 Date	Health & Safety Coordinator — 07/21/17 Date
Quality Assurance Manager — 09/27/17 Date	Technical Director — 09/08/17 Date

This SOP was previously identified as SOP No. NC-OP-039, Rev 4, dated 6/23/16

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1. SCOPE AND APPLICATION

1.1. This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in soil matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS) using Sonication Extraction. The procedures are based on SW846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8270C, 8270D, 8015B, 8015C, and 8015D.

1.1.2. The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

2. SUMMARY OF METHOD

2.1. Sonication Extraction

2.1.1. A measured weight of sample is mixed with anhydrous sodium sulfate until free flowing. This is solvent extracted three times using an ultrasonic horn.

2.2. Concentration

2.2.1. Procedures are presented for drying and concentration of the extract to final volume for analysis.

3. DEFINITIONS

3.1. Definitions of terms and acronyms used in this SOP may be found in the glossary of the current version of the TestAmerica Canton Quality Assurance Manual (QAM).

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

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5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut-resistant gloves must be worn doing any task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded. Other gloves must be cleaned immediately when contaminated.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds must be prepared in the hood.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause light-headedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Exposure to hazardous chemicals must be minimized as much **as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.6. The preparation of hazardous standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride must be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints which can become stuck. Technicians must use Kevlar or other cut/puncture-resistant gloves when separating stuck joints.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware must be cleaned per Glassware Washing, SOP NC-QA-014.

6.2. Equipment and supplies for extraction procedures:

EQUIPMENT AND SUPPLIES	Soni	Conc
Solvent dispenser pump or 100 mL graduated cylinder		√
Boiling chips: contaminant-free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent)		√
450mL wide-mouth glass jars	√	√
Balance: >100 g capacity, accurate ± 0.1 g	√	√
Sonicator (at least 300 watts)	√	
Sonicator horn, 3/4 inch	√	
Micro-tip sonicator horn	√	
Kuderna-Danish (K-D) Apparatus: 500 mL		√
Concentrator tube: 10 mL, attached to K-D with clips		√
Snyder column: three-ball macro		√
Water bath: heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.		√
Vials: glass, 2 mL, and 40 mL capacity with Teflon®-lined screw-cap		√
Nitrogen blowdown apparatus		√
Nitrogen: reagent grade		√
Culture tubes: 10 mL, 16 mmx100 mm		√

EQUIPMENT AND SUPPLIES	Soni	Conc
Microliter pipette , syringe 1 mL	√	
Glass wool	√	√
Glass funnel: 75 X 75 mm	√	√
Disposable pipettes, 5 ¾ in, and 9in.	√	√
Aluminum foil	√	√
Paper towels	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for extraction procedures:

7.1.1. All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Soni	Conc
Sodium sulfate (Na_2SO_4), granular, anhydrous: Purify by heating at 800°C a minimum of one hour.	√	√
Magnesium sulfate	√	
Extraction/exchange solvents: Methylene chloride, hexane, acetone, pesticide quality or equivalent	√	√
Acetone, methylene chloride: used for cleaning	√	√

7.2. Standards

7.2.1. Stock Standards

7.2.1.1. Stock standards are purchased as certified solutions. Semivolatile stock standards are stored according to manufacturer's instructions. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is opened if purchased). Standards must be allowed to come to room temperature before use.

7.2.2. Surrogate Spiking Standards

7.2.2.1. Prepare or purchase surrogate spiking standards at the concentrations listed in Table 4. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light or stored according to manufacturer's instructions. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.3. Matrix Spiking and Laboratory Control Spiking Standards

7.2.3.1. The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 5. Spiking standards are purchased or prepared as dilutions of the stock standards.

7.2.3.2. Spiking solutions must be refrigerated and protected from light or stored according to manufacturer's instructions. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps. Sample containers other than glass, must be documented in a Non-Conformance Memo.

8.3. Holding Times

8.3.1. The holding time for solid and waste samples is 14 days from sampling to extraction.

8.3.2. Unless otherwise specified by regulatory or client programs, the holding time for PCB samples is 1 year from sampling to extraction.

8.3.3. Analysis of the extracts must be completed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike / matrix spike duplicate (MS/MSD). (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS / MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. See Policy QA-003 for further definition of the batch.

9.2. Sample Count

9.2.1. Laboratory-generated QC samples (MB, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.3. Method Blank (MB)

9.3.1. A solid MB consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the MB at the same level as the samples. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.3.2. Solid MBs use approximately 10 g to 30 g of sodium sulfate spiked with the surrogates. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB goes through the entire analytical procedure.

9.4. Laboratory Control Sample (LCS)

9.4.1. Laboratory Control Samples are well-characterized laboratory-generated samples used to monitor the laboratory day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure.

9.4.2. The LCS is made up in the same way as the MB (see Sections 9.3.1 through 9.3.2), but spiked with the LCS standard and the surrogates. See Tables 2 and 3 for the appropriate amount of spike to use for each analytical method.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Each applicable sample, blank, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. See Table 2 for the appropriate amount of surrogate spike to use for each analytical method.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. An MS is an environmental sample to which known concentrations of target analytes have been added. An MSD is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and MS to

demonstrate precision. See Tables 2 and 3 for the appropriate amount of spike to use for each analytical method.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are accessible via the LIMs.

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volumes of solvents into the appropriate sized glass culture tubes gravimetrically. The “standard” glass culture tubes are sealed, and the meniscus is noted by marking a line on the bottles. The glass culture tubes containing the sample extracts are then compared against the “standard” glass culture tubes of the appropriate volume and solvent to ensure the volumes are consistent. (See Table 1 for final volumes)

11. PROCEDURE

11.1. Procedural Variations

11.1.1. Procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance memo. The Nonconformance memo will be filed in the project file. Procedural variations are not allowed for Ohio VAP projects.

11.2. Sonication

11.2.1. Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature if cold stored.

11.2.2. If sample can be mixed easily in the sample jar, mix thoroughly by stirring with a clean plastic or wooden spoon or spatula. If the sample cannot be easily mixed (i.e., clay samples or samples of various and very different particle sizes), use the spoon or spatula to select enough separate portions from locations within the jar to produce a representative sample. Analyst judgment is important in determining how many portions and which locations are used to produce a representative aliquot. If the sample is uniform clay, at least 3 portions should be selected from different locations in the sample jar, if particle sizes or materials indicate a very non-homogenous sample, selection should be made carefully to collect an aliquot that represents the relative percentages of the various particle sizes and types in the sample jar.

11.2.3. Sediment samples require that the water layer is not decanted. Sediment samples must be weighed at a higher weight to account for the dry weight correction.

11.2.4. Weigh approximately 30 g of sample ± 0.5 g (or more for sediments) into a 250 or 400 mL beaker or wide-mouth jar. For PCB extraction, weigh approximately 10g of sample ± 0.5g. Record the weight to the nearest 0.01 g in the appropriate column in LIMS.

Note: Alternate sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

11.2.5. Mix the weighed sample with a spatula adding enough anhydrous sodium sulfate (approximately 10 g to 30 g) to be free flowing. (If the sample is not free flowing, extraction efficiency may be reduced.) If free flowing media cannot be obtained, sample weight may need to be reduced. Add the appropriate spike and surrogate solution.

11.2.6. Add an appropriate volume of spiking solution to any LCS and MS/MSD samples (see Table 3). Add the appropriate volume of the surrogate spiking solution to each sample, MB, LCS, and MS/MSD (see Table 2 for appropriate amounts). Refer to Table 5 for details of the surrogate spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions that are cold stored promptly to refrigerator.

11.2.7. Prepare a MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP. Use 10 g to 30 g of sodium sulfate for the method blank and LCS. Use 10 g to 30 g ± 0.5 g each of parent sample for the MS and MSD samples.

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11.2.8. Immediately add approximately 100 mL of solvent to the beaker.

Solvents:

Semivolatile GC/MS, TPH,	1:1 v/v Methylene Chloride / Acetone
Organochlorine pesticides and PCBs	1:1 v/v Hexane / Acetone
8270 (MS) Concrete matrix	Methylene Chloride

Note: Steps 11.2.5 through 11.2.9 must be performed rapidly to avoid loss of the more volatile extractables.

11.2.9. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.2.10. Sonicate for three minutes, making sure the entire sample is agitated.

Note: Do ***not*** use ***Micro-tip*** probe.

11.2.11. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.2.12. Place the prepared funnel on a labeled collection apparatus (beaker or K-D apparatus).

11.2.13. Decant and filter extract through the prepared funnel into the collection apparatus (a clean beaker or K-D Apparatus).

11.2.14. Repeat the extraction two more times with approximately 100 mL portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication, pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the appropriate solvent (refer to table in Section 11.2.7).

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.2.15. Cover with aluminum foil and refrigerate if the extract is not concentrated immediately. Refer to Section 11.5 for concentration.

11.3. Medium Level Sonication (PCB only)

11.3.1. Remove surrogate and matrix spiking solutions from refrigerator if cold stored, and allow to come to room temperature.

11.3.2. Sediment samples require that the water layer is not decanted. Sediment samples must be weighed at a higher weight to account for the dry weight correction. Homogenize the sample by mixing it thoroughly in the container. If this is not possible, place the sample in clean beaker and homogenize. Upon completion of homogenization in the beaker, return sample to original container. Discard foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials, consult with the client (via the Project Manager or Administrator).

11.3.3. Weigh 5 g of sample ± 0.1g (or more for sediments) into a 40 mL vial. Record the weight to the nearest 0.01 g in LIMS.

11.3.4. Mix the weighed sample with a spatula adding enough anhydrous sodium sulfate to be free flowing.

11.3.5. Add appropriate volume of spiking solution to any LCS and MS/MSD samples (see Table 3). Add the appropriate volume of the surrogate spiking solution to each sample, MB, LCS, and MS/MSD (see Table 2 for appropriate amounts). Refer to Table 5 for details of the surrogate spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions that are cold stored promptly to refrigerator.

11.3.6. Prepare a MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP. Use 5 g of sodium sulfate for the MB and LCS. Use 5 g ± 0.1g each of the parent sample for the MS and MSD samples.

11.3.7. Immediately add the appropriate mLs of solvent to the vial.

LCS, MS/MSD	18 mL Hexane
Sample and blank	19 mL Hexane

Note: Steps 11.3.5 - 11.3.9 must be performed rapidly to avoid loss of the more volatile extractables.

11.3.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.3.9. Sonicate for two minutes continuous disruption, making sure the entire sample is agitated.

Note: Use ***Micro-tip*** probe.

11.3.10. The samples are now ready for analysis.

11.4. Concentration

11.4.1. According to the type of sample, different solvents and final volumes will be required. Refer to Table 1 for the appropriate final volumes and solvents.

11.4.2. Kuderna-Danish (KD) Method:

11.4.2.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. Label the CT and KD. Transfer the sample to the labeled K-D flask, filtering samples through funnels filled with sodium sulfate. Rinse the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

11.4.2.2. Add one or two clean boiling chips to the extract and attach a three-ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column. (This is important to ensure that the balls are not stuck, and the column will work properly). Attach to the KD flask.

11.4.2.3. Place the KD apparatus on a water bath [90ºC ± 4ºC for MS Semi samples, 94ºC ± 4ºC for other analyses] so the tip of the concentrator tube is submerged. The water level must not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter; but the chambers should not flood.

11.4.2.4. Concentrate to 15-20 mL. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.4.2.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. Rinse the KD and Snyder column with 1-2 mL of solvent. If the level of the extract is above the level of the concentrator tube (CT) joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.5. Nitrogen Evaporation to Final Concentration

11.5.1. Transfer the CT to the evaporation apparatus.

11.5.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but must not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C
Toluene	111°C

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.5.3. Refer to Table 1 to determine the final volume needed for a specific test method. Evaporate to slightly less than the required final volume.

11.5.4. Quantitatively transfer the extract to the appropriate final container and dilute to the appropriate final volume using the “standard” glass vial noted in Section 10.1. Cap the sample and affix the appropriate label. The sample is now ready for analysis.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.6. Analytical Documentation

11.6.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.6.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.6.3. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

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12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which must contain all of the analytes of interest. The spiking level must be equivalent to a mid-level calibration. (For certain tests, more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. See SOPs NC-GC-038, NC-MS-018, NC-MS-003, and NC-GC-007 for detailed information on the determinative methods.

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management And Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with federal, state and local laws and regulations. Where reasonably feasible, technological changes have been

implemented to minimize the potential for pollution of the environment. Employees will abide by this method the policies in section 13 of the Corporate Environmental Health And Safety Manual (CW-E-M-001) for "Waste Management And Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.2. **Assorted flammable solvent waste from various rinses**: These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.3. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.4. **Hexane-Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.5. **Waste Hexane in vials:** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.6. **Waste Methylene Chloride sample vials**: These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Extracted solid samples contaminated with methylenechloride/acetone or acetone/hexane:** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.8. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCBs must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB, and PCB vial waste.

15.2.9. Solvent Recovery System Waste: Methylene Chloride waste from the Solvent Recovery System is collected and disposed of in the liquid-liquid separation unit. Acetone/Methylene Chloride waste from this system is disposed of in the flammable waste containers located in the laboratory.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B and 3550C.

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. Federal Register – Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

16.1.6. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

16.1.7. Revision History

Historical File:		Revision 3.4: 10/16/98		Revision 0: 03/12/08 (NC-OP-032)
(formerly CORP-OP-0001NC		Revision 3.5: 04/22/99		Revision 1: 01/07/09 (NC-OP-032)
		Revision 3.6: 05/13/99		Revision 0: 03/03/11 (NC-OP-039)
		Revision 3.7: 03/20/01		Revision 1-A: 04/21/12
		Revision 3.8: 05/23/01		Revision 2: 02/21/14
		Revision 3.9: 04/22/02		Revision 3: 06/25/15
		Revision 4.0: 02/04/03		Revision 4: 06/23/16
		Revision 4.1: 10/07/03		
		Revision 4.2: 01/30/06		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.6. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.7. Gas Chromatographic Analysis Based on Methods 8082 and 8082A, NC-GC-045

16.2.8. GC/MS Analysis based on Method 8270C and 8270D, NC-MS-018

16.2.9. Analysis of Pesticides and PCBs by EPA Method 608, NC-GC-007

16.2.10. GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Method 625, NC-MS-003

16.2.11. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Spiking and surrogating occurs after the sodium sulfate has been homogenized with the sample rather than before, as stated in SW-846.

17.1.3. True sediment matrices are not decanted as stated in SW-846.

17.2. Tables

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TABLE 1

Final Volumes

Type	Final Volume for Analysis in mL
BNA	2.0
PCB	10.0
Pesticides	10.0
BNA – SIM	2.0
TPH	5.0

Note: Different final volumes may be necessary to meet special client reporting limit requirements.

TABLE 2

Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	20 ppm BNA Surrogate	1.0
BNA / SIM	20 ppm BNA Surrogate	0.1
PEST	0.2 ppm DCB/TCX	1.0
TPH	40ug/mL o-Terphenyl	1.0
PCB	0.2 ppm DCB/TCX	1.0

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TABLE 3

Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	20 ppm BNA All-Analyte Spike	1.0
BNA / SIM	20 ppm BNA All-Analyte Spike	0.1
PEST	Pest NPDES Spike	1.0
PCB	10 ppm PCB Spike	1.0
TPH	See Spike List – Table 5	1.0

TABLE 4

Surrogate Spike Components

Analyte Group	Compounds
BNA	2-Fluorobiphenyl
	Nitrobenzene-d_5
	p-Terphenyl-d_{14}
	2-Fluorophenol
	Phenol-d_6
	2,4,6-Tribromophenol
	1,2-Dichlorobenzene-d_4
	2-Chlorophenol-d_4
PEST PCB	Decachlorobiphenyl
	Tetrachloro-m-xylene
TPH	o-Terphenyl

TABLE 5

LCS and Matrix Spike Components

Type	Compounds
BNA	1,1'Biphenyl
	1,2,4,5-Tetrachlorobenzene
	1,2,4-Trichlorobenzene
	1,2-DICHLOROBENZENE
	1,2-Diphenylhydrazine
	1,3-Dichlorobenzene
	1,3-Dinitrobenzene
	1,4-Dichlorobenzene
	1,4-Dioxane
	1-Methylnaphthalene
	2,2'-oxybis[1-chloropropane]
	2,3,4,6-Tetrachlorophenol
	2,4,5-Trichlorophenol
	2,4,6-Trichlorophenol
	2,4-Dichlorophenol
	2,4-Dimethylphenol
	2,4-Dinitrophenol
	2,4-Dinitrotoluene
	2,6-Dichlorophenol
	2,6-Dinitrotoluene
	2-Chloronaphthalene
	2-Chlorophenol
	2-Methylnaphthalene
	2-Methylphenol
	2-Nitroanaline
	2-Nitrophenol
	3&4-Methylphenol
	3,3'-Dichlorobenzidine
	3-Methylphenol
	3-Nitroanaline
	4,6-Dinitro-2-methylphenol

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Type	Compounds
BNA	4-Bromophenyl phenyl ether
	4-Chloro-3-methylphenol
	4-Chloroanaline
	4-Chlorophenyl phenyl ether
	4-Methylphenol
	4-Nitroanaline
	4-Nitrophenol
	Acenaphthene
	Acenaphthylene
	Acetophenone
	Aniline
	Anthracene
	Azobenzene
	Benzidine
	Benzo[a]anthracene
	Benzo[a]pyrene
	Benzo[b]fluoranthene
	Benzo[g,h,i]perylene
	Benzo[k]fluoranthene
	Benzoic acid
	Benzyl alcohol
	Bis(2-chloroethoxy)methane
	Bis(2-chloroethyl)ether
	Bis(2-ethylhexyl)phthalate
	Butyl benzyl phthalate
	Carbazole
	Chrysene
	Dibenz(a,h)anthracene
	Dibenzofuran
	Diethyl phthalate
	Dimethyl phthalate
	Di-n-butyl phthalate
	Di-n-octyl phthalate
	Fluoranthene

Type	Compounds
BNA	Fluorene
	Hexachlorobenzene
	Hexachlorobutadiene
	Hexachlorocyclopentadiene
	Hexachloroethane
	hexadecane
	Indene
	ideno[1,2,3-cd]pyrene
	isophorone
	Naphthalene
	n-Decane
	Nitrobenzene
	N-Nitrosodimethylamine
	N-Nitrosodi-n-propylamine
	N-Nitrosodiphenylamine
	n-Octadecane
	Pentachlorophenol
	Phenanthrene
	Phenol
	Pyrene
	Pyridine

Type	Compounds
Pest NPDES/Pest	Alrin
	Alpha-BHC
	beta-BHC
	delta-BHC
	gamma-BHC (Lindane)
	4,4'-DDD
	4,4'-DDE
	4,4'-DDT
	Dieldrin

	alpha-Endosulfan
	beta-Endosulfan
	Endosulfan Sulfate
	Endrin
	Heptachlor
	Heptachlor Epoxide

Diesel Range Organics (8015B) (8015C)Spike
Compound
Diesel Fuel

Title: SOXHLET (TRADITIONAL) EXTRACTION OF ORGANIC COMPOUNDS FROM SOILS BASED ON METHOD SW846 3540C

[Method: SW846 3540C]

Approvals (Signature/Date):

Technology Specialist	03/02/17 Date	Health & Safety Coordinator	03/06/17 Date
Quality Assurance Manager	04/28/17 Date	Technical Director	04/10/17 Date

This SOP was previously identified as SOP No. NC-OP-040, Rev 4, dated 1/18/16

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1. SCOPE AND APPLICATION

1.1. This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in soil, sediment, waste and wipe matrices for analysis by Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS) using Soxhlet Extraction. The procedures are based on SW846 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1.1. Extraction procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8270C, 8270D, 8015B, 8015C, and 8015D.

1.1.2. The extraction procedures herein may be appropriate for other determinative methods when appropriate spiking mixtures are used.

2. SUMMARY OF METHOD

2.1. Soxhlet Extraction (Traditional)

2.1.1 A 30 g sample (10 g for Pesticides and PCBs) is mixed with anhydrous sodium sulfate until free flowing, or a 1 wipe sample is placed in an extraction thimble. They are extracted by refluxing with solvent.

2.2. Concentration

2.2.1 Procedures are presented for drying the extract and concentration of the extract to final volume for analysis.

3. DEFINITIONS

3.1. Definitions of terms and acronyms used in this SOP may be found in the glossary of the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be

documented.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.3. The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, dibenz(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyl compounds. Primary standards of these toxic compounds must be prepared in the hood.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride must be conducted in a fume hood with the sash closed as far as the operations will permit. If more than 500 mL of methylene chloride is spilled, evacuate the area until the area has been cleaned by EH&S.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.8. During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints that can become stuck. Technicians must use Kevlar or other cut/puncture-resistant gloves when separating stuck joints.

6. EQUIPMENT AND SUPPLIES

6.1. Glassware must be cleaned per Glassware Washing, SOP NC-QA-014.

6.2. Equipment and supplies for extraction procedures:

EQUIPMENT AND SUPPLIES	Sox	Conc
Graduated cylinder: 1 liter. (other sizes may be used as needed)		√
Erlenmeyer flask: 250 mL (other sizes optional)		√
Solvent dispenser pump or 100 mL graduated cylinder	√	√
Round or flat bottom: 250 mL	√	
Boiling chips: contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent)	√	√
Cooling condensers	√	
Heating mantle: rheostat controlled or equivalent	√	
Auto-timer for heating mantle	√	
Soxgriddle or equivalent	√	
Beakers: 450mL wide-mouth glass jars		√
Balance: >100 g capacity, accurate to ±1.00 g	√	√
Soxhlet extractor	√	
Cellulose and glass thimbles	√	

EQUIPMENT AND SUPPLIES	Sox	Conc
Kuderna-Danish (K-D) apparatus: 500 mL		√
Concentrator tube: 10 mL, attached to K-D with clips		√
Snyder column: three-ball macro		√
Water bath: heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.		√
Vials: glass, 2 mL and 40 mL capacity with Teflon®-lined screw-cap		√
Clean wipes for wipe matrix method blanks and laboratory control samples		
Nitrogen blowdown apparatus		√
Nitrogen: reagent grade.		√
Culture Tubes: 10 mL, 16 x100 mm		√
Microliter pipette and/or syringe 1 mL	√	
Glass wool	√	
Glass funnel: 75 X 75 mm	√	√
Disposable pipettes, 5 ¾ in, and 9in.	√	√
Aluminum foil	√	√
Paper towels	√	√

7. REAGENTS AND STANDARDS

7.1. Reagents for Extraction Procedures

7.2. All reagents must be ACS reagent grade or better, unless otherwise specified.

REAGENTS	Sox	Conc
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 800°C a minimum of one hour.	√	√
Magnesium sulfate	√	
Extraction Solvents (pesticide quality or equivalent): Methylene chloride, Methylene Chloride/acetone hexane/acetone,	√	√
Hexane/Acetone:, reagent grade: Used for cleaning glassware.	√	√

7.3. Standards

7.3.1. Stock Standards

7.3.1.1. Stock standards are purchased as certified solutions. S tock standards are stored according to manufacturer's instructions. All stock standards must be protected from light. Stock standard

solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampoule is opened, if purchased). Standards that are cold stored must be allowed to come to room temperature before use.

7.3.2. Surrogate Spiking Standards

7.3.2.1. Prepare or purchase surrogate spiking standards at the concentrations listed in Table 2. Surrogate spiking standards are purchased or prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced every six months at a minimum, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3. Matrix Spiking and Laboratory Control Spiking Standards

7.3.3.1. The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 3. Spiking standards are purchased or prepared as dilutions of the stock standards.

7.3.3.2. Spiking solutions must be refrigerated and protected from light, or stored according to manufacturer's instructions. The standards must be replaced every six months at a minimum, or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4. See SOP NC-QA-017 for additional information on Standards and Reagents.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps.

8.3. Holding Times

8.3.1. The holding time for solid and waste samples is 14 days from sampling to extraction.

8.3.2. Analysis of the extracts is completed within 40 days of extraction.

9. QUALITY CONTROL

9.1. Quality Control Batch

9.1.1. The batch is a set of up to 20 client samples and appropriate QC that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank (MB), an LCS, and a matrix spike/matrix spike duplicate (MS/MSD). (In some cases, at client request, it may be appropriate to process a matrix spike and un-spiked sample duplicate in place of the MS/MSD). If clients designate specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs. See Policy QA-003 for further definition of the batch.

9.2. Method Blank (MB)

9.2.1. An MB consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the MB at the same level as the samples. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB is used to identify any background interference or contamination of the analytical system which may lead to the reporting of elevated concentration levels or false positive data.

9.2.2. For a solid MB, use approximately 30 g of sodium sulfate spiked with the surrogates. For PCB and Pesticides, use approximately 10 g ± 0.5 g of sodium sulfate. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB goes through the entire analytical procedure.

9.2.3. For a wipe MB, use 1 clean wipe spiked with the surrogates. See Table 2 for the appropriate amount of surrogate to use for each analytical method. The MB goes through the entire analytical procedure.

9.3. Laboratory Control Sample (LCS)

9.3.1. LCSs are well-characterized laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure.

9.3.2. The LCS is made up in the same way as the MB (see Sections 9.2.1 through 9.2.3), but spiked with the LCS standard and the surrogates. See Table 3 for the appropriate amount of spike to use for each analytical method.

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9.4. Surrogates

9.4.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.4.2. Each applicable sample, MB, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits of the applicable determinative method. See Table 2 for the appropriate amount of surrogate spike to use for each analytical method.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. An MS is an environmental sample to which known concentrations of target analytes have been added. An MSD is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and MS. See Table 3 for the appropriate amount of spike to use for each analytical method.

9.6. QC requirements can be found in the various associated analytical SOPs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically, unless method specified. Control limits are easily accessible via the LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established and performed by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are easily accessible via the LIMs.

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. On a weekly basis, measure the appropriate volumes of solvents into the appropriate sized glass culture tubes gravimetrically. The “standard” glass culture tubes are sealed, and the meniscus is noted by marking a line on the tubes. The glass culture tubes containing the sample final extracts are then compared against the “standard” glass culture tubes of the appropriate volume and solvent to ensure the volumes are consistent. (See Table 1 for final volumes)The bottle top dispenser is calibrated quarterly and must be within ±5% of the target volume with an RSD ≤ 1%.

10.2. All labware, pipettes, and balances are calibrated according to SOPs NC-QA-004 and NC-QA-015.

11. PROCEDURE

11.1. Procedural Variations

11.1.1. Procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance memo and approved by a supervisor. The Nonconformance memo will be filed in the project file. Procedural variations are not allowed for Ohio VAP projects.

11.2. Soxhlet

11.2.1. Remove surrogate and matrix spiking solutions from refrigerator if cold stored, and allow to warm to room temperature.

11.2.2. If sample can be mixed easily in the sample jar, mix thoroughly by stirring with a clean plastic or wooden spoon or spatula. If the sample cannot be easily mixed (i.e., clay samples or samples of various and very different particle sizes), use the spoon or spatula to select enough separate portions from locations within the jar to produce a representative sample. Analyst judgment is important in determining how many portions and which locations are used to produce a representative aliquot. If the sample is uniform clay, at least 3 portions should be selected from different locations in the sample jar, if particle sizes or materials indicate a very non-homogenous sample, selection should be made carefully to collect an aliquot that represents the relative percentages of the various particle sizes and types in the sample jar.

11.2.3. Do not decant the water layer from sediment samples. The entire sample is used. A higher weight of sample portion must be weighed for sediment samples to account for the dry weight correction (see 11.2.3). Record and document in the LIMS if a water layer was present in the sample.

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11.2.4. If the sample cannot be prepared using a Soxhlet due to matrix issues, a waste dilution may be required. Refer to SOP NC-OP-043 for the waste dilution procedure.

11.2.5. Place approximately 200mL of solvent into a 250 mL flat bottom flask containing one or two clean boiling chips. Weigh 30g ± 0.5 g of sample into a thimble or in a jar, recording the weight to the nearest 0.01g in LIMS. For PCB or Pesticides Extraction, weigh approximately 10 g of sample ± 0.5 g. Sample weights less than 30g, but over 1g, may be used if the appropriate reporting limits can be met. For sediment samples that contain excessive moisture, weigh 50 g ±0.5 g. For wipe samples, the wipe is placed in an extraction thimble. For concrete samples, weigh 5 g of sample ± 0.5g.

Note: Waste samples with difficult matrices (such as caulk) are extracted at 1g.

Note: Alternate sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the sample to reagent ration. All samples and standards must be processed similarly.

11.2.6. Prepare an MB, LCS, and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate or a clean wipe as the matrix for the LCS and MB. The parent sample is used for the MS/MSD. The weight of sodium sulfate used must be approximately the weight of soil used for samples.

11.2.7. Add anhydrous sodium sulfate to each solid, sediment or waste sample and mix well. The mixture must have a free-flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet extractor thimble, but do not pack the thimble tightly. The soxhlet extractor or extraction thimble must drain freely for the duration of the extraction period. Thimbles are only used for PCB and Pesticide extraction. A glass wool plug below the sample in the soxhlet extractor is used for other extractions.

11.2.8. Add the appropriate amount of surrogate and matrix spiking solution as indicated in Tables 2 and 3.

11.2.9. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

Note: If a reduced quantity of sample is extracted, it is usually necessary to increase the amount of sodium sulfate added or increase the solvent boiling rate to properly set the cycling rate.

Solvents:

Semivolatile GC/MS and TPH	1:1 v/v Methylene Chloride / Acetone
8270 (MS) Concrete	Methylene Chloride
PCB and Pesticides	1:1 v/v Hexane / Acetone
8082 Concrete	1:1 v/v Methylene Chloride/Acetone

11.2.10. Allow the extract to cool after the extraction is complete then disassemble by gently twisting the soxhlet from the flask.

11.2.11. The sample is now ready for the concentration step (Section 11.3).

11.2.12. Cover the extracts with aluminum foil and store at 4°C ± 2°C if the extract will not be concentrated immediately. Refer to Section 11.3 for concentration.

11.3. Concentration: According to the type of sample, different solvents and final volumes will be required. Refer to Table 1 for the appropriate final volumes and concentrations.

11.3.1. Kuderna-Danish (KD) Method:

11.3.1.1. Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube (CT) to the 500 mL KD flask. Label the CT and KD. Transfer the sample to the labeled K-D flask filtering the extracts through funnels filled with sodium sulfate. Rinse the sample flasks from the soxhlet setups with approximately 10 – 20 mL of methylene chloride Transfer the rinsate through the funnel and rinse the funnel with 20-30 mL of methylene chloride to complete the quantitative transfer.

11.3.1.2. Add one or two clean boiling chips to the KD flask and attach a three-ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column. **Note:** It is important to wet with MeCl to ensure that the balls in the Snyder column do not stick, and the column will work properly.

11.3.1.3. Place the KD apparatus on a water bath (90-98^{o}C) so the tip of the concentrator tube is submerged. The water level must not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter; but the chambers should not flood.

11.3.1.4. Concentrate to 15-20 mL. If the determinative method requires a solvent exchange, add the appropriate exchange solvent to the top of the Snyder Column, and then continue the water bath concentration back down to 5-8 mL. Refer to Table 1 for details of exchange solvents and final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.3.1.5. Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the CT joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

11.4. Nitrogen Evaporation to Final Concentration

11.4.1. Transfer the CT to the evaporation apparatus.

11.4.2. Place the tube in a warm water bath that is at least 5°C below the boiling temperature of the solvent being evaporated and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but must not create splattering of the extract.

Boiling points of commonly used solvents are:

Methylene chloride	40°C
Acetone	56°C
Hexane	69°C
Acetonitrile	82°C

Note: It is very important not to concentrate to dryness as analytes will be lost.

11.4.3. Refer to Table 1 to determine the final volume needed for a specific test method. Evaporate to slightly less than the required final volume.

11.4.4. Rinse the CT and quantitatively transfer the extract with the rinsate to the appropriate final container, rinse the CT and transfer the rinsate to the final container and dilute to the appropriate final volume using the “standard” glass vial noted in Section 10.1. Cap the sample and affix the appropriate label. The sample is now ready for analysis.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Record sample and associated QC information into LIMs. Level I and Level II technical reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Initial Demonstration

13.1.1. Each analyst must make an initial demonstration of capability (IDOC) for each individual method. This requires analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which must contain all of the analytes of interest. The spiking level must be equivalent to a mid-level calibration. (For certain tests, more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

13.1.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.1.3. Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs. See SOPs NC-GC-038, NC-MS-018, NC-MS-003, and NC-GC-007 for detailed information on the determinative methods.

13.1.4. Method validation information (where applicable) in the form of analyst demonstrations of capabilities is maintained for this method in the analyst's training files

13.2. Training Qualification

13.2.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State, and local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride/acetone or acetone/hexane from the extract drying step. These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.2. **Assorted flammable solvent waste from various rinses**. These wastes are put into the halogenated/non-halogenated 25 gallon solvent waste container located under the fume hood in extractions.

15.2.3. **Methylene chloride waste from various rinses:** These wastes are disposed of in the liquid-liquid separation unit.

15.2.4. **Hexane-Hexane waste:** These samples are to be disposed in the flammable waste.

15.2.5. **Waste Hexane in vials.** These vials are placed in the vial waste located in the GC prep laboratory.

15.2.6. **Waste Methylene Chloride sample vials**. These vials are placed in the vial waste located in the GC prep laboratory.

15.2.7. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane.** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.

15.2.8. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCBs must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB, and PCB vial waste.

15.2.9. Solvent Recovery System Waste. Methylene Chloride waste from the Solvent Recovery System is collected and disposed of in the liquid-liquid separation unit. Acetone/Methylene Chloride waste from this system is disposed of in the flammable waste containers located in the laboratory.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3540C, and 3580A

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version16.1.5 Federal Register - Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

16.1.5. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

16.1.6. Revision History

Historical File:		Revision 3.4: 10/16/98		Revision 0: 03/12/08 (NC-OP-032)
(formerly CORP-OP-0001NC)		Revision 3.5: 04/22/99		Revision 1: 01/07/09 (NC-OP-032)
		Revision 3.6: 05/13/99		Revision 0: 03/24/11 (NC-OP-040)
		Revision 3.7: 03/20/01		Revision 1-A: 01/24/12
		Revision 3.8: 05/23/01		Revision 2: 08/28/13
		Revision 3.9: 04/22/02		Revision 3: 08/25/14
		Revision 4.0: 02/04/03		Revision 4: 01/18/16
		Revision 4.1: 10/07/03		
		Revision 4.2: 01/30/06		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.6. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.7. Gas Chromatographic Analysis of PCBs Based on Methods 8082 and 8082A, NC-GC-045

16.2.8. GC/MS Analysis based on Method 8270C and 8270D, NC-MS-018

16.2.9. Analysis of Pesticides and PCBs by EPA Method 608, NC-GC-007

16.2.10. GC/MS Semivolatile Organic Compounds Capillary Column Technique Based on EPA Method 625, NC-MS-003

16.2.11. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS

17.1. Modifications from Reference method

17.1.1. Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.1.2. Sodium sulfate is heated for 1 hour at 800°C to purify. The reference method lists a minimum of 4 hours at 400°C.

17.2. Tables

TABLE 1

Final Volumes and Exchange Solvents

Type	Exchange Solvent for Analysis*	Final Volume for Analysis in mL
Semivolatiles	N/A	2.0 mL
PCB	Approximately 36 mL Hexane	10.0
Pesticides	Approximately 18 mL Hexane	10.0
BNA – SIM	N/A	2.0 mL
TPH	N/A	5.0

Note: *PCBs and Pesticides only need the solvent exchange step when they are extracted in methylene chloride / acetone. If they are extracted in hexane / acetone, no solvent exchange is necessary.*
Note: *Different final volumes may be necessary to meet special client reporting limit requirements.*

TABLE 2

Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA	20 ppm BNA	1.0
BNA / SIM	20 ppm BNA	0.1
PEST	0.2 ppm DCB/TCX	1.0
TPH	o-Terphenyl	1.0
PCB	0.2 ppm DCB/TCX	1.0

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TABLE 3
Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	20 ppm BNA All-Analyte Spike	1.0
BNA / SIM	20 ppm BNA All-Analyte Spike	0.1
PEST	Pest NPDES Spike	1.0
PCB	10 ppm PCB Spike	1.0
TPH	Diesel Spike	1.0

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Title: Waste Dilution

[Method: SW846 Method 3580A]

Approvals (Signature/Date):

Technology Specialist	02/22/18 Date	Health & Safety Coordinator	02/26/18 Date
Quality Assurance Manager	05/10/18 Date	Technical Director	05/14/18 Date

This SOP was formerly known as NC-OP-043 Rev. 2, dated 2/22/18

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1. SCOPE AND APPLICATION

1.1. Method 3580A is a procedure for diluting nonvolatile and semivolatile organic compounds from organic, non-aqueous wastes that are **soluble** in the dilution solvent

1.2. This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory QA department.

2. SUMMARY OF METHOD

2.1. The waste sample is weighed into a culture tube and diluted to an appropriate final volume using hexane or methylene chloride.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current edition.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. The use of high purity reagents and solvents helps minimize interference problems. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Test America associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the

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Safety Data Sheets (SDS) maintained in the laboratory. The following specific hazards are known:

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Exposure to chemicals must be maintained **as low as reasonable achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a Test America associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Culture tubes with Teflon®-lined caps: 10 mL capacity

6.2. Balance: capable of accurately weighing ± 0.01g

6.3. Vortex mixer

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Extraction solvent is hexane or methylene chloride, pesticide quality or

equivalent.

7.2. Standards

7.2.1. Surrogate Standard

7.2.1.1. Prepare surrogate solutions at the appropriate concentration which allows detection of each compound within the linear range of the analysis (see Tables 1 and 3). Surrogate solutions are made in the solvent which is compatible with the dilution solvent. Store at 4°C ± 2° C.

7.2.2. Matrix Spike Standard

7.2.2.1. Prepare a matrix spike standard of the appropriate concentration for each target analyte group using the same procedures found in Section 7.2.1.1 (See Table 2).

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are stored at 4°C ± 2°C.

8.2. Waste samples for PCB analysis, unless otherwise specified by regulatory or client programs, have a holding time of 1 year.

8.3. All other waste samples are extracted within fourteen days of the sampling date and the extracts analyzed within forty days of extraction.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, and MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of the appropriate dilution solvent containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated

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analyte concentrations or false positive data. The MB should not contain any analyte of interest at or above the reporting limit.

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS consisting of the appropriate dilution solvent must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.5. Surrogates

9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.5.2. Each sample, MB, LCS, and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Not Applicable

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Summary

11.3.1. The waste sample is weighed into a culture tube and diluted to appropriate final volume using hexane or methylene chloride.

11.4. Sample Preparation Procedure

11.4.1. Sample Handling

11.4.1.1. Determine solubility of the waste in the appropriate dilution solvent.

Note: If the waste is not soluble in the dilution solvent do not proceed. The sample will have to be extracted as a solid waste. Alternately, the sample may be prepared as a water sample, dependent on the nature of the matrix.

Note: The phases of multiphase samples must be prepared separately.

11.4.1.2. Weigh approximately 1.0 g of the sample into the labeled and calibrated culture tube. Record the weight in the extraction log.

11.4.1.3. Add the appropriate volume of each required surrogate standard solution onto the sample. For the LCS and the sample in each analytical batch selected for matrix spiking, add the appropriate volume of the matrix spiking solution (see Section 9 for details on the surrogate standards and matrix spiking solutions).

11.4.1.4. Bring the sample to volume (10 mL) in the labeled and calibrated culture tube using the appropriate solvent. The dilution solvent for BNA and TPH analyses is methylene chloride. The dilution solvent for PCB and Pesticide analyses is hexane.

11.4.1.5. Mix thoroughly with vortex.

11.4.1.6. The sample is now ready for cleanup and analysis.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the analytical logbook/logsheet and LIMs system, including the analytical data from standards, MBs, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file and the laboratory must maintain corresponding method detection limit files.

13.2. Training Qualifications:

13.2.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with federal, state and local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method the policies in section 13 of the corporate environmental health and safety manual (cw-e-m-001) for “waste management and pollution prevention**.”**

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Sulfuric acid from acid stripping goes into Sulfuric Acid Waste #13.

15.2.2. TBA waste goes into Waste #26.

15.2.3. Extracts go into Vial Waste #4.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Method 3580A

16.1.2. Revision History

Historical File:		Revision 0: 08/19/13		
		Revision 1: 10/29/15		

16.2. Associated SOPs

16.2.1. Gas Chromatographic Analysis of Pesticides Based on Methods 8081A and 8081B, NC-GC-042

16.2.2. Gas Chromatographic Analysis of Diesel Range Organics Based on Methods 8015B, 8015C, and 8015D, NC-GC-043

16.2.3. Gas Chromatographic Analysis Based on Methods 8082 and 8082A, NC-GC-045

16.2.4. GC/MS Analysis Based on Methods 8270C and 8270D, NC-MS-018

16.2.5. Gas Chromatographic Analysis of Herbicides Based on Method 8151A, NC-GC-044

17. MISCELLANEOUS (TABLES, APPENDICES, ETC...)

17.1. Reporting limits

17.1.1. Refer to the individual methods listed in Table 4 for specific analyte reporting limits.

17.2. Tables

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TABLE 1
Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
BNA Waste Dilution	20 ppm BNA Surrogate Spike	2.5
PEST	0.2 ppm DCB/TCX	1.0
TPH	40ng o-Terphenyl	2.0
Herbicide	2 ppm 2,4-Dichlorophenylacetic Acid	1.0
PCB	0.2 ppm DCB/TCX	1.0

TABLE 2
Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
BNA	20 ppm BNA Spike	0.5
BNA / SIM	20 ppm BNA Spike	0.1
PEST	Pest NPDES Spike	1.0
PCB	10 ppm PCB Spike	1.0
Herbicide	Herbicide Standard Spike	1.0
TPH	Diesel	2.0

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TABLE 3
Surrogate Spike Components

Analyte Group	Compounds	Conc. (µg/mL)
BNA	2-Fluorobiphenyl	20
	Nitrobenzene-d_5	20
	p-Terphenyl-d_{14}	20
	2-Fluorophenol	20
	Phenol-d_6	20
	2,4,6-Tribromophenol	20
	1,2-Dichlorobenzene-d_4	20
	2-Chlorophenol-d_4	20
PEST	Decachlorobiphenyl	0.2
PCB	Tetrachloro-m-xylene	0.2
Herbicide	2,4-Dichlorophenylacetic Acid	0.2
TPH	o-Terpphenyl	40.0

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TABLE 4
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
BNA	1,1'Biphenyl	20
	1,2,4,5-Tetrachlorobenzene	20
	1,2,4-Trichlorobenzene	20
	1,2-Dichlorobenzene	20
	1,2-Diphenylhydrazine	20
	1,3-Dichlorobenzene	20
	1,3-Dinitrobenzene	20
	1,4-Dichlorobenzene	20
	1,4-Dioxane	20
	1-Methylnaphthalene	20
	2,2'-oxybis[1-chloropropane]	20
	2,3,4,6-Tetrachlorophenol	20
	2,4,5-Trichlorophenol	20
	2,4,6-Trichlorophenol	20
	2,4-Dichlorophenol	20
	2,4-Dimethylphenol	20
	2,4-Dinitrophenol	40
	2,4-Dinitrotoluene	20
	2,6-Dichlorophenol	20
	2,6-Dinitrotoluene	20
	2-Chloronaphthalene	20
	2-Chlorophenol	20
	2-Methylnaphthalene	20
	2-Methylphenol	20
	2-Nitroanaline	20
	2-Nitrophenol	20
	3&4-Methylphenol	20
	3,3'-Dichlorobenzidine	40
	3-Methylphenol	10
	3-Nitroanaline	20
	4,6-Dinitro-2-methylphenol	40
	4-Bromophenyl phenyl ether	20
	4-Chloro-3-methylphenol	20
	4-Chloroanaline	20
	4-Chlorophenyl phenyl ether	20
	4-Methylphenol	10
	4-Nitroanaline	20
	4-Nitrophenol	40
	Acenaphthene	20

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TABLE 4 LCS and Matrix Spike Components		
Type	**Compounds**	**Conc. (µg/mL)**
BNA	Acenaphthylene	20
	Acetophenone	20
	Aniline	20
	Anthracene	20
	Azobenzene	20
	Benzidine	40
	Benzo[a]anthracene	20
	Benzo[a]pyrene	20
	Benzo[b]fluoranthene	20
	Benzo[g,h,i]perylene	20
	Benzo[k]fluoranthene	20
	Benzoic acid	40
	Benzyl alcohol	20
	Bis(2-chloroethoxy)methane	20
	Bis(2-chloroethyl)ether	20
	Bis(2-ethylhexyl)phthalate	20
	Butyl benzyl phthalate	20
	Carbazole	20
	Chrysene	20
	Dibenz(a,h)anthracene	20
	Dibenzofuran	20
	Diethyl phthalate	20
	Dimethyl phthalate	20
	Di-n-butyl phthalate	20
	Di-n-octyl phthalate	20
	Fluoranthene	20
	Fluorene	20
	Hexachlorobenzene	20
	Hexachlorobutadiene	20
	Hexachlorocyclopentadiene	20
	Hexachloroethane	20
	hexadecane	20
	Indene	40
	ideno[1,2,3-cd]pyrene	20
	isophorone	20
	Naphthalene	20
	n-Decane	20
	Nitrobenzene	20
	N-Nitrosodimethylamine	20
	N-Nitrosodi-n-propylamine	20
	N-Nitrosodiphenylamine	40

TABLE 4
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
	n-Octadecane	20
	Pentachlorophenol	40
	Phenanthrene	20
	Phenol	20
	Pyrene	20
	Pyridine	20
Pesticides TCLP	Heptachlor	0.5
	Heptachlor epoxide	0.5
	Lindane	0.5
	Endrin	0.5
	Methoxychlor	1.0
Pesticides NPDES	Aldrin	1.0
	Alpha-BHC	1.0
	beta-BHC	1.0
	delta-BHC	1.0
	gamma-BHC (Lindane)	1.0
	4,4'-DDD	1.0
	4,4'-DDE	1.0
	4,4'-DDT	1.0
	Dieldrin	1.0
	alpha-Endosulfan	1.0
	beta-Endosulfan	1.0
	Endosulfan Sulfate	1.0
	Endrin	1.0
	Heptachlor	1.0
	Heptachlor Epoxide	1.0
Herbicide	2,4,5-T	0.25
	2,4-D	1.0
	2,4-DB	1.0
	Dalapon	1.0
	Dicamba	0.5
	Dichlorprop	1.0
	Dinoseb	1.0
	MCPA	100
	MCPP	100
	Pentachlorophenol	0.25
	Picloram	1.0
	Silvex (2,4,5-TP)	0.25

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TABLE 4
LCS and Matrix Spike Components

Type	Compounds	Conc. (µg/mL)
TPH	Diesel Fuel	2500 **µg/mL**

Title: TOTAL SOLIDS, PERCENT MOISTURE, AND TOTAL SETTLEABLE SOLIDS

[Method: Standard Method 2540F and ASTM D2216-80]

Approvals (Signature/Date):

Technology Specialist	04/23/18 Date	Health & Safety Coordinator	04/26/18 Date
Quality Assurance Manager	04/25/18 Date	Technical Director	04/27/18 Date

This SOP was previously identified as SOP No. NC-WC-0004, Rev 5, dated 5/23/16

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total Solids; Percent Moisture; and Settleable Solids in wastewaters, sludges, and solids. It is based on Standard Method 2540F and ASTM D2216-80.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Total Solids/Percent Moisture: A homogenous sample is dried at 104 °C ± 2°C, and the difference in the weight loss of the sample represents the Total Solids.

2.2. Settleable Solids: Settleable matter is measured volumetrically with an Imhoff cone.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Samples high in concentrations of minerals must be dried longer, desiccated, and weighed quickly to prevent any excess weight added due to absorption of water from the atmosphere.

4.3. Non-homogeneous samples may give erratic results.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Oily samples or those that contain volatile chemicals may ignite during this procedure. In the case of a fire, the oven should be turned off and allowed to cool before the sample can be removed and put under a hood.

5.3. There are no materials used in this method that have a significant or serious hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. Therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Drying Oven

6.2. Desiccators

6.3. Evaporating dishes: various

6.4. Tongue blades

6.5. Sample containers

6.6. Top loading balance: capable of accurately weighing ± 0.01 g

6.7. Analytical balance: capable of accurately weighing ±0.0001 g

6.8. Beakers: glass, various

6.9. Volumetric flasks: various

6.10. Imhoff cones: Graduated to 20 mL, marked at 900 mL, 1000 mL, and at 1100 mL

6.11. Labels

6.12. Graduated Cylinder, 1000 mL, 2000 mL, 10mL, Class A

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water

7.1.2. Ottawa sand: cleaned and dried

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. The holding time is 48 hours for settleable solids.

8.4. There is no recommended holding time for non-water samples.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, sample duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch of Settleable Solids samples. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest at or above the reporting limit.

Note: There is no MB applicable for Total Solid or Percent Moisture.

9.2.2. Corrective Action for MBs

9.2.2.1. If the analyte level in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or

other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. For the Settleable Solids method, an LCS sample is required.

9.3.1.1 One mL of sand will be added to a 10 mL graduated cylinder. 1000 mL of water is added to a liter container. The sand mixture is added to the liter container and mixed. The resulting mixture is transferred to an Imhoff cone and allowed to settle for one hour. Control limits will be 90-110%.

9.4. Duplicates (DU)

9.4.1. A DU is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, DUs are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.4.2. DUs are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.4.3. DUs are not applicable for Settleable Solids.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.6. Nonconformance and Corrective Action

9.6.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Imhoff Cone Calibration Procedure

10.1.1. The Imhoff Cones are checked on an annual basis. Each Imhoff Cone is checked against a Class A graduated cylinder at the following volumes: 1 mL, 20 mL, and 1000 mL. Verification is visual.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Total Solids (TS) and Percent Moisture

11.3.1. For solid and sludge samples, label and weigh an evaporating dish on an analytical balance that measures to ±_0.0001 g. Record the weight in the LIMS. For solid samples (TS and % Moisture), a universal tare weight is recorded in the LIMS. For solid samples, Sample Receiving will divide the soil sample into a pre-tared container with a label. Weigh and record the wet weight in the LIMS.

11.3.2. DU for solid samples (TS and % Moisture), Sample Receiving will supply the sample duplicate. If the sample duplicate is not supplied from Receiving, split some sample off from another container into a new container with a label. Weigh and record the weight in the LIMS.

11.3.3. Place dishes with sample in the drying oven (103° - 105°C) until dry (minimum of 12 hours). Document the time samples were placed in the oven in the LIMS.

11.3.4. Remove the samples from the drying oven when they are dry. Document the time samples were removed from the oven in the LIMS.

11.3.5. Place the dishes in the desiccator for at least one hour. Weigh the sample and dish on the top loading balance. Record the weight in the LIMS.

11.4. Settleable Solids

11.4.1. An MB is prepared from one liter of reagent water. An MB must be analyzed with each batch of 20 or fewer samples to ensure Imhoff cones are clean and free of particulate contamination. An LCS sample must be analyzed as noted in Section 9.3.

11.4.2. Shake one liter of sample vigorously for ten seconds.

11.4.3. Pour the sample into an Imhoff cone, filling the cone to the one-liter mark.

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Note: For samples containing volume less than 900 mL or greater than 1100 mL: After analysis is complete, pour the sample into a 1000 or a 2000 mL graduated cylinder to determine the exact sample volume. The exact sample volume must be entered into the LIMS, and RLs will be adjusted accordingly.

11.4.4. Allow the sample to settle for forty five minutes, gently agitate sample near the sides of the cone with a glass stir-rod. Then allow the sample to settle for another fifteen minutes.

11.4.5. Measure the volume of settleable solids by observing the location of the border between the settled matter and the supernatant liquid.

11.4.5.1. If pockets of liquid are trapped beneath large settled particles, estimate the volume of the pockets and subtract from the total measured volume.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Total Solids

$$\textit{Total Solids, \% (non-waters)} = \frac{(A - B) \times 100}{(C - B)}$$

Where: A = Final weight of dried sample and dish, g
B = Initial weight of dish, g
C = Initial weight of wet sample and dish,

12.2. Dry Weight

$$\textit{Dry Weight} = \frac{\textit{Sample Test Result x 100}}{\textit{(\%) Total Solid Results}} = \textit{Dry Weight}$$

12.3. Percent Moisture

$$\textit{\%Moisture} = 100 - \textit{\%TS (Section 12.1)}$$

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of capability data on file for Settleable Solids. Initial Demonstrations of Capability (IDOCs) and Continuing Demonstrations of Capability (CDOCs) are filed and tracked in the analyst's technical training file.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State, and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. Weighing containers and residue generated by solid sample analysis. This waste is collected in the laboratory in a designated container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Standard Methods for the Evaluation of Waters and Wastewaters, Method 2540F, Settleable Solids, current version

16.1.2. Annual Book of ASTM Standards, Volume 04.08, 1990

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Ohio Bureau of Underground Storage Tank Regulations (BUSTR) Technical Guidance Manual, April 2005

16.1.7. Revision History

Historical File:		Revision 3.0: 08/04/00		Revision 3.5: 4/23/12
		Revision 3.1: 11/06/04		Revision 4: 05/08/14
		Revision 3.2: 02/02/06		Revision 5: 05/23/16
		Revision 3.3: 09/10/07		
		Revision 3.4: 12/22/09		

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Detection and Quantitation Limits, CA-Q-S-006

16.2.5. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The reporting limit for Method SM2540F is 0.1 ml/L/hr. The reporting limit for Percent Moisture by ASTM D2216-80 is 0.1%.

17.1.2. For Settleable Solids: If sample volumes other than the volumes specified in this SOP are used, the RL will be adjusted accordingly.

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Title: pH ELECTROMETRIC METHOD

[Methods: SW846 Methods 9040B, 9040C, 9041A, 9045C and 9045D, and SM4500 H^+B]

Approvals (Signature/Date):

Technology Specialist	06/28/17 Date	Health & Safety Coordinator	06/29/17 Date
Quality Assurance Manager	07/17/17 Date	Technical Director	07/20/17 Date

This SOP was previously identified as SOP NC-WC-010, Rev 14 dated 6/15/15

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of pH in waters, drinking waters, wastewaters, and solids. It is based on SW846 Methods 9040B, 9040C. 9041A, 9045C, 9045D, SM4500 H^+B, Method 9040B/9040C should be used if the aqueous phase constitutes at least 20% of the total volume of the waste. Method 9045C/9045D should be used for measuring pH in soils and waste samples. If water is present, it must constitute less than 20% of the total volume of the sample. See Section 11 for details on determining the correct method.

1.2. The approximate working range is 1 - 14 pH units.

1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The pH is determined electrometrically by using an electrode. The pH meter is calibrated with a series of pH buffers.

2.2. For Method 9041A, an aliquot of sample is analyzed for pH using pH paper. Samples are mixed with water prior to analysis.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low sodium error electrode.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. There are no materials used in this method that have a serious or significant hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other

gloves will be cleaned immediately

5.4. Exposure to chemicals must be minimized as much as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. pH meter with electrode(s) and temperature compensation

6.2. Disposable beakers: various

6.3. Top loading balance: Capable of accurately weighing ±0.01 g

6.4. Stir plate and stir bars

6.5. Shaker or mechanical tumbler

6.6. Autotitrator

6.7. Centrifuges tubes

6.8. pH paper: Various pH ranges

6.9. Disposable snap top containers

7. REAGENTS AND STANDARDS

7.1. Standards

7.1.1. A commercially available control standard (LCS)

7.1.2. Target Calibration Standards

7.1.2.1. pH 2, 4, 7, 10, and 12 buffers--purchased

7.1.2.1.1. Fresh buffers are poured and used each working day.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. Samples should be analyzed as soon as possible after sampling, but not to exceed one day after sampling.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS and Sample Duplicates) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Sample Duplicate

9.2.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, a sample duplicate pair is processed as two independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process.

9.2.2. Sample duplicates are performed at a frequency of 10% per matrix, and must meet laboratory-specific limits for precision. For 9041A, all samples will be analyzed in duplicate.

9.3. Laboratory Control Sample (LCS)

9.3.1. One second source aqueous LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A commercially available (Environmental Resource Associates or equivalent) control standard will be analyzed. Recovery must be within +/-3% of true value.

9.3.3. Corrective Action for LCS

9.3.3.1. If the pH is outside the established control limits the system is out of control and corrective action must occur.

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9.3.3.2. Corrective action consists of identification and correction of the cause for the out of control situation and reanalysis of all effected samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. Refer to the manufacturer's manual for instrumental calibration.

10.1.2. The following procedure is applicable for use with the Orion Star A211 pH meter.

10.1.2.1. Five pH buffers will be used for calibrating this meter, 2, 4, 7, 10, and 12.

10.1.2.2. After calibration, run a pH 7, then an LCS, allowing the electrode to stabilize for each. Record results on analytical logsheet.

10.1.3. The pH meter must be calibrated daily. The calibration date is recorded on the analytical logsheet.

10.1.4. If the pH meter has been turned off, it must be calibrated prior to use.

10.1.5. The calibration slope must be 95 – 105 %. If the slope does not meet criteria, perform maintenance and recalibrate.

10.1.5.1. Maintenance can include, but is not limited to, changing the solution in the probe, cleaning the probe, or refreshing the buffer solutions.

10.2. An NCM will be created for samples with results outside of the calibration range.

10.3. Continuing Calibration

10.3.1. A pH 7 buffer is analyzed before sample analysis, every ten samples, and at the end of the analysis to ensure the calibration remains linear.

10.3.2. The pH meter must be recalibrated if the reading for the pH 7 buffer deviates by more than ±0.05. If this range is exceeded, re-analyze all samples analyzed since the last pH buffer that met criteria.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Sample Preparation

11.2.1. At the time of sample receipt, the sample must be inspected to determine the correct method reference. General Chemistry staff members will determine the percent of aqueous phase present and notify the Project Management staff if a method change is needed. Methods 9040B and C should be used if the aqueous phase constitutes at least 20% of the total volume of the waste. Method 9045C and 9045D should be used for measuring pH in soils and waste samples with less than 20% water present (as percent of total sample volume).

Note: The analyst will note in the comments section in LIMS which method was used and if a method change was required.

11.2.2. Waters and aqueous wastes where the aqueous phase constitutes at least 20% of the total volume of the waste

11.2.2.1. No preparation necessary for waters and wastewaters.

11.2.3. Solids and Sludges

11.2.3.1. Place 10 g (± 0.5 g) of sample in a beaker or other suitable container.

11.2.3.2. Add approximately 10 mL of reagent water and mix for five minutes in a shaker or mechanical tumbler.

11.2.3.3. Allow sample to stand for about one hour to allow the solids to settle out.

11.2.4. Non-aqueous Waste and liquids

11.2.4.1. Place 10 g (± 0.5 g) of sample in a beaker or other suitable container.

11.2.4.2. Add approximately 10 mL of reagent water and mix for five minutes in a shaker or mechanical tumbler.

11.2.4.3. Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension. Filter or centrifuge and decant off aqueous phase for pH measurement.

Note: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned gently with acetone if it becomes coated with an oily material.

11.2.5. Method 9041A Sample Preparation (solids, sludges, and oils)

11.2.5.1. Place 10 g (± 0.5 g) of sample in a snap top container.

11.2.5.2. Add approximately 10 mL of reagent water to the sample and mix.

11.2.5.3. If the sample is multiphasic decant the oily phase and analyze only the

aqueous layer.

11.2.5.4. Allow the sample and water layers to separate and carefully decant the water layer into another snap cap for analysis. If it is not possible to decant without decanting some of the sample (in the case of oils or oily sludges), it is permissible to use a disposable transfer pipette to remove the water layer for analysis.

11.3. Sample Analysis

11.3.1. Manual Procedure

11.3.1.1. Waters and aqueous wastes where the aqueous phase constitutes at least 20% of the total volume of the waste

11.3.1.1.1. Place the sample in a clean beaker using a sufficient volume to cover the sensing elements of the electrode(s). Allow the pH to stabilize (swirling or stirring may quicken stabilization). Record the pH in LIMS. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 7 buffer when not in use.

11.3.1.1.2. For 9040B and 9040C,– Continuously stir the sample while obtaining a stable reading.

11.3.1.1.3. For Method 9040B and 9040C note and record the sample pH of the first aliquot. Repeat the measurement on successive aliquots of sample until the values differ by < 0.1 pH units. Two or three volume changes are usually sufficient. If more than three measurements are required, contact the Group Leader.

11.3.2. Solids and Non-aqueous Waste and liquids

11.3.2.1. Immerse the pH electrodes in the supernatant layer of the sample - be careful not to stir up solids. Allow pH to stabilize and record the value in LIMS. Remove and rinse the electrodes between each measurement. Store the electrode in the pH 7 buffer.

Note: If the sample contains oil or other substances that will coat and damage the electrodes analyzing the pH by pH Paper Method 9041A should be considered.

11.3.3. Automated Procedure (aqueous samples only)

11.3.3.1. Load the appropriate schedule on the autotitrator starting with the pH calibration.

11.3.3.2. Pour a homogenized sample into the centrifuge tubes and place the tubes in the appropriate position on the autosampler. Remember to include a pH 7 buffer check after every ten positions.

11.3.3.3. Start the autotitrator.

11.3.4. Method 9041A Sample Analysis Procedure (aqueous samples)

11.3.4.1. Immerse the wide range pH paper into the decanted water layer of the sample for several seconds. Remove the paper and determine the pH range from the manufacturer's pH chart. Using the appropriate narrow range pH paper read the sample pH and record the pH in LIMS. Reading with the narrow range pH paper will be done in duplicate.

11.3.4.2. pH paper used for analysis will also be checked against certified buffers and the lot of pH paper recorded in the batch information.

Note: The initial pH range check that is performed with the wide range pH paper does **not** count as a duplicate analysis.

11.4. Analytical Documentation

11.4.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.4.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.4.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

11.4.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Method validation information (where applicable) in the form of analyst demonstrations of capabilities are maintained for this method in the analysts' training files.

13.2. Training Qualifications

13.2.1. Each analyst must have initial demonstration of competence (IDOC) data on file and corresponding continuing DOCs.

13.2.2. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic and alkaline sample waste and exhausted buffer solutions can be poured down the drain if the pH is between 5 and 10. Any sample waste generated that is not in this pH range is collected in a designated container identified as "Acid Waste".

15.2.1.2. Exhausted soil or oil samples analyzed by the method. The liquid layer is decanted and disposed of in a designated container identified as "Acid Waste". The remaining solid layer is disposed of by placing it in a container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, pH Electrometric Measurement, Method 9040B, Revision 2, January 1995

16.1.2. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Soil pH, Method 9045C, Revision 3, January 1995.

16.1.3. SW846, Test Methods for Evaluating Soil Waste, Soil and Waste pH Method 9045D, Revision 4, November 2004

16.1.4. SW846, Test Methods for Evaluating Solid Waste, pH Electrometric Measurement , Method 9040C, Revision 3, November 2004.

16.1.5. SW846, Test Methods for Evaluating Solid Waste, Third Edition, pH paper, Method 9041A, Revision 1, July 1992

16.1.6. Standard Method for pH Electrometric Method, SM4500 H^+B, 2000

16.1.7. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.8. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.9. Corporate Quality Management Plan (CQMP), current version

16.1.10. Ohio EPA Laboratory Manual for Chemical Analyses of Public Drinking Water 2000

16.1.11. Revision History

Historical File:		Revision 4.0: 01/04/99		Revision 10: 11/24/10
		Revision 4.1: 11/28/00		Revision 11: 04/16/12
		Revision 5: 02/05/03		Revision 12: 03/21/13
		Revision 6: 10/27/04		Revision 13: 03/13/14
		Revision 7: 03/23/06		Revision 14: 06/15/15
		Revision 8: 04/30/08		
		Revision 9: 05/26/10		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. A minimum reporting limit of 0.1 SU (standard units) is listed in LIMS. Units are reported as “SU”.

17.2. Method Deviations

17.2.1. Method 9041A requires a procedure to identify interferences. The laboratory does not perform this procedure.

17.2.2. Method 9041A requires each batch of pH paper to be calibrated versus certified pH buffers or a pH meter which has been calibrated with certified pH buffers. The pH paper is not calibrated by the laboratory.

17.2.3. Method 9041A does not call for any kind of sample preparation; however, due to the various matrices encountered, the laboratory preps the samples as described in section 11.2.5.

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Title: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

[Method: SW846 Method 9012A, 9012B, EPA Method 335.4, and Standard Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G]

Approvals (Signature/Date):

Technology Specialist	Date	Health & Safety Coordinator	Date
Quality Assurance Officer	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-WC-031, Rev 12a, dated 03/06/17

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total, Amenable, and Weak Acid Dissociable Inorganic Cyanide in solids, liquids, and waters. It is based on SW846 Methods 9012A, 9012B, EPA Method 335.4, and Standard Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G. The working linear range is 0.005 – 0.2 mg/L for waters and 0.25-10 mg/kg for solids.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and then trapped in a sodium hydroxide solution.

2.2. The sodium hydroxide solution is analyzed colorimetrically on an autoanalyzer using the pyridine-barbituric acid method.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Sulfides interfere, but can be eliminated by treating the sample with cadmium carbonate or bismuth nitrate prior to analysis.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials

used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Potassium Cyanide	Poison Corrosive	5 mg/m^3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 mg/m^3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Potassium Phosphate	Flammable	None	Inhalation causes severe irritation to the respiratory tract. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. .
Sodium Phosphate		None	Inhalation may cause respiratory tract irritation. Can produce delayed pulmonary edema. Causes mild skin and eye irritation. Ingestion may cause gastrointestinal irritation.

Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Cadmium Carbonate	Probable carcinogen	0.01 mg/ m^3 as Cd	Ingestion causes increased salivation, choking, vomiting, stomach pains and diarrhea. Inhalation may cause respiratory irritation, nausea and dyspnea.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Must be treated as potential health hazard; do not ingest.
Potassium Hydroxide	Poison Corrosive Reactive	2 mg/m^3 – Ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness.
Chloramine T Hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution, if possible. If glass containers are used, they must be free of any cracks or irregularities.

5.4. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas--hydrogen cyanide. Cyanide and cyanide salts such as Potassium cyanide and Sodium cyanide are extremely toxic. Addition of acid can generate hydrogen cyanide gas, which can be extremely dangerous. Inhalation of cyanide gas can cause irritation, dizziness, nausea, unconsciousness, and potentially death.

5.5. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the Department Manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal.

5.6. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded. Other gloves must be cleaned.

5.7. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Cuvettes

6.2. 100 mL, 250 mL, 1000 mL volumetric flasks

6.3. Volumetric pipettes: various, ranging from 0.01 mL to 20 mL

6.4. Top loading balance: capable of accurately weighing $\pm$ 0.01g

6.5. Balance: Analytical, capable of accurately weighing 0.0001g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Glacial Acetic Acid ($C_2H_4O_2$): Reagent grade

7.1.2. Phosphate buffer: Add 136 g of potassium phosphate - monobasic (KH_2PO_4) and 2.8 g of sodium phosphate – dibasic anhydrous (Na_2HPO_4) to 800 mL of reagent water in a 1 liter volumetric flask. Mix, bring to volume with reagent water. This reagent may be purchased commercially.

7.1.3. Chloramine-T reagent: Add 1.0 g of chloramine-T to a 250 mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily. This reagent may be purchased commercially.

7.1.4. Pyridine reagent: Add 15.0 g of barbituric acid to a 1 liter volumetric flask. Add 75 mL of pyridine and 15 mL of concentrated hydrochloric acid (HCl) and mix. Bring to volume with reagent water and store at 4°C $\pm$ 2°C in an amber glass bottle. The maximum shelf life is six months or the vendor's expiration date, whichever is earlier

Note: The pyridine barbituric acid may be purchased commercially. Filter 50 ml of the pyridine barbituric acid, and bring up to 250 ml with DI water.

7.1.5. Sodium Hydroxide (NaOH): reagent grade

7.1.6. 1.0 N Sodium hydroxide: Carefully add 40 g of NaOH to 800 mL reagent water. Dilute to 1 liter with reagent water.

7.1.7. 0.25 N sodium hydroxide: Add 250 mL of 1N NaOH to a 1 liter volumetric flask, and dilute to volume with reagent water.

Note: 0.25 N NaOH may be purchased instead.

7.2. Standards

7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in amber glass container. Stable for 1-3 months. Additional information can be found in SOP NC-QA-017.

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I (SOP NC-WC-032)

7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow Section 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I (SOP NC-WC-032).

7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1. Pipette the appropriate amount of cyanide standard into 100 mL volumetric and bring to volume with 0.25N NaOH. The low standard must be at, or below, the reporting limit. Prepare weekly.*

Concentration CN- Calibration Standards	ML CN-	Final Volume
10 mg/L	1 mL of 1000 mg/L	100 mL Dilution from stock primary and secondary
1.0 mg/L (Secondary only)	20 mL of 10 mg/L	200 LCS/MS
0.25mg/L (Secondary only)	2.5 mL of 10 mg/L	100 mL ICV

Concentration CN- Calibration Standards	ML CN-	Final Volume
0.01 mg/L	0.1 mL of 10 mg/L	100 mL MRL check
* 0.5 mg/L	5 mL of 10 mg/L	100 mL Calibrant
0.25 mg/L	2.5 mL of 10 mg/L	100 mL CCV Solution

*Denotes calibration standards

***Note:** Cyanide samples from West Virginia will be prepared and analyzed on the day that the standards are prepared.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Solid samples are not chemically preserved. Water samples are preserved with NaOH to a pH >12. All samples are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time for samples is 14 days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike/Matrix Spike Duplicate (MS/ MSD)), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water or 0.25N NaOH and must contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated Cyanide concentrations or false positive data. The MB must not contain Cyanide at, or above, the reporting limit. For Ohio VAP Projects, the MB must not contain Cyanide above the reporting limit.

9.2.2. Corrective Action for MBs

9.2.2.1. If the level in the MB exceeds the reporting limit for Cyanide, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the

corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no Cyanide result greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS spiked with an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

Note: A purchased complex cyanide solution may be used instead as the midrange LCS for Total Cyanide analysis only.

9.3.2. Corrective Action for LCSs

9.3.2.1. If Cyanide recovery is outside established control limits, the system is out of control and corrective action must occur.

9.3.2.2. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP samples, the LCS must be redistilled, unless the LCS is biased high and the samples are non-detect.

9.3.2.3. The only exception is if the LCS recoveries are biased high and the associated sample is ND for Cyanide. In this case, the batch is acceptable. **This must be addressed in the project narrative.**

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each analytical batch. A Matrix Spike (MS) is a field sample to which known concentrations of Cyanide have been added. A Matrix Spike Duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, MS/MSD pairs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. Corrective action for MS/MSDs

9.4.2.1. If Cyanide recovery or RPD falls outside the acceptance range, the results should be evaluated to determine the cause.

9.4.2.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability. Re-preparation and re-analysis may be necessary.

9.4.2.3. If matrix interference is suspected, the recovery of Cyanide must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.4.2.4. If the Cyanide concentration in the sample used to prepare the MS/MSD exceeds four times the spike level, the recovery data is automatically flagged with a "4" in TALS.

9.5. MRL Standard

9.5.1. The MRL Standard is a standard at the same concentration as the RL. It is run daily immediately after the calibration. The calibration curve cannot be accepted unless the MRL falls within ± 30% of the true value.

9.6. Additional information on QC samples can be found in QA Policy QA-003.

9.7. QC Acceptance Criteria

9.7.1. Control limits are established by the laboratory as described in NC-QA-018.

NOTE: Control limits for LCS and MS/MSD for Method 335.4 are 90% to 110%.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. The latest version is easily accessible via the LIMs

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are easily accessible via the LIMs

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1 The instrument is calibrated daily using the 0.2 ppm standard, which is diluted by the instrument to the following concentrations: 0.002, 0.005, 0.010, , 0.050,

0.100, 0.500. The calibration is verified by running a midrange ICV. The ICV is composed of the 0.25 ppm secondary standard. The ICV must not vary from the original curve by more than ± 10%, or recalibration is required. The correlation coefficient of the original curve must be ≥ 0.995, or recalibration is required. The curve must not be forced through the origin. An ICB sample is analyzed after the ICV. It cannot contain a Cyanide level above the reporting limit or recalibration is required.

10.2. Continuing Calibration

10.2.1. The run is checked every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than ± 10%, or re-analysis of all samples bracketed by the failing CCV is required. If CCVs continually fail to meet criteria, this would indicate a possible issue with the calibration standard or with the CCV standard solution, and re-preparation and re-analysis of the calibration curve and/or CCV solution is required. The CCV is composed of the 0.25 mg/L primary standard.

10.2.2. System cleanliness is checked every ten samples and at the end of the run using a CCB. It cannot contain a Cyanide level above the reporting limit, or reanalysis of all bracketed samples is required. If CCBs continually fail to meet criteria, immediately stop the analysis and take corrective action. Corrective action can include, but is not limited to, the following: refreshing the CCB solution, recalibration, or instrument maintenance as deemed necessary. The CCB is 0.25N NaOH.

10.3. High and Low Standard

10.3.1. The distillation technique is checked by distilling a high and low standard daily and comparing the values obtained to the standard curve. The method recommends that the HI/LO standards be compared to the curve with a ±10% agreement. Re-analysis must occur if the standards do not meet criteria.

10.4 Linear Calibration Range

10.4.1 The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be re-established. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

10.4. All supportive laboratory equipment is calibrated as specified in SOPs NC-QA-004 and NC-QA-015.

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11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, Operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. This is not applicable for OVAP.

11.3. Sample Preparation

11.3.1. See Cyanide Distillation SOP NC-WC-032.

11.3.1.1. The sample is distilled/refluxed under acidic conditions for 30 minutes. The released HCN is trapped in 2 mL of 0.25 N NaOH solution.

11.3.2. Sample Preparation Procedure

11.3.2.1 All Solid Samples: Test each sample for the presence of sulfides using lead acetate test paper. If sulfides are present (indicated by the lead acetate test paper turning a medium to dark brown in color), dilute the sample. Repeat this operation until a drop of the diluted sample does not darken the lead acetate test paper. Document this in the LIMS.

Note: Water samples must be tested prior to distillation. See Cyanide Distillation SOP NC-WC-032.

11.4. Sample Analysis

11.4.1. Recommended Instrument Conditions

11.4.1.1. See manufacturer's information for operation instructions.

11.4.1.2. Perform instrument startup.

11.4.1.3. Add reagents to the RapidT reagent tray.

11.4.1.4. Insert standards and samples into the autosampler segments.

11.4.2. Sample Analysis Procedure

11.4.2.1. See manufacturer's information for operating instructions.

11.4.2.2. Calibrate the instrument (see section 10.1.1). The correlation coefficient must be $>$ 0.995 to continue.

11.4.2.3. The ICV (from the secondary source) and the ICB are analyzed after the calibration and followed by an MRL check. CCVs (from the primary source) and CCBs are analyzed between every ten samples and at the end of the run.

11.4.2.4. Sample distillates higher than the highest calibration standard (0.5 mg/L) must be diluted with 0.25 N NaOH and re-analyzed.

11.4.2.5. Any samples analyzed after a high sample must be re-analyzed if carryover is suspected.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC directly into the LIMS. Level I and Level II review is performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1.1.1. Linear Regression

The linear fit uses the following functions:

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

12.2. $$\textit{Total}\ \text{Cyanide, mg/L} = \frac{\text{mg/L } CN^- \textit{ from}\ \text{printout x 6}}{\text{mL of sample distilled}}\ \text{x D}$$

12.3. $$\text{Total Cyanide, mg/kg} = \frac{\text{mg/L } CN^- \text{ from printout x 6}}{\text{g of sample distilled.}}\ \text{x D}$$

12.4. ***Amenable Cyanide, mg / L = Total CN^- (mg / L) - Chlorinated CN^- (mg / L)***

Where:

mg/L = can also be mg/kg

D = Dilution Factor $\dfrac{\textit{Final Volume of Dilution}}{\textit{Volume of Sample Distillate Used}}$

Note: Weak Acid Dissociable Cyanide has the same calculations as Total Cyanide

12.5. Laboratory Control Sample (LCS) Recovery:

$$\frac{\text{Instrument Value}}{0.25(\textit{true})}\ \text{x } 100 = \%\ \text{Recovery}$$

Note: The true value may vary by manufacturer or analysis.

12.6. CCV Recovery:

$$\frac{\textit{Instrument Value}}{\textit{0.25 (true)}}\ \textit{x 100 = \% Recovery}$$

NOTE: *CCV recovery must be between 90-110% for data to be acceptable. If CCV recovery is not within these limits, re-analysis is required.*

12.7. MS/MSD Recovery for Waters and solids

$$\frac{\textit{A - B}}{\textit{0.040 (true)}}\ \textit{x 100 = \% Recovery}$$

Where:

A	=	Instrument value for MS/MSD
B	=	Sample instrument value

12.7 Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file and the laboratory must maintain corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The waste from RapidT analysis is collected in the waste bucket housed in the instrument. The waste container is emptied at the end of the day in the "Acid Waste" container.

15.2.2. Aqueous rinsates from distillation tube clean up. This waste is collected in the lab and disposed of in a container labeled "Acid Waste".

15.2.3. Standard Waste and High Concentration Samples: This waste is disposed of in the designated container labeled “High Cyanide/Basic Waste.” NO ACID is added to this container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste Method 9012A, Revision 1, 1996

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Method 9012B, Revision 2, 2004

16.1.3. EPA 600; Determination of Total Cyanide by Semi-Automated Colorimetry, 335.4, Revision 1.0, August 1993

16.1.4. Standard Methods for the Examination of Water and Wastewater, Total, Amenable, and Weak Acid Dissociable Cyanide; Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G, 1999

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File:		Revision 5: 06/24/99		Revision8.4-A: 04/16/12
		Revision 6: 06/28/99		Revision 9: 3/22/13
		Revision 7: 05/31/01		Revision 10: 08/19/15
		Revision 8: 11/08/04		Revision 11: 10/23/15
		Revision8.1: 05/30/08		Revision 12a: 3/6/17
		Revision 8.2: 12/30/08		
		Revision 8.3: 06/15/10		

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Pipette, Repeater, and Bottle-Top Dispenser Calibrations, NC-QA-004

16.2.4. Balance and Thermometer Calibration, Container Verification, NC-QA-015

16.2.5. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.6. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.7. Cyanide Preparation Method, NC-WC-032

16.2.8. Standards and Reagents, NC-QA-017

16.2.9. Selection of Calibration Points, CA-T-P-002

16.2.10. Calibration Curves (General), CA-Q-S-005

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The reporting limit (RL) is 0.01 mg/L for waters (6 mL used) and 0.50 mg/kg for solids (0.25 g used). The lowest level of the calibration curve can be used as the reporting limit upon request.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviation

17.2.1. Method of Standard Addition is not performed for samples with matrix interference (sulfides).

17.2.2. Methods 9012A and 9012B state that the CCV must be within $\pm$15%, or recalibration is required. The laboratory reanalyzes all samples bracketed by CCVs that are outside of $\pm$10%, and recalibrates only if deemed necessary by continual failures.

Company Confidential & Proprietary

Title: CYANIDE PREPARATION METHOD

[Method: EPA Method 335.4, Standard Methods 4500-CN-I, 4500-CN-E, 4500-CN-G, and SW846 Methods 9012A and 9012B]

Approvals (Signature/Date):

Technology Specialist	11/20/17 Date	Health & Safety Coordinator	11/20/17 Date
Quality Assurance Manager	11/20/17 Date	Technical Director	11/20/17 Date

This SOP was previously identified as SOP No. NC-WC-032, Rev 12, dated 10/13/16

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Total, Amenable, and Weak Acid Dissociable Cyanide in solids, liquids, and waters. It is based on SW 846 Methods 9012A, 9012B, EPA 335.4, and Standard Methods 4500-CN-E, 4500-CN-G, and 4500-CN-I. The working linear range is 0.005 - 0.2 mg/L for waters and 0.25 to 10 mg/kg for solids.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory.

2. SUMMARY OF METHOD

2.1. Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid, and is trapped in a sodium hydroxide solution.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Interferences are eliminated or reduced by using the distillation procedure. Oxidizing agents, such as chlorine, will decompose most cyanides. Sulfide will distill over with the cyanide and could affect colorimetric, titrimetric, and electrode procedures. Refer to the preparation section on how to screen and treat samples appropriately. The possibility of interferences from nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation.

4.3. Aldehydes convert cyanide to cyanohydrin which could result in the loss of cyanide. If the presence of aldehydes is suspected, stabilize the sample with NaOH at the time of collection and add 2 mL 3.5% ethylenediamine solution per 100 mL of sample.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Latex, vinyl, nitrile, or similar gloves may be used.

5.3. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution if possible. If glass containers are used, they must be free of any cracks or irregularities.

5.4. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas, hydrogen cyanide.

5.5. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the Department Manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal. **Potassium cyanide and sodium cyanide will give off Hydrogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.**

5.6. Cyanide and cyanide salts are extremely toxic. Addition of acid can generate hydrogen cyanide gas, which can be extremely dangerous.

5.7. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
Potassium Cyanide	Poison Corrosive	5 mg/m^3 TWA as CN	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3 2 mg/m^3-Ceiling	This material will cause burns if comes into contact with the skin or eyes. Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose.

			Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Magnesium Chloride	Health	No PEL est.	Inhalation of dust may cause mild irritation to the mucous membranes.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Sulfamic Acid	Corrosive Poison	No PEL est.	Symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. Can be fatal if ingested.
Sodium Cyanide	Poison Corrosive	5 mg/m^3 TWA as CN (skin)	**This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death.** Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heartbeat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.
Zinc Acetate	Irritant	None Listed	Symptoms of skin or eye contact include redness, itching and pain.
Silver Nitrate	Corrosive Poison Oxidizer	0.01 mg/m^3 (TWA) for silver metal dust and fume as 0.02 Ag	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire. Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit			

5.8. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

5.9. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must

be kept closed unless transfers are being made.

5.10. The preparation of hazardous standards and reagents must be conducted in a fume hood with the sash closed as far as the operation will permit.

5.11. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. MicroDist Distillation Apparatus

6.2. Analytical balance, capable of accurately weighing ± 0.0001 g

6.3. Calibrated Class B Disposable Beakers: 50 mL

6.4. Volumetric flasks: 100 mL, 200 mL, 500 mL, 1 L

6.5. Volumetric pipettes: range from 0.01 to 20 mL

6.6. Balance: Top loading, capable of accurately weighing ± 0.01 g

6.7. Lead Acetate Indicator Paper

6.8. Potassium Iodide (KI) Indicator Paper

6.9. Buret: Class A 10 mL

6.10. pH strips

6.11. Snap seal containers: 120 mL

6.12. Plastic bottles with lids: 250mL or 500mL

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfamic Acid: reagent grade

7.1.2. Sulfamic Acid Solution: Add 10 g of sulfamic acid to 80 mL reagent water and dilute to 100 mL with reagent water

7.1.3. Sodium Thiosulfate: reagent grade

7.1.4. Sodium Thiosulfate Solution (0.02 g/L)

7.1.5. Sodium Thiosulfate Solution (500 g/L)

7.1.6. Hydrogen Peroxide (H_2O_2) (3%): purchased.

7.1.7. Sodium Hydroxide: (NaOH), high purity grade.

7.1.8. Sodium Hydroxide, 0.25 N: Add 10 g of NaOH to 900 mL reagent water and dilute to 1 liter with reagent water. Purchased reagent may also be used.

7.1.9. Magnesium Chloride: ($MgCl_2 \cdot 6H_2O$), reagent grade.

7.1.10. Calcium Hypochlorite: [Ca ($OC_1)_2$] reagent grade

7.1.11. Calcium Hypochlorite Solution: Add 5 g of $Ca(ClO)_2$ to 100 mL of reagent water. Store in an amber glass bottle in the dark. Prepare monthly.

7.1.12. Methyl Red Indicator: Add 0.25 g of methyl red to 250 mL of glacial acetic acid and dilute to 500 mL with reagent water.

7.1.13. Methyl red reagent grade glacial

7.1.14. Acetic Acid: (CH_3COOH), glacial reagent grade

7.1.15. Zinc Acetate: [$Zn(C_2H_3O_2)$], reagent grade

7.1.16. Sodium Acetate: [$NaC_2H_3O_2 \cdot 3H_2O$] reagent grade

7.1.17. Rhodanine: reagent grade

7.1.18. 0.0192 N Silver Nitrate: reagent grade

7.1.19. Cyanide Releasing Reagent: Add 32.2 magnesium chloride to 110.8g of reagent water. Slowly add 139g of sulfuric acid. Solution is good for 6 months

7.1.20. Weak Acid Releasing Reagent: Add 35.49g of sodium acetate trihydrate and 5g zinc acetate dihydrate to 475mL of reagent water. Slowly add 26.25mL of glaciel acetic acid. Solution is good for 6 months.

7.2. Standards

7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months. Additional information can be found in SOP NC-QA-017.

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I

7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow Section 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I.

7.2.3. Spiking Standards (Water and Solid Matrices)

7.2.3.1. If using the purchased 0.25N NaOH: Pipette the appropriate amount of cyanide standard into 100 mL volumetric, and bring to volume with 0.25N NaOH. Prepare weekly.*

Standard	Concentration CN-	mL CN-	Final Volume
Primary Intermediate CN- Std	10 mg/L	1.0 mL of 1000 mg/L	100 mL
Calibration Solution	0.5 mg/L	5 mL of 10 mg/L	100 mL
CCV Solution	0.25 mg/L	2.5 mL of 10 mg/L	100 mL
MRL Solution	0.01 mg/L	0.1 mL of 10 mg/L	100 mL
Secondary Intermediate CN- Standard	10 mg/L	1.0 mL of 1000 mg/L	100 mL
MS/MSD solution	1 mg/L	10 mL of 10 mg/L	100 mL
ICV Solution	0.25 mg/L	2.5mL of 10 mg/L	100 mL

***Note:** Cyanide samples from West Virginia will be prepared and analyzed on the day that the standards are prepared.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Solid and non-aqueous samples are not chemically preserved. Aqueous samples are preserved with NaOH to a pH≥12. All samples are stored at 4ºC ±2ºC in plastic or glass containers.

8.2. The holding time for samples of all matrices is 14 days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (Laboratory Control Sample, Method Blank, Matrix Spike, and Matrix Spike Duplicate) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same process.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB must contain all reagents specific to the method and be carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated cyanide concentrations or false positive data. The MB must not contain any cyanide at or above the reporting limit.

9.2.1.1. A MB consists of 6 mL 0.25N NaOH for Total Cyanide analysis or 6 mL reagent water for Weak Acid Dissociable and Amenable Cyanide analysis. The MB for solids consists of 5 mL 0.25N NaOH or reagent H_2O and 0.25g Ottawa sand. The MB must be distilled per Section 11.4.3 and analyzed with each analytical batch of samples.

9.2.2. Corrective Action for Method Blanks

9.2.2.1. If the Cyanide level in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no cyanide level greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. For Method 335.4, LCS recoveries must be within 90% to 110%, or corrective action is required.

9.3.2. A mid-range LCS consisting of a 0.25 mg/L (6.0 mL of 0.25 mg/L secondary source) must be distilled per Section 11.4.3 and analyzed with each analytical batch of samples for Total, Non-Amenable, and Weak Acid Dissociable Cyanide analysis.

Note: A purchased complex cyanide solution may be used instead as the mid-range laboratory control sample for **Total Cyanide** analysis only.

9.3.3. Corrective Action for Laboratory Control Samples

9.3.3.1. If recovery for cyanide is outside established control limits, the system is out of control and corrective action must occur.

9.3.3.2. Corrective action must be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP samples, the laboratory control sample must be re-distilled, unless the LCS is biased high and the samples are non-detect. **This must be addressed in the project narrative**.

9.3.3.3. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for cyanide, the batch is acceptable. **This must be addressed in the project narrative**.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A MS is a field sample to which a known concentration of cyanide has been added. A MSD is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of un-spiked sample duplicates in place of or in addition to MS/MSD pairs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.1.1. An MS/MSD pair consisting of 6 mL or 0.25 g of sample with 5mL of reagent water added and 0.24 mL of the 1.0 mg/L of secondary standard must be distilled with each analytical batch of samples. For samples requiring Amenable analysis no MS/MSD will be performed.

9.4.2. Corrective action for Matrix Spike/Matrix Spike Duplicates

9.4.2.1. If the analyte recovery or Relative Percent Difference (RPD) falls outside the acceptance range, the results should be evaluated to determine the cause of the error.

9.4.2.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability. Re-preparation and /or re-analysis may be necessary.

9.4.2.3. If matrix interference is suspected, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.4.2.4. If the native cyanide concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is flagged with a "4" in LIMS.

9.5. Additional information on QC samples can be found in QA Policy QA-003.

9.6. Control Limits

9.6.1. Control limits are established by the laboratory as described in SOP NC-QA-018, with the exception of Method 335.4, which has stated control limits of 90% to 110%.for the LCS, MS, and MSD recoveries.

9.6.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established and performed by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.7.2. MDLs are easily accessible via the LIMs.

9.8. Non-conformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a non-conformance, with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. A low and high standard from the same source as the calibration curve are distilled each day. Prepare the low standard (0.025 mg/L) by diluting 0.3 mL of 0.5 ppm standard with 0.25N NaOH to a final volume of 6 mL. Prepare the high standard (0.1 mg/L) by diluting 1.2 mL of 0.5 ppm standard with 0.25N NaOH to a final volume of 6 mL. If distilled standards do not agree within 10% of the un-distilled standards, the analyst must find the cause of the apparent error before proceeding. The instrument is calibrated daily using the 0.5 ppm standard (see SOP NC-WC-031), which is diluted by the instrument into the following concentrations: 0.002, 0.005, 0.010, , 0.050, 0.100, and 0.500.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Non-conformance Memo. This is not applicable for Ohio EPA/VAP.

11.2. Sample Preparation Procedure Applicable For Use With The Midi Distillation Unit

11.2.1. Checking for Interferences

11.2.1.1. Using pH paper strips, check the pH of the sample and document in the LIMS worksheet if the pH is <12. If pH is <12, the deviation **must be addressed in the project narrative.**

11.2.1.2. Test each sample for the presence of sulfides using lead acetate test paper. If sulfides are present (indicated by the lead acetate test paper turning a medium to dark brown in color), dilute the sample. Repeat this operation until a drop of the diluted sample does not darken the lead acetate test paper.

11.2.1.3. Test each sample for the presence of chlorine using potassium iodide test strips. If chlorine is present, add small portions of sodium thiosulfate solution (0.02 g/L) with constant re-testing until the oxidizers are neutralized. Avoid any excess thiosulfate solution. . **Note:** The analyst must create an NCM for samples that test positive for chlorine stating the possibility of low bias.

11.2.1.4. Reagent cleanliness verification:

11.2.1.4.1. One MB and one LCS must be treated with sodium thiosulfate solution per lot of reagent to demonstrate reagent cleanliness. This verification must be performed each time a new lot of reagent is used. The data for the MB and LCS must be scanned and attached to the reagents in the LIMS Reagents module if any of these reagents are used to treat interferences in any sample in the batch.

11.2.2. Amenable Cyanide (Chlorinated Aliquot)

11.2.2.1. Place 50 mL (waters) or 0.25 g (solids/non-aqueous liquids) into a snap cap container. Add a stir bar to the snap seal container. Add 50 mL of reagent water to non-waters. Place the snap cap container on a stir plate and begin mixing. Test the pH of the solution. If less than 12, add 1.25 N NaOH, drop by drop until pH ≥12. Drop by drop, add calcium hypochlorite until an excess of chlorine is reached. Test for chlorine excess using KI paper. Allow the sample to chlorinate for one hour maintaining excess chlorine and pH between 11 and 12. If necessary, add more $Ca(ClO)_2$ and/or NaOH. Either cover snap cap containers with aluminum foil, or place box over snap cap containers to keep them in the dark during the chlorination process. At the end of the chlorination period, add 8 drops of H_2O_2 (3%) followed by 4 drops $Na_2S_2O_3$ solution (500g/L) to destroy excess chlorine. Test using KI paper until there is no color change. Pour the sample into a distillation flask and follow the total cyanide preparation method (Section 11.4.3). Also set up an un-chlorinated aliquot of sample (50 mL or 1.0 g)

following the total cyanide method. **Reminder**: Do not use the purchased complex cyanide standard for the Amenable LCS.

11.2.3. Total Cyanide

11.2.3.1. See Appendix II for a diagram of the distillation tube apparatus

11.2.3.2. Add 6 mL or 0.25 g of the sample to the sample tube. Add 5mL of reagent water to solids. Add 2 mL of 0.25 N NaOH solution to the collector tube. Then place a membrane and cap on top of the collection tube.

11.2.3.3. Waste Procedure - Sometimes waste samples will stick to the weigh pan making it difficult to rinse all of the sample into the distillation tube, causing a biased low result. In this case, aliquot the sample onto a Whatman 47mm filter instead of a weigh pan. If the sample is bleeding through the filter, use extra filters to prevent sample loss due to over-saturation of the filter. It may be helpful to form the filter into a bowl shape before aliquoting to keep the sample from running off the filter. Place the filter(s) on the top-loading balance and tare the balance. Weigh 0.2 g of the waste sample in the filter(s). Once the sample is weighed, the filter can be wrapped around the sample and dropped into the distillation tube. When preparing waste samples in this way, an extra blank must be distilled with a filter added to the distillation tube. This blank must be analyzed and shown to be free of cyanide to prove the filters do not contain cyanide. Proceed with the rest of the distillation as usual.

11.2.3.4. Turn on the MicroDist apparatus allowing it to warm up to 120 degrees C..

11.2.3.5. Add 0.25mL sulfamic acid to each sample tube. Then individually add 0.75mL releasing reagent and immediately push the collector tube onto the sample tube with the press.

11.2.3.6. Put the distillation tube into the hot block. Push the tube down until the collector tube ring touches the block.

11.2.3.7. Set a timer for 30 minutes. Do not pull the tubes out before the 30 minutes are up to check them.

11.2.3.8. After 30 minutes have passed put on heat resistant gloves. Remove the first tube from the block and immediately pull the sample tube off of the bottom. Failure to do so can create suck-back causing low recoveries, ruining the sample. Dispose of the sample tube contents in the acid waste container.

11.2.3.9. Place the tubes in a rack with the “M” end up. Allow them to cool for 10 minutes. Slowly roll the distillate around the tube to gather droplets clinging to the walls.

11.2.3.10. With the "D" end up break the collector tube in half. Bring the distillate up to the 6mL final volume marked on the tube with NaOH. If the sample is not going to be analyzed immediately it should be sealed with parafilm.

11.2.4. Weak Acid Dissociable

11.2.4.1. Add 6 mL or 0.25 g of sample to the distillation tube. Add 5mL of reagent water to solids. Add 2 mL of 0.25 N NaOH solution to the collection end of the distillation tube.

11.2.4.2. Add 1 drop of methyl red to samples. Then add 0.75 of the weak acid releasing solution. If the sample is not pink add acetic acid dropwise. **Reminder:** Do not use the complex purchased cyanide solution standard as the LCS for Weak Acid Dissociable cyanide analysis.

11.2.4.3. Prep will continue just like that for total cyanide starting in section 11.2.3.

11.2.5. Cyanide Unit Cleanup

11.2.5.1. All distillation tubes can be recycled once all samples and distillates have been put in the appropriate waste container.

11.3. Analytical Documentation

11.3.1. Record all analytical information appropriately in the LIMS, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.3.2. All standards are logged into the LIMS reagent module. All standards are assigned a unique number for identification.

11.3.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.3.4. Sample results and associated QC are transferred directly into the LIMS from the instrument. Level I and Level II review is done in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file and the laboratory must maintain corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Total cyanide waste is disposed of in the designated container labeled "Acid Waste". Weak Acid dissociable waste is disposed of in a designated container labeled "Weak Acid Dissociable Waste".

15.2.1.2. Standard Waste and High Concentration Samples: This waste is disposed of in the designated container labeled "High Cyanide/Basic Waste." NO ACID is added to this container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total and

Amenable Cyanide, Automated UV; Method 9012A, Revision 1, 1996

16.1.2 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total and Amenable Cyanide, Automated UV; Method 9012B, Revision 2, 2004

16.1.3 EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Method 335.4

16.1.4. Standard Methods for the Examination of Water and Wastewater, Weak Acid Dissociable Cyanide; Method 4500-CN-I, 1999

16.1.5. Standard Methods for the Examination of Water and Wastewater, Complex Cyanide; Method 4500-CN-E, 4500 CN-G, 1999

16.1.6. Standard Methods for the Examination of Water and Wastewater, Colorimetric Method; Method 4500-CN-E, 4500 CN-E, 1999

16.1.7. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.8 TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.9 Corporate Quality Management Plan (CQMP), current version

16.1.10 Revision History

Historical File:		Revision 7.0: 03/19/98		Revision 8.8-A: 4/16/12
		Revision 8.0: 02/04/99		Revision 9: 03/21/13
		Revision 8.1: 03/20/00		Revision 10: 8/27/14
		Revision 8.2: 05/31/01		Revision 11: 09/21/15
		Revision 8.3: 06/17/03		Revision 12a: 10/13/16
		Revision 8.4: 12/08/04		
		Revision 8.5: 05/30/08		
		Revision 8.6: 12/30/08		
		Revision 8.7: 06/16/10		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.3 Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4 Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5 Standards and Reagents, NC-QA-017

16.2.6 Cyanide, Automated Method, NC-WC-031

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Method Deviation [9012A]

17.1.1. The reflux distillation apparatus used is the MicroDistillation.

17.1.2. The volume of sample used is reduced to 6 mL vs. 500 mL using the midi-distillation apparatus.

17.1.3. Samples are refluxed for 30 minutes instead of 1.5 hrs. per 335.4.

17.1.4. Samples will not be treated for sulfide interference with bismuth nitrate or other reagents prior to distillation. The sulfide will be diluted out instead.

17.1.5. Method of Standard Addition is not performed for samples with matrix interference (sulfides).

17.2 Method Deviation [SM4500CN_G]

17.2.1 No MS/MSD will be performed for non-amenable cyanide analysis

Appendix I

CYANIDE STANDARDIZATION

1. Pipette 10.0 mL of the 1000 ppm stock cyanide standard into a 250 mL Erlenmeyer flask and add 90 mL of reagent water.
2. Add 0.5 mL (10 drops) of Rhodanine indicator.
3. Titrate with 0.0192 N silver nitrate (using a micro burette) until the color changes from yellow to pink/orange.
4. Titrate a blank (100 mL reagent water) following Steps 2 and 3.
5. Calculation

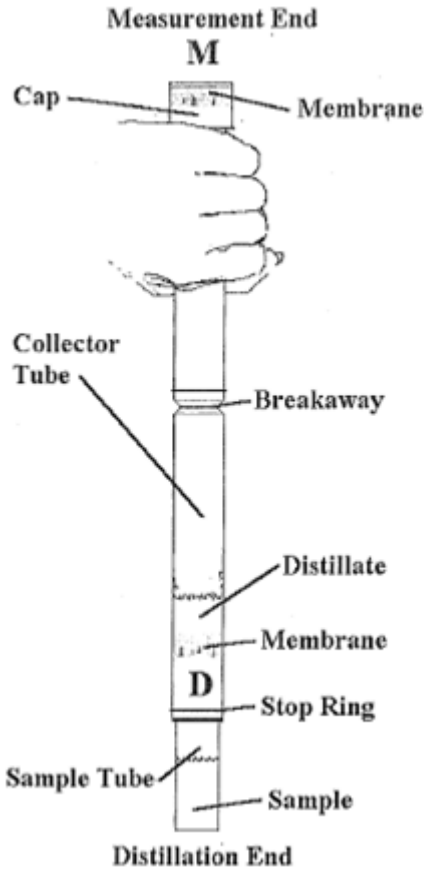
$$\text{Cyanide, mg / L} = \frac{\text{(A - B) (1000)}}{\text{mL Cyanide Solution (10)}}$$

Where:
A = mL titrant for standard
B = mL titrant for blank

6. If the cyanide concentration is not 1000 ppm ± 10%, the standard should be re-made and re-standardized.

Appendix II

Diagram of the Distillation Tube Apparatus



Title: FLASHPOINT CLOSED CUP

[Method: SW846 Method 1010, 1010A, and ASTM D93-80]

Approvals (Signature/Date):

Technology Specialist	12/11/17 Date	Health & Safety Coordinator	12/12/17 Date
Quality Assurance Manager	12/27/17 Date	Technical Director	12/28/17 Date

This SOP was previously identified as SOP No. NC-WC-0034, Rev 4, dated 6/15/16

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Flashpoint by Pensky-Martens closed cup tester in a variety of wastes, liquids, and solids. It is based on ASTM D93-80, SW846 Method 1010, and 1010A. The approximate working range is 20-200 ºF.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The sample is heated at a slow constant rate with continual stirring if it is a liquid or water. A small test element is directed into the sample cup at regular intervals. The Flashpoint is the lowest temperature at which the test element causes the vapor above the sample to ignite.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Not Applicable

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
p-Xylene	Flammable Irritant	100 ppm-TWA	Inhalation of vapors may be irritating to the nose and throat. Inhalation of high concentrations may result in nausea, vomiting, headache, ringing in the ears, and severe breathing difficulties, which may be delayed in onset. High vapor

			concentrations are anesthetic and central nervous system depressants. Skin contact results in loss of natural oils and often results in a characteristic dermatitis. May be absorbed through the skin. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves MUST be worn when doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to a Laboratory Supervisor and the EH&S Coordinator.

5.6. In the event a sample ignites in the test apparatus do not attempt to remove the sample. Turn off the apparatus and flame. The flame should go out when the cup is closed. If this does not happen the flame may be extinguished by covering the sample with a non-flammable material. After the apparatus has cooled the sample may be removed.

5.7. **When testing a sample, the analyst shall remain within eyesight of the flash point tester and will manually shut down the tester if it fails to automatically shut down following ignition.**

6. EQUIPMENT AND SUPPLIES

6.1. Igniter and detector

6.2. Pensky-Martens closed cup tester with stirrer, stirring motor, internal barometer, and thermocouple or equivalent

6.3. Flash point sample cup with lid

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. p-Xylene

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in glass containers at 4ºC ± 2ºC. Samples are not to be stored in plastic containers since volatile materials may diffuse through the walls of the container.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS and sample duplicates) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Laboratory Control Sample (LCS)

9.2.1 One LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process and the accuracy of the Flashpoint Apparatus. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.2.2 One LCS consisting of p-Xylene will be analyzed at the beginning of every batch. p-Xylene has a flashpoint of 81 ^{o}F. If the flashpoint of the p-Xylene varies by more than $\pm$ 2 ^{o}F, corrective action is required before samples can be analyzed.

Note: Dependent upon ambient temperature, p-Xylene may have to be cooled to just above the freezing point in order to achieve accurate results.

9.2.3 Corrective Action for LCS

9.2.3.1 If the p-Xylene flashpoint temperature is outside of established control limits, the system is out of control and corrective action must occur.

9.2.3.2 Corrective action consists of troubleshooting the apparatus for errors and cleanliness, followed by re-analysis of the p-Xylene LCS.

9.3. Duplicates

9.3.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.3.2. Sample duplicates are performed at a minimum frequency of 10% per matrix (water, waste, solid) and must meet laboratory-specific limits for precision. Soil and Waste matrices may be combined for batching purposes.

9.4. Control Limits

9.4.1. For this test method, the RPD value is used to assess the sample duplicate.

9.5. Nonconformance and Corrective Action

9.5.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration of tester

10.1.1. Determine the flash point of p-Xylene following the procedures outlined in Section 11.3.

10.1.2. The tester is operating properly when a value of 81± 2ºF is obtained (See section 9.2).

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-Conformance Memo. The Non-Conformance Memo shall be filed in the project file in LIMS.

11.2. Sample Preparation Procedure

11.2.1. Not Applicable

11.3. Sample Analysis Procedure

11.3.1. Operate the Pensky-Martens tester according to the manufacturer's specifications, in a well-ventilated area away from flammable materials and

significant air movement. Operating manuals are located in the laboratory near the tester. Performing this analysis under a hood is the best approach - ensure that the air intake and hood lights are turned off. Inspect the igniter coil closely to ensure the filaments are not touching. Proper placement of the igniter coil in the flashpoint apparatus is crucial to achieving accurate results. Fill the sample cup to the designated line with sample, and assemble the tester as directed.

11.3.1.1. Solid samples require a modified cover for the sample cup. The solid material is placed in the cup until even with the designated line. The sample is not stirred.

11.3.2. A flash check (LCS) must be analyzed with each analytical batch of samples. The compound p-Xylene is used to provide the analyst a reference true value for flashpoint. The flash temperature is recorded in LIMS. - The true flashpoint temperature for p-Xylene is 81ºF. The acceptable range for p-Xylene flashpoint is 79 to 83°F. If the measured p-Xylene flashpoint is outside of this range, troubleshoot the system and rerun the p-Xylene. Sample analysis will not proceed until a passing p-Xylene flashpoint is achieved.

11.3.3. Pour the sample into the cup, assemble the apparatus, and record the initial temperature. Start the flashpoint apparatus.

11.3.3.1. If sample flashes, record the temperature at which the flash occurred in LIMS. Re-analyze the sample using a fresh aliquot for confirmation using the observed flashpoint as the estimated flashpoint.

Note: Confirmation analyses are run using a program that is specifically built for known flashpoints. Reference the apparatus user manual to choose the appropriate program.

11.3.3.2. If the temperature reaches 200ºF and no flash occurs (see manual), turn off flashpoint instrument and record >200ºF as the flashpoint in LIMS.

11.3.4. If solvents are used to clean sample cups, be sure to clean thoroughly with reagent water to prevent contamination.

Note: Some samples may burn, but not flash. If possible, record the initial temperature at which the sample begins to burn in the comments section of the worksheet. Report these samples at the initial temperature the sample starts to burn and include an NCM.

11.3.5. Some samples have a flashpoint below room temperature. If this is known, the sample should be chilled to just above freezing and then analyzed promptly to confirm a true flashpoint.

11.3.6. Waters, distillate fuels, and homogeneous petroleum products will be analyzed with a stir rate of 105 rpm. This is program #3 on the flashpoint apparatus.

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11.3.7. Used oils and other highly viscous materials will be analyzed with a stir rate of 205 rpm. This is program #8 on the flashpoint apparatus.

11.4. Analytical Documentation

11.4.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.4.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.4.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.4.4. Record all sample results and associated QC directly into LIMS during analysis. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. If the sample did not flash, report > 200 ^{o}F.

12.2. If the sample flashes, record and report the observed flashpoint.

13. METHOD PERFORMANCE

13.1. Method validation information (where applicable) in the form of analyst demonstrations of capabilities are maintained for this method in the analysts' training files.

13.2. Training Qualifications

13.2.1. Each analyst must have initial demonstration of competence (IDOC) data on file and corresponding continuing DOCs.

13.2.2. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

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15. WASTE MANAGEMENT

15.1. Refer to the Laboratory Sample and Waste Disposal plan.

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

15.3. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.4. Waste Streams Produced by the method

15.4.1. The following waste streams are produced when this method is carried out.

15.4.1.1. **Solid samples.** Solids are put into the red can for the debris waste stream

15.4.1.2. **Liquid samples and waste solvents.** Flammable wastes including the Xylene standard are disposed of in the solvent waste stream located in the red can in the hood**.** Adding water to the solvent waste stream should be avoided.

16. REFERENCES

16.1. References

16.1.1. Annual Book of ASTM Standards, ASTM Method D93-80, Flashpoint by Pensky-Martens Closed Tester

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Pensky-Martens Closed Cup Method for Determining Ignitability, Method 1010, Revision 0, September 1986.

16.1.3. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Pensky-Martens Closed Cup Method for Determining Ignitability, Method 1010A, Revision 1, November 2004.

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. Revision History

Historical File:		Revision 0: 10/24/97		Revision 4: 06/15/16
		Revision 1.0: 09/25/03		
		Revision 1.1: 06/28/07		
		Revision 1.2: 09/18/09		
		Revision 1.2: 09/18/09		
		Revision 1.3: 04/09/12		
		Revision 2: 03/21/13		
		Revision 3: 03/12/14		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Deviations from Method

17.1.1. Methods SW846 1010, 1010A, and ASTM D93-80 do not reference solid materials. Section 11.3.1.1 notes the procedure for solid samples.

Title: PAINT FILTER

[Method: SW846 Method 9095A and 9095B]

Approvals (Signature/Date):

Technology Specialist	12/12/17 Date	Health & Safety Coordinator	12/18/17 Date
Quality Assurance Manager	12/27/17 Date	Technical Director	12/15/17 Date

This SOP was previously identified as SOP No. NC-WC-046, Rev 7, dated 12/10/15

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of the presence of free liquid in a variety of wastes. It is based on SW846 Methods 9095A and B.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory.

2. SUMMARY OF METHOD

2.1. An aliquot of sample is placed in a paint filter. If any liquid portion of the material passes through the filter in five minutes, the sample is deemed to contain free liquids.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. There are no materials used in this method that have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

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5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Conical paint filter: Mesh 60 x 48

6.2. 150 mL plastic beakers

7. REAGENTS AND STANDARDS

7.1. Not applicable

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in glass containers at 4°C $\pm$ 2°C.

8.3. Holding Times - Not Applicable

9. QUALITY CONTROL

9.1. Duplicates

9.1.1. Sample duplicates are performed at a minimum frequency of 10% and must meet laboratory-specific limits for precision.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample

matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-conformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Not applicable

11.4. Sample Analysis

11.4.1. Place an aliquot of representative sample in the paint filter up to the level where the sample covers the mesh of the filter. Place the filter containing the sample aliquot in a 150 mL plastic disposable beaker.

11.4.2. Allow the sample to drain for five minutes into the graduated cylinder. If any free liquid is collected in the graduated cylinder, the sample is considered positive. If no free liquid is collected, the sample is negative. Data entry into LIMS is CFL (Contains Free Liquids) and CNF (Contains No Free Liquids).

Note: If fine or dry solid samples are analyzed, any particles that fall through the filter that are not liquid will not be considered a positive result.

Note: If sample quantity is limited, a visual procedure may be performed and documented accordingly.

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.5.2. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) is available for each data file.

11.5.3. Record all sample results and associated QC in LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Training Qualifications

13.1.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.5. Waste Streams Produced by the Method

15.5.1. The following waste streams are produced when this method is carried out.

15.5.1.1. Spent sample is to be disposed of in the non-hazardous solids container located in the prep lab near the sink.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Paint Filter Liquids Test, Method 9095A

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Method 9095B, Revision 2,

August 2002

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.6. Revision History

Historical File:		Revision 0: 06/08/95		Revision 7: 12/10/15
		Revision 1: 09/25/03		
		Revision 2: 10/30/07		
		Revision 3: 12/31/09		
		Revision 4: 04/05/11		
		Revision 5: 08/27/12		
		Revision 6: 08/07/13		

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Method Deviations

17.1.1. SW846 Method 9095 requires a paint filter size 60 mesh. This size is no longer commercially available. Mesh size 60 x 48 has been deemed acceptable by the EPA, and will be used for analysis.

17.1.2. SW846 Method 9095 specifies that 100 g or more of sample should be used. Due to the size of the available filters and varying sample volume received, the laboratory uses approximately 20 to 50 g of sample.

Title: SULFIDE

[Methods: SW846 Methods 9030B and 9034, and SM4500 S2-F]

Approvals (Signature/Date):

Lucas Grossman	02/17/18		02/19/18
Technology Specialist	Date	Health & Safety Coordinator	Date
	02/15/18		03/01/18
Quality Assurance Manager	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-WC-060, Rev 11, dated 2/16/17

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1. SCOPE AND APPLICATION

1.1. This SOP is applicable to the determination of the concentration of Sulfide in waters, liquids, solids, and sludges. It is based on SW846 Method 9030B/9034, Methods for Chemical Analysis of Water and Wastes. This method measures Total Sulfide which is usually defined as the acid-soluble fraction of a waste. SM4500 S2-F measures Sulfide in undigested aqueous matrix samples. For 9030B/9034 analysis, the working range is 3 to 30 mg/L for waters and 30-650 mg/kg for solids and sludges. Method SM4500 S2-F is suitable for measuring sulfide in concentrations above 1 mg/L.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Samples may be analyzed undigested by SM4500 S2-F, or digested by 9030B/9034.

2.2. For digested 9030B/9034 acid soluble (Total) sulfide samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70^0C and the hydrogen sulfide (H_2S), which is formed, is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate scrubbing bottles where it is precipitated as zinc sulfide.

2.3. For methods SM4500 S2-F and 9034 (after the digestion process): An excess of iodine is added to a sample, which oxidizes the Sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), latest version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Reducing substances such as thiosulfite, sulfites, and various organic compounds cause interferences, but treatment with zinc acetate solution will eliminate some of these interferences. (Use approximately 15 drops of 2 N zinc acetate per 500 mL of sample if not already preserved with it.)

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4.3. Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an immeasurable form.

4.4. Samples that contain strong oxidizers or reducers will interfere with this method.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table.** A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Iodine	Poison Corrosive Oxidizer	0.1 ppm-Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	2 mg/ m^3 - Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/ m^3 - TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose, throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.

Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
Note: Always add acid to water to prevent violent reactions.			
1- Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. **Sodium Sulfide will form Hydrogen Sulfide (HS) gas if combined with water moisture or strong acids. Inhalation of HS gas may be fatal.**

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

5.9. Sulfide titration must be performed in a fume hood.

6. EQUIPMENT AND SUPPLIES

6.1. Volumetric pipettes: various

6.2. Burette: 10 mL and 25 mL Class A

6.3. Erlenmeyer flasks: 500 mL

6.4. Graduated cylinder: 50 mL and 200 mL

6.5. Top loading balance: capable of accurately weighing ± 0.01 g

6.6. Volumetric flasks: various

6.7. Distillation apparatus containing: Boiling tubes, inlet adapters, dropping/addition funnels, gas inlets, impinged bubblers, bubbler/scrubber vessels, Westclips®, gas line "T" connectors, Easy Midi Distillation heating block or equivalent

6.8. Ottawa sand

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. 6N Hydrochloric Acid (1:1 HCl): Add 250 mL concentrated hydrochloric acid (HCl) to 250 mL of reagent water.

7.1.2. Starch Indicator: Add 10 mL of reagent water to 5 g starch (potato) and mix. Add starch mixture to 500 mL of boiling reagent water. Mix, cool, and store in a well-labeled squirt bottle. Alternately, use purchased starch solution.

7.1.3. 0.025 N Sodium Thiosulfate (stored in desiccator): Add 0.4 g NaOH and 6.205 g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$) to 500 mL of reagent water in a 1 liter volumetric. Dilute to volume with reagent water. Store in a dark container. This reagent is also available commercially.

Note: If the 0.025 N Sodium Thiosulfate solution is a purchased certified solution, standardization is not necessary.

7.1.3.1. Standardization of 0.025 N Sodium Thiosulfate Solution: *To make 0.025N Biodate Solution, dissolve 0.462 g $KH(IO_3)_2$ in 500 mL with reagent water. Weigh 2 g KI in a 500 mL Erlenmeyer flask. Add 100 to 150 mL reagent water, 5 drops H_2SO_4 and 20 mL Biodate solution using a volumetric pipette. Dilute to 200 mL with reagent water. Titrate with Sodium Thiosulfate. When a pale straw yellow color is reached, add 1-2 mL starch. Continue titrating from a blue to a clear end point. **If a certified solution is purchased, standardization is not necessary.**

Note: Biodate Solution may be purchased.

Calculation:

$$Na_xS_2O_3\ Normality = \frac{(a)\ (b)}{c}$$

Where:
a = mLs Biodate (20 mL)
b = Normality Biodate (0.025N)
c = mLs of $Na_2S_2O_3$ used to titrate Repeat two more times

7.1.4. 0.0282 N Iodine Solution: Add 20 g KI (potassium iodide) and 3.2 g iodine to a 1 liter volumetric flask. Add 500 - 700 mL of reagent water and dissolve. Dilute to volume with reagent water. Store in a dark container. This reagent is also available commercially.

Note: If the 0.0282 N Iodine solution is a purchased certified solution, standardization is not necessary.

7.1.4.1. Standardization 0.0282 N Iodine Solution: Perform three method blanks daily. Refer to method blank section in SOP.

Calculation:

$$\textit{Normality Iodine} = \frac{(\textit{Normality } Na_2S_2O_3)(\textit{mL of titrant } Na_2S_2O_3)}{20 \textit{ mL Iodine}}$$

7.1.5. Zinc Acetate Solution (approximately 0.5M): Dissolve 55g of zinc acetate in 400 mL reagent water. Add 0.5 mL HCl and dilute to 500 mL with reagent water.

7.1.6. Sulfuric acid – Concentrated.

7.1.7. Nitrogen – High Purity Grade

7.2. Standards

7.2.1. Laboratory Control Sample

7.2.1.1. 2000 ppm Sulfide: Add 3.5 g of sodium sulfide to 100 mL of reagent water in a 250mL volumetric flask. Dilute to volume with reagent water. The sulfide standard must be verified each working day. If the resulting value is <75% of the original standard, a new solution must be prepared.

7.2.2. Matrix Spike Standard

7.2.2.1. Prepare a midrange matrix spike standard as described in 7.2.1 for use as a MS/MSD.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Waters are preserved to a pH > 9 with NaOH and zinc acetate. Non-water samples are unpreserved. All matrices are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time is 7 days from sampling to analysis for aqueous and solid samples. Samples must be analyzed as soon as possible if arrived in the laboratory without proper chemical preservation.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, and MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated sulfide concentrations or false positive data. The MB should not contain any sulfide at or above the reporting limit.

9.2.2 For Method 4500-S2-F, a MB consisting of 200 mL reagent water must be analyzed with each analytical batch of samples.

9.2.3 For Method 9030B/9034, a MB consisting of 50 mL reagent water, or 5g Ottawa sand and 50 mL reagent water for solids and wastes must be analyzed with each analytical batch of samples.

9.2.4 Corrective Action for MBs

9.2.4.1. If the sulfide level in the MB exceeds the reporting limit for the sulfide in the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, this **must be addressed in the project narrative.**

9.2.4.2. If there is no sulfide level greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

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9.3.2. For Method 4500-S2-F, a mid-range LCS is prepared by adding 2.5 mL of the 2000 ppm sulfide standard to 200 mL reagent water.

9.3.3. For Method 9030B/9034, a mid range LCS is prepared by adding 0.25 mL of 2000 ppm sulfide standard to 50mL reagent water or 5g Ottawa sand and 50 mL reagent water for solids or wastes.

9.3.4. LCS standard must be analyzed with each analytical batch of samples.

9.3.5. Corrective Action for LCS

9.3.5.1. If the sulfide recovery is outside established control limits the system is out of control and corrective action must occur.

9.3.5.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for sulfide, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.5.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. If re-preparation and re-analysis are not possible due to limited sample quantity or other considerations, this must be addressed in the project narrative.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of sulfide have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. For Method 4500-S2-F, an MS/MSD pair consisting of 200 mL sample and 2.5 mL 2000 ppm sulfide standard must be analyzed with every 20 samples.

9.4.3. For Method 9030B/9034, an MS/MSD pair consisting of 50 mL sample for waters, 5g sample and 50 mL reagent water for solids and wastes, and 0.25 mL 2000 ppm sulfide standard must be analyzed with every 20 samples.

9.4.4. Corrective Action for MS/MSDs

9.4.4.1. If the sulfide recovery or RPD falls outside the acceptance range, the results should be evaluated to determine the cause.

9.4.4.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability.

9.4.4.3. If matrix interference is suspected, the recovery of sulfide must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.4.4.4. If the native sulfide concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported and flagged with a "4" in LIMS.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. LCS limits are easily accessible via the LIMs.

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.6.2. MDLs are easily accessible via the LIMs.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. NA.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Aqueous Sample Method 9030B

11.3.1.1. For an efficient distillation, prepare the sample using one of the procedures in this section. Then proceed with the distillation step.

11.3.1.2. If the sample is aqueous, shake the sample container to suspend any solids, and then quickly decant the appropriate volume (50 mL) of the sample to a graduated cylinder. Transfer the contents of the graduated cylinder into the boiling tube.

11.3.1.3. If the sample is aqueous, but contains a large proportion of solids, the sample may be roughly separated by phase and the amount of each phase measured and weighed to the nearest milligram into the distillation flask in proportion to their abundance in the sample. Reagent water may be added up to a total volume of 50 mL.

11.3.2. Solids and Waste Samples, Method 9030B

11.3.2.1. Weigh out 5g $\pm$ 0.1 g of homogenized sample and put into the reaction flask.

11.3.2.2. Samples that are not water miscible (oils, various solvents) should not be analyzed using this method.

11.3.3. Method 9030B Distillation

11.3.3.1. Acid Soluble Sulfides

11.3.3.1.1. Place the boiling tube containing the sample in the heater block, and assemble the acid-soluble distillation apparatus as shown in Figure 1.

11.3.3.1.2 Place 2.0 mL of 0.5M zinc acetate solution and 25 mL reagent water in each of two bubbler/scrubber vessels. (The method also requires the addition of formaldehyde, but this has been found to cause interferences; therefore, it is not used.) Place an impinged bubbler (front) in the first vessel, a fritted bubbler (back) in the second vessel, and seal them with size 24/40 WestClips®. The sealed vessels and impingers function as the gas scrubbers. Connect the first scrubber to the inlet adapter, and place the second bubbler vessel in the bubbler vessel rack. Connect the two impingers in series using Tygon® tubing.

11.3.3.1.3 Close stopcock of addition/dropping funnel. Place 10 mL concentrated sulfuric acid in addition/dropping funnel.

11.3.3.1.4 Connect a high-purity (GC grade) nitrogen gas source to the main inlet of the gas manifold of the aluminum heater block as specified in the Heater Block Operation manual. Use a

two-stage gas tank regulator, and set the pressure into the gas manifold to 20 psi.

11.3.3.1.5 Connect a black gas line from each gas manifold valve to a "T" connector and a Tygon® gas line from manifold valve to a "T" connector and a Tygon® gas line from the "T" to each of the two gas inlets of the apparatus--one at the top of the addition/dropping funnel, and one at the inlet adapter as shown in Figure 1.

11.3.3.1.6 Purge assembled apparatus with high-purity nitrogen for ten minutes to remove atmospheric oxygen from the apparatus and contained solutions. During purge, adjust nitrogen flow such that approximately five bubbles per second exit the base of the inlet adapter. A proper flow rate is indicated by a vigorous foaming action at the fritted bubbler.

11.3.3.1.7 Following instructions in the Easy Dist Heat Block manual set the program to "P1". Open the stopcock of the dropping/addition funnels and allow all the sulfuric acid to drop into the boiling tube at a rate of approximately 1 mL/min. Continue to observe the boiling tube contents as acid is added to monitor for excessive foaming, swelling of solids, or formation of a non-homogeneous mixture that is not suspended by the bubbling action in the tube. It may be necessary to use a smaller sample aliquot under such conditions. Once dropping/addition funnel is empty, close the stopcock to ensure sample is not lost into the funnel. It may also be necessary to add antifoam to known swelling solids and waters.

11.3.3.1.8 After the 90-minute heating period, the heat will automatically shut off. Remove the bubbler vessels. Turn off the nitrogen flow. Carefully combine the gas scrubber solutions. Do not shake or mix the solutions to avoid loss of sulfide. Determine the concentration of acid-soluble sulfide in the zinc acetate gas scrubber solutions by using the titrimetric-iodine method (9034).

11.4. Sample Analysis

11.4.1. Method 4500-S2-F

11.4.1.1. Place 200 mL of homogenized sample in a 500 mL Erlenmeyer flask. At this time, add any spiking solutions if necessary for the filtered water samples.

11.4.1.2. Add 20.0 mL 0.028 N Iodine solution and approximately 2 mL 1:1 HCl solution (watch for fumes). Check the pH prior to titration to make sure it is less than 2. If the pH is not <2, add additional acid.

11.4.1.3. Add 1 squirt (1-2 mL) of starch indicator and mix. Titrate from blue to clear with 0.025 N sodium thiosulfate titrant. Record the amount of titrant used in LIMS.

Note: Some matrices may be turbid or colored and the color change from blue to clear may not be easily seen. In this case, look for a shade change.

11.4.1.4. After adding 20 mL iodine, the color should be orange/red. If the color remains yellow, add additional 20 mL aliquots until the orange/red color persists (adjust the calculation accordingly). If the sample requires more than 60 mL of iodine, the sample must be re-prepped at a dilution.

11.4.2. Methods 9030B/9034 Titrations

11.4.2.1. Add 8 mL of 0.0282 N iodine solution to scrubber solution and 1-2 mL 1:1 HCl (check pH prior to titration to make sure it is less than 2).

11.4.2.2. After adding 8 mL iodine, the color should be orange/red. If the color remains yellow, add additional 8 mL aliquots until the orange/red color persists (adjust the calculation accordingly). If the sample requires more than 24 mL of iodine, the sample must be re-prepped at a dilution.

11.4.2.3. Add 1 squirt of starch indicator and mix. Titrate from blue to clear with 025 N sodium thiosulfate titrant.

11.4.2.4. Using a 10 mL Class A burette, titrate scrubber solution in 150 mL disposable beaker.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC into the LIMS. Level I and Level II reviews are performed in the LIMS.

11.6. Glassware Washing and Cleaning

11.6.1. Boiling tubes and bubbler/scrubber vessels must be cleaned with hot soapy water between each setup.

11.6.2. Impingers and inlet adapters must be cleaned with hot soapy water, and may require additional 1:1 HCl rinse if sulfide contamination is suspected. If 1:1 HCl rinse is required, many rinses with reagent water must follow to ensure all 1:1 HCl is completely rinsed away. Alternately, rinsing with 1N NaOH solution is acceptable.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$\textit{Sulfide, mg / L or mg / kg} = \frac{\textit{[(A x B) - (C x D)] x 16,000}}{\textit{mL or g of sample used}}$$

Where:
A = mL of iodine solution
B = Normality of iodine solution
C = mL of sodium thiosulfate titrant
D = Normality of sodium thiosulfate titrant

12.1.1. LCS Recovery

$$LCS\,\%\,\text{Recovery} = \frac{\text{mg/L (from 12.1.1)}}{\text{20 (true)}}\,\text{x}\,100$$

Note: The true value of the standard is determined daily.

12.1.2. MS/MSD Recovery

$$\text{MS/MSD \% Recovery} = \frac{\text{A - B}}{\text{20 (waters) or 1000 (solids)}}\,\text{x}\,100$$

Where:
A = (20 - mL titrant for MS/MSD) x 400
B = Concentration from 12.1.1 x mL or g of sample used

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

15.3. Waste Streams Produced by the Method

15.3.1. The following waste streams are produced when this method is carried out.

15.3.1.1. Acidic waste generated by sample titration. Waste material is disposed of in the 55-gallon waste stream called "Acid Waste" located in the lab.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Sulfide, Method 9030B.

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. SW846, Test Methods of Evaluating Solid Waste, Third Edition, Titrimetric Procedure for Acid-soluble and Acid-insoluble Sulfides, Method 9034

16.1.5. Standard Methods for the Examination of Water and Wastewater, Sulfide, Iodometric Method 4500-S2-F, 2000.

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Revision History

Historical File:		Revision 0: 02/14/96		Revision 10: 12/14/15
		Revision 1: 11/20/00		Revision 11: 02/16/17
		Revision 2: 09/17/02		
		Revision 3: 06/17/03		
		Revision 4: 09/24/04		
		Revision 5: 10/22/07		
		Revision 6: 03/05/09		
		Revision 7: 11/16/10		
		Revision 8: 08/12/14		
		Revision 9: 09/15/14		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting Limits

17.1.1. The lower reporting limit for Method 4500-S2-F is 1 mg/L for water. The acid-soluble sulfide reporting limit is 3 mg/L for water and 30 mg/kg for solid.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

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17.2. Method Deviations

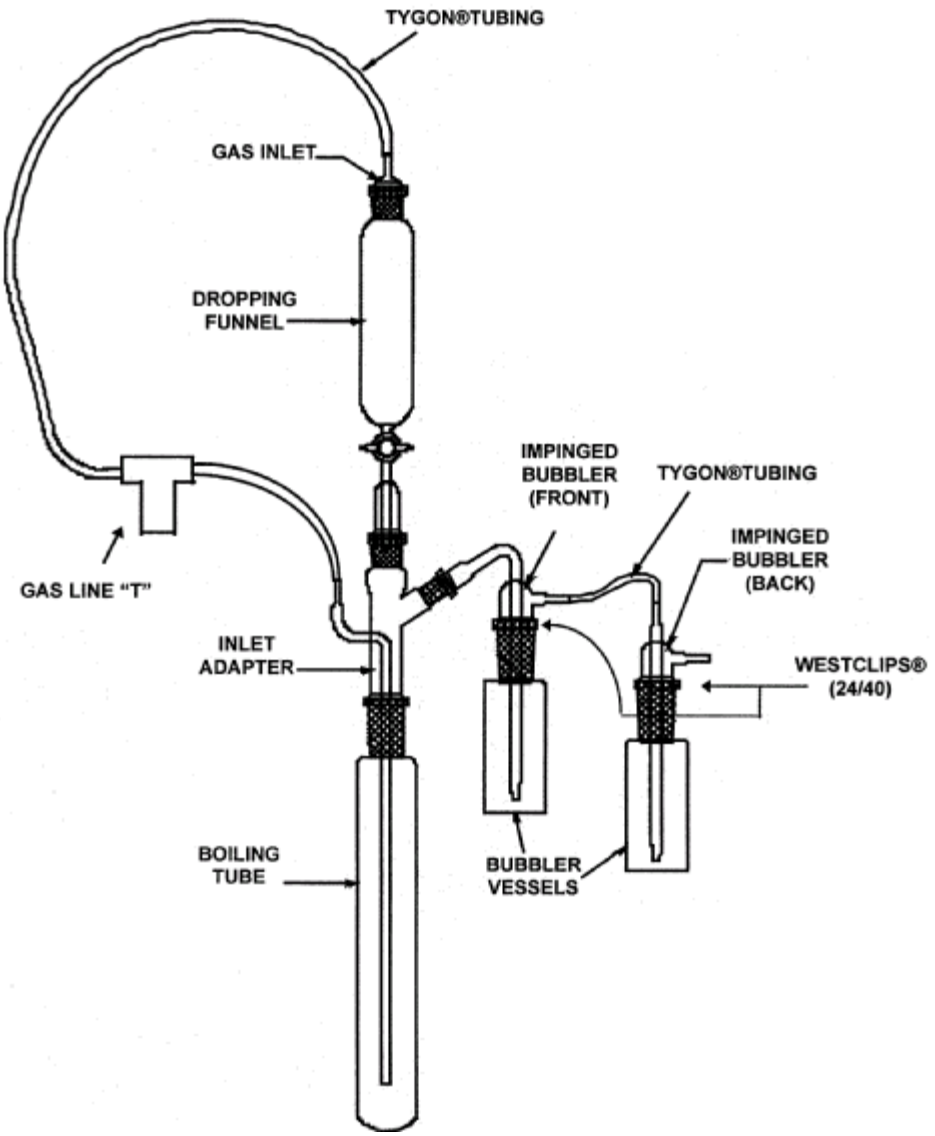
17.2.1. The laboratory does not add formaldehyde due to interferences with the analysis.

17.2.2. Methods 9034 and SM4500 S2-F call for pipetting the sample below the surface of the iodine solution. The laboratory does not pipette the sample below the surface of the iodine solution.

17.2.3. Method 9030B states that solid samples should be preserved in the field by filling the surface of the solid with 2N zinc acetate until moistened. The laboratory does not receive preserved solids for this method.

17.2.4. Method 9030B does not assign a holding time to the solid samples. The laboratory has defaulted to a 7-day hold time for prep and analysis.

FIGURE 1
ACID-SOLUBLE SULFIDE DISTILLATION APPARATUS



Title: SPECIFIC CONDUCTANCE

[Method: EPA Method 120.1, SW846 9050A and Standard Method 2510B]

Approvals (Signature/Date):

Technology Specialist	12/12/17 Date	Health & Safety Coordinator	12/18/17 Date
Quality Assurance Manager	12/27/17 Date	Laboratory Director	12/15/17 Date

This SOP was previously identified as SOP No. NC-WC-079, Rev 10, dated 12/10/15

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1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of Specific Conductance in waters and wastewater. It is based on EPA Method 120.1, SW846 9050A and Standard Method 2510B. The approximate working range is 1 μmhos/cm to 200,000 μmhos/cm.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. The Specific Conductance of a sample is measured using a Wheatstone bridge-type conductivity meter or equivalent. The sample is analyzed at a temperature of 25°C or temperature corrections are made.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica North Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

4.1. Not Applicable

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. There are no materials used in this method that have a significant or serious hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened,

transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Conductivity meter with conductivity probe with temperature correction

6.2. Beakers: various

6.3. Centrifuge tubes

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Not applicable

7.2. Standards

7.2.1. Reference Standards

7.2.1.1. Potassium Chloride Standard Solution: purchased (1,000 and 1409 µmhos/cm)

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C

8.3. Holding times

8.3.1. The holding time for samples is 28 days from sampling to completion of analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, sample duplicate, and method blank) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest at or above the reporting limit.

9.2.2. Corrective Action for MBs

9.2.2.1. If the analyte level in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Corrective Action for LCS

9.3.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.3.2.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.2.3. Corrective action will be repreparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

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9.4. Duplicates (DU)

9.4.1. A DU is a second aliquot of an environmental sample taken from the same sample container, when possible, that is processed with the first aliquot of that sample. That is, DUs are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.4.2. DUs are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.6.2. MDLs are easily accessible via the LIMs.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. The conductivity meter must be calibrated each day of use and noted in the conductivity Maintenance Logbook.

10.1.2. The conductivity meter is calibrated per manufacturer's instructions.

10.2. Continuing Calibration

10.2.1. The run is checked at the beginning, every ten samples and at the end of the run using a 1000 ppm Continuing Calibration Verification (CCV) standard to verify continued linearity. It cannot vary from the theoretical conductivity by

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more than ± 10% of the theoretical value or recalibration and re-analysis of all samples analyzed since the last CCV that met criteria is required.

10.3. Temperature Calibration Check

10.3.1. Quarterly, the temperature readings from the conductivity probe must be verified against a NIST certified thermometer. See NC-QA-015, current version.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Sample Preparation Procedure

11.3.1. Not applicable

11.4. Sample Analysis Procedure

11.4.1. Measure the sample directly or pour a homogenized sample into a beaker. Place the electrode in the sample. Record the conductivity on the analytical logsheet.

11.4.2. Rinse the electrode with reagent water between measurements. Place the electrode in 1000 ppm standard for storage.

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC into the LIMS. Level I and Level II reviews are performed in the LIMS.

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12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

12.1.1. Not applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this method is carried out.

15.2.1. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

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15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. EPA 600, Methods for Chemical Analysis of Water and Wastes, Conductance (Specific Conductance, μmhos at 25°C), Method 120.1

16.1.2. Standard Methods for the Examination of Water and Wastewater, Conductivity, Method 2510B, 1997

16.1.3. Test Methods for Evaluating Solid Waste, Physical /Chemical Methods, SW-846, 3rd Edition, September 1986, Method 9050A

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Revision History

Historical File:		Revision 1: 01/16/97		Revision 6: 08/04/10
		Revision 2: 04/24/02		Revision 7: 11/17/10
		Revision 3: 02/05/03		Revision 8: 11/30/12
		Revision 4: 09/27/04		Revision 9: 09/19/13
		Revision 5: 11/09/07		Revision 10: 12/10/15

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

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16.2.5. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) is 1 μmho/cm.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Deviations

17.2.1. EPA Method 120.1 specifies that samples will be filtered and stored if not analyzed within 24hrs. The lab does not filter samples that are not run within 24 hours of sampling, and defaults to a 28 day hold time as per methods 9050A and SM2510B.

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Title: DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

[Method: EPA Method 300.0A and SW846 Method 9056A]

Approvals (Signature/Date):

Technology Specialist	03/08/18 Date	Health & Safety Coordinator	03/12/18 Date
Quality Assurance Manager	03/16/18 Date	Technical Director	03/12/18 Date

This SOP was previously identified as SOP No. NC-WC-084, Rev 15, dated 4/13/17

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1. SCOPE AND APPLICATION

1.1. This method covers the determination of fluoride, chloride, nitrite, bromide, nitrate, and sulfate in surface waters, mixed domestic, and industrial wastewaters, groundwater, reagent waters, solids (after extraction Section 11.10) and leachates (when no acetic acid is used). This SOP is based on EPA Methods 300.0A and SW846 9056A.

1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. A 25 µL volume of sample is introduced into the ion chromatograph. The sample is then pumped through two different ion exchange columns, a suppressor device, and into a conductivity detector. The first two columns, a pre-column or guard column and a separator column, are packed with low-capacity, strongly basic anion exchange resin. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppresser column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions, in their acid forms, are measured using an electrical conductivity cell. Anions are identified based on their retention times as compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3. DEFINITIONS

3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version

4. INTERFERENCES

4.1. Interferences can be caused by substances with retention times that are similar to and/or overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or an elevated baseline in the ion chromatograms.

4.3. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known co-elution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not

be significant; however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.4. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5. SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2 Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.3 A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

5.4 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5 Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore; unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation when possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6 The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g and top-loading capable of accurately weighing to the nearest 0.01 g

6.2 Ion Chromatograph: Analytical system complete with ion chromatograph and all required accessories including analytical columns, compressed gases, and detectors.

6.2.1 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter as will the life of the separator column. Usually packed with the same substrate as the separator column. 4 x 50mm, Dionex IonPac AG19 P/N 062887, or equivalent.

6.2.2 Anion separator column: The separation shown in Figure 1 was generated using a 4 x 250mm Dionex IonPac AS19 column (P/N 062885) An equivalent column may be used if comparable resolution is obtained and the requirements of Section 9.2 can be met.

6.2.3 Anion suppressor device: Dionex anion micro membrane suppressor ERS 500 Suppressor (4mm) P/N 082540 or equivalent.

6.2.4 Detector -- Conductivity cell: Approximately 1.25 uL internal volume, Dionex, or equivalent.

6.2.5 Dionex-Chromeleon Data Chromatography software or equivalent.

6.2.6 Chrom software for data processing.

6.3 Pipettes: Ranging from 10 uL to 20 mL

6.4 Volumetric Flasks: 10 mL, 200 mL

6.5 Filters: 0.45 um

6.6 Syringes: 10 mL

6.7 Polyvials with caps

7. REAGENTS AND STANDARDS

7.1. Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain no particles larger than 0.20 microns.

7.2. Clean Ottawa Sand

7.2.1. Weigh 100 g of Ottawa sand into a 500 mL Erlenmeyer flask. Bring up to volume (500 mL) with DI water. Using a clean stir bar, stir for one hour. Allow to settle. Decant.

7.2.2. Bring up to volume (500 mL) with DI again, stir for one hour, settle, decant

7.2.3. Repeat Step 7.2.2

7.2.4. Place sand in a clean beaker and let sit overnight in a 104 ± C oven.

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7.2.5. Store covered in a desiccator until needed.

7.3. Eluent for the ICS-2100/Integrion is generated using a Dionex KOH eluent generator cartridge, and high purity deionized water. This instrument allows the use of a gradient so the concentration of the eluent can change throughout the run.

7.4. All stocks are purchased from commercial sources. Primary and secondary sources are required for each target analyte.

7.4.1. Commercial stock solution A: F^- - 25 mg/L, Cl^- - 500 mg/L, Br^-- 100 mg/L, NO_3^- - N- 25 mg/L, SO_4^{-2}- 500 mg/L. The stock solution may also be at the following concentrations: F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^-- 500 mg/L, NO_3^- - N- 125 mg/L, SO_4^{-2}- 2500 mg/L.

7.4.2. Commercial stock solution B: NO_2^- - N- 25 mg/L. The spike solution may also be at 125 mg/L.

7.4.3. Commercial IC Spike solution A: F^- - 125 mg/L, Cl^- - 2500 mg/L, Br^-- 500 mg/L, NO_3^- - N- 125 mg/L, SO_4^{-2}- 2500 mg/L

7.4.4. Commercial IC Spike solution B: NO_2^- - N- 125 mg/L

7.5. Working standards: Prepare Cal standard #9 by mixing 1.6 mL commercial stock A, 1.6 mL commercial stock B, and 16.8 mL of DI; or if the less concentrated solution is used, by mixing 8.0 mL A, 8.0 mL B, and 4.0 mL of DI.

7.5.1. In 5 mL polyvials prepare the following calibration standards in DI using the appropriate pipettes. Final concentrations of working standards are shown below.

7.5.1.1. Calibration Standard #1: Take 25.0 µL of calibration standard #9, and add 4.975 mL of DI.

7.5.1.2. Calibration Standard #2: Take 125 µL of calibration standard #9, and add 4.875 mL of DI.

7.5.1.3. Calibration Standard #3: Take 250 µL of calibration standard #9, and add 4.75 mL of DI.

7.5.1.4. Calibration Standard #4: Take 0.5 mL of calibration standard #9, and add 4.5 mL of DI.

7.5.1.5. Calibration Standard #5: Take 1.25 mL of calibration standard #9, and add 3.75 mL of DI.

7.5.1.6. Calibration Standard #6: Take 2.00 mL of calibration standard #9, and add 3.00 mL of DI.

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7.5.1.7. Calibration Standard #7: Take 2.50 mL of calibration standard #9, and add 2.50 mL of DI.

7.5.1.8. Calibration Standard #8: Take 3.75 mL of calibration standard #9, and add 1.25 mL of DI.

Calibration Standards

Level	Fluoride	Nitrite	Nitrate	Chloride	Sulfate	Bromide
1	0.05	0.05	0.05	1	1	0.2
2	0.25	0.25	0.25	5	5	1
3	0.5	0.5	0.5	10	10	2
4	1	1	1	20	20	4
5	2.5	2.5	2.5	50	50	10
6	4	4	4	80	80	16
7	5	5	5	100	100	20
8	7.5	7.5	7.5	150	150	30
9	10	10	10	200	200	40

7.5.2. Prepare or purchase a secondary stock standard(s) using a standards source other than that used for the primary standards as described in Section 7.5. Dilute these stock standards as indicated in the table below to prepare the mixture to be used for the laboratory control sample (LCS) and continuing calibration verification (CCV) solution. The CCV solution may be prepared by mixing 2.0 mL of A(if the more concentrated solution is used) and 2.0 mL of B (if the more concentrated solution is used) and diluting to 100 mL with DI. The LCS solution may be prepared by mixing 10 mL of A and 10 mL of B and diluting to 100 mL with DI.

LCS & Continuing Calibration Verification Solution Analyte	Final Conc. (V_f=5ml)
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Sulfate	50. mg/L

7.5.2.1. Whenever BP samples are analyzed on a day that a calibration is not run, a second CCV with the following concentrations will be prepared and analyzed.

LCS & Continuing Calibration Verification Solution Analyte	Final Conc. (Vf=5ml)
Fluoride	5 mg/l
Chloride	100 mg/L
Nitrite	5 mg/L
Bromide	20 mg/L
Nitrate	5 mg/L
Sulfate	100 mg/L

7.5.3. Prepare or purchase a primary stock standard(s). Dilute these stock standards to prepare the mixture to be used for the Matrix Spike solution. Alternatively purchase these mixes (ready to use) from a commercial source. Add 100 uL of each IC Spike solution (the more concentrated) to 5 mL of sample when preparing the MS. Dilute as needed after spiking the sample.

Matrix Spike "True" Values

Analyte	Final Conc.
Fluoride	2.5 mg/L
Chloride	50. mg/L
Nitrite	2.5 mg/L
Bromide	10. mg/L
Nitrate	2.5 mg/L
Sulfate	50. mg/L

Note: Stock standards, calibration standard #9 and LCS standard should be stored in the dark at 4° ±2°C. Replace these standards when instrument response indicates target analyte degradation may have occurred or after the standard has expired (12 months commercial mix or six months in-house mix), whichever occurs first. Nitrite is particularly light and oxygen-sensitive.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. The volume collected should be sufficient to ensure a representative sample; allow for replicate analysis, if required; and minimize waste disposal.

8.2 Sample preservation and holding times for the anions that can be determined by this method for water samples are as follows:

Analyte	Preservation	Holding Time
Fluoride	4° ± 2°C	28 days
Chloride	4° ± 2°C	28 days
Nitrite	4° ± 2°C	48 hours
Bromide	4° ± 2°C	28 days
Nitrate	4° ± 2°C	48 hours
Sulfate	4° ± 2°C	28 days

Note: Soil leachates will follow the same preservation and holding times as the water samples, starting from the time extraction ends.

9. QUALITY CONTROL

9.1. The TestAmerica Quality Control (QC) Program document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

9.2. Linear Calibration Range (LCR)

9.2.1. The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of three standards. If any verification data exceeds the initial values by ±10%, linearity must be re-established. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.3. Batch definition: Preparation and QC batch definitions are provided in the TestAmerica QC Policy.

9.4. Method Blank (MB) or Laboratory Reagent Blank (LRB):

9.4.1. One MB must be processed with each preparation batch. The MB consists of deionized water that has been taken through the entire preparation and analytical process. For DI leach samples, the MB consists of 10 g of clean Ottawa sand (see section 7.3) with 100 mL of deionized water. The MB must go through the entire leaching process with the samples. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest above the reporting limit.

9.4.2. Corrective Action for MBs

9.4.2.1. If the analyte level in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.4.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.5. Laboratory Control Sample (LCS) or Laboratory Fortified Blank (LFB):

9.5.1. One LCS must be processed with each preparation batch and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. If the result is outside established control limits the system is out of control and corrective action must occur. A control limit of 90 – 110% recovery must be applied. Corrective action will be re-preparation and reanalysis of the batch. The LCS is prepared from a separate stock standard, or neat material, of a different manufacturer than the stock, or neat material, used to prepare the calibration standard. For DI leach samples, the LCS consists of 10 g of clean Ottawa sand and 100 mL of LCS prepared solution. The LCS must go through the entire leaching process with the samples.

9.5.2. Corrective Action for LCS

9.5.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.5.2.2. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.5.2.3. The only exception is if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1. One MS/MSD pair must be analyzed with every ten samples. A matrix spike (MS) is a field sample to which a known concentration of target analyte has been added. Some client-specific DQOs may require the use of un-spiked sample duplicates in place of, or in addition to the MS. The MS result is used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Spiking levels will be the same as the LCS values.

9.6.1.1. If the MS/MSD recovery or relative percent difference (RPD) falls outside the acceptance range, the results must be evaluated to determine the cause of the failure. A control limit of 80-120% recovery and 15% RPD will be applied to the MS/MSD.

9.6.1.2. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact of data usability. Re-analysis may be

necessary.

9.6.1.3. If matrix interference is suspected and the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.6.1.4. If the recovery of the LCS is outside the limits, corrective action must be taken. Corrective action will include re-analysis of the batch.

9.6.1.5. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is automatically flagged with a "4" flag.

9.7. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB):

9.7.1. Continuing calibration is verified by analyzing the calibration standard after every ten samples. The CCV must fall within ± 10% of the true value for each target analyte. A CCB is analyzed immediately following the CCV to monitor low level accuracy and system cleanliness. The CCB result must be below the reporting limit for that analyte. If either the CCV or CCB fail to meet criteria, the analysis must be terminated, the problem corrected and re-preparation and re-analysis of all samples following the last CCV and CCB which were in control must be performed.

9.8. Control Limits

9.8.1. Control limits are specified in the method.

9.8.2. Control limits are easily accessible via the LIMs

9.9. Method Detection Limits (MDLs) and MDL Checks

9.9.1. MDLs and MDL Checks are established and performed by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.9.2. MDLs are easily accessible via the LIMs

9.10. Nonconformance and Corrective Action

9.10.1. Any deviation from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Establish ion chromatographic operating parameters equivalent to those indicated in Table 1. Refer to Table 2 for typical standard run retention times.

10.2. For each analyte of interest, prepare a **minimum** of three calibration standards by adding

accurately measured volumes of one or more stock standards to a volumetric flask and diluting to volume with DI. If a sample analyte concentration exceeds the calibration range the sample may be diluted to bring the concentration within the range. If this is not possible, then three new calibration concentrations must be chosen—two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3. Using an injection volume of 25 µL of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. All analytes will be calibrated using a least squares-linear regression, weighted least squares, quadratic regression, or average response that is not forced through the origin. Correlation coefficients (R^2) must be 0.995 or better. An average response criterion is ± 20%.

10.4. Initial Calibration Verification (ICV) – The Initial Calibration is verified immediately following calibration, prior to sample analysis. The acceptance criterion is ±10% of the true value. If this criterion is not met, the instrument must be re-calibrated.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Sample preparation

11.3.1. Waters: None

11.3.2. Solids: See Appendix 1 for the solid leaching procedure.

11.4. Table 1 summarizes the recommended operating conditions for the ICS-2100/Integrion ion chromatograph. Included in table 2 are estimated retention times that can be achieved by this method for this instrument.

11.5. Check system calibration daily as outlined in table 3; and, if required, recalibrate as described in Section 10.

11.6. Prescreening may be performed using a conductivity meter to determine dilutions for chloride and sulfate. Visual anomalies in the sample and analyst judgment determine the need for prescreening. Follow this formula to approximate required dilutions:

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$$\frac{\textit{Conductivity}}{400} = \textit{DILUTION FACTOR}$$

11.7. Load and inject a fixed amount (25 µL) of sample. If the sample is cloudy then it should be filtered prior to loading into the autosampler. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.8. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of various concentrations. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms since retention time is concentration dependent for most analytes.

11.9. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of deionized water and re-analyze.

11.10. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and re-analyze.

Note: Retention time is affected by concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. See Table 2. In some cases, this peak migration may produce poor resolution or identification.

11.11. The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed for one hour using a magnetic stirring device or tumbler. Filter the resulting slurry before injecting, using a 0.45 µm membrane type filter. This can be the type that attaches directly to the end of the syringe

11.12. Analytical Documentation

11.12.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.12.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.12.3. Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

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11.12.4. Record all sample results and associated QC in the LIMS. Level I and level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply the answer by the appropriate dilution factor. The Average curve uses the following function:

12.1.1. Calibration Factor for external calibration

$$CF = \frac{Peak\ Area\ (or\ height)\ of\ the\ compound\ in\ the\ standard}{Mass\ of\ the\ compound\ injected}$$

12.1.2. Standard Deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}}$$

12.1.3. Average Calibration Factor

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

n = number of calibration standards

12.1.4. Relative Standard Deviation

$$RSD = \frac{SD}{\overline{CF}} x\ 100$$

12.1.5. Calculated Concentration using Average Calibration

$$X_s = \frac{A_s}{\overline{CF}}$$

X_s = Calculated mass of the analyte in the sample aliquot introduced into the instrument

A_s = Peak area (or height) of the analyte in the sample

$\overline{CF}$ = The average calibration factor from the most recent initial calibration

12.2. A linear curve uses the following function:

$$Y = m \cdot x + b$$

Y = Instrument response
m = slope
x = Concentration
b = Intercept

12.3. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and re-analyzed. Estimated values may be reported by client request. The following equations are used to calculation sample concentrations.

12.4. Aqueous and Non-Aqueous samples

Final Result (Mg/L or Mg/Kg) = (C) (D)

Where:

C=Concentration from Calibration Curve

D=Dilution Factor (If Needed)

12.5. Report results in mg/l for aqueous samples and mg/kg for DI leachates and mg/l for 18-hour leachates of solid samples.

12.6. Report NO_2 as “Nitrite as N” and NO_3 as “Nitrate as N”.

13. METHOD PERFORMANCE

13.1. The reporting limits for the following analytes are based on a 25 ul injection volume:

Analyte	Water RL (mg/L)	Soil RL (mg/kg)
Fluoride	0.05	0.5
Chloride	1.0	10
Nitrite	0.1	5
Bromide	0.5	5

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Analyte	Water RL (mg/L)	Soil RL (mg/kg)
Nitrate	0.1	5
Sulfate	1.0	10

13.2. The group/team leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The group/team leader must document the training, and submit the results to the QA dept. for inclusion in the associate's training files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in section 13 of the corporate environmental health and safety manual (cw-e-m-001) for "waste management and pollution prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.3. The following waste streams are produced when this method is carried out.

15.3.1. Spent samples**:** Solid samples are disposed of as solid debris waste in the container labeled "Solid Waste."

15.3.2. Alkaline and/or acidic waste generated by the analysis. Aqueous waste can be poured down the drain if the pH is between 5 and 10. Any sample waste generated that is not in this pH range must be collected and disposed of in the designated acid waste drum located in the lab. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.3.3. Contaminated plastic materials such as IC syringes, filters, caps and vials utilized for sample preparation. This waste is disposed of in containers labeled "Solid Waste."

16. REFERENCES

16.1. References

16.1.1. Method 300.0A, “Determination of Inorganic Anions by Ion Chromatography”, Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio, Revision 2.1, August 1993

16.1.2. Method 9056A, “Determination of Inorganic Anions by Ion Chromatography”, SW846, Test Methods for Evaluating Solid Waste, Third Edition, Draft Revision 1, September 1999

16.1.3. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.4. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.5. Corporate Quality Management Plan (CQMP), current version

16.1.6. Revision History

Historical File:		Revision 3: 10/03/00		Revision 10: 10/20/10
		Revision 4: 11/06/04		Revision 11: 1/10/12
		Revision 5: 05/26/06		Revision 12: 08/28/13
		Revision 6: 06/27/08		Revision 13: 08/25/15
		Revision 7: 09/15/09		Revision 14: 11/24/15
		Revision 8: 04/29/10		Revision 15: 04/13/17
		Revision 9: 08/16/10		

16.2. Associated SOPs and Policies

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Detection and Quantitation Limits, CA-Q-S-006

16.2.5. Standards and Reagents SOP, NC-QA-017

16.2.6. Selection of Calibration Points, CA-T-P-002

16.2.7. Calibration Curves (General), CA-Q-S-005

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16.2.8. Acceptable Manual Integration Practices, CA-Q-S-002

17. METHOD DEVIATIONS, MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. The CCV and Laboratory Control Sample (LCS) solutions are made fresh weekly

17.2. Due to limitations in the data acquisition system, no zero point is run in the calibrations. The Linear Calibration Range will be determined using three standards.

17.3. Reporting limits

17.3.1. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.4. The lab defaults to holding times from Method 300.0.

17.5. Tables, appendices, etc.

17.5.1. Appendix 1: DI Leaching Procedure for Solid Samples

17.5.2. Tables

17.5.2.1. Table 1 - Standard Instrument Operating Parameters for ICS-2100 / Integrion

17.5.2.2. Table 2 - Retention Time Matrix for ICS-2100 / Integrion

17.5.3. Figures

17.5.3.1. Figure 1 - Example Ion Chromatogram – ICS 2100 / Integrion

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Appendix 1: Leaching Procedure for Solid Samples

The solids leaching procedure is only applicable for Anions by method 300.

- Weigh approximately 10 g of sample into a clean plastic bottle or a calibrated snap cap container (see SOP NC-QA-015 Balance and Thermometer Calibration, Container Verification). Record sample weight.
- Add 100 mL of reagent water to the sample.
- Prepare a leachate blank of 100mL DI water, and 10 g clean Ottawa sand. The procedure for cleaning sand is in section 7.3
- Prepare a leachate LCS by adding 100mL of LCS solution to 10g clean Ottawa sand (or a lesser amount in the same proportion)
- Properly label the bottle or beaker and record the preparation procedure in LIMS.
- Place the capped bottles securely in the tumbler or shaker and tumble or shake for 10 minutes, or place the sample and beaker on a stir plate and mix for 10 minutes.
- After the tumbling, shaking, or stirring period, remove the bottles or beakers and allow the contents to settle for approximately one hour.
- If necessary due to turbidity or sample particulates that will not settle, filter the supernatant through a Whatman #4 or 0.45 μm filter into a clean container.
- Cap and label the bottle. Submit the sample extract for analysis.

NOTE: Some samples/extracts may need to be filtered a second time to further remove particulates or turbidity. Be sure to properly document if extra filtering is necessary.

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TABLE 1

Example Standard Instrument Operating Parameters

Standard Conditions:

Eluent Pump Rate: 1.00 mL/min

Sample Loop: 25 uL

Eluent: Varies due to gradient used during analysis, Startup concentration is 20 M.

Detector Output: Baseline conductivity should be >1 uS prior to sample analysis

Suppressor Current: 50mA

TABLE 2

Standard Run Retention Time Matrix (minutes)*

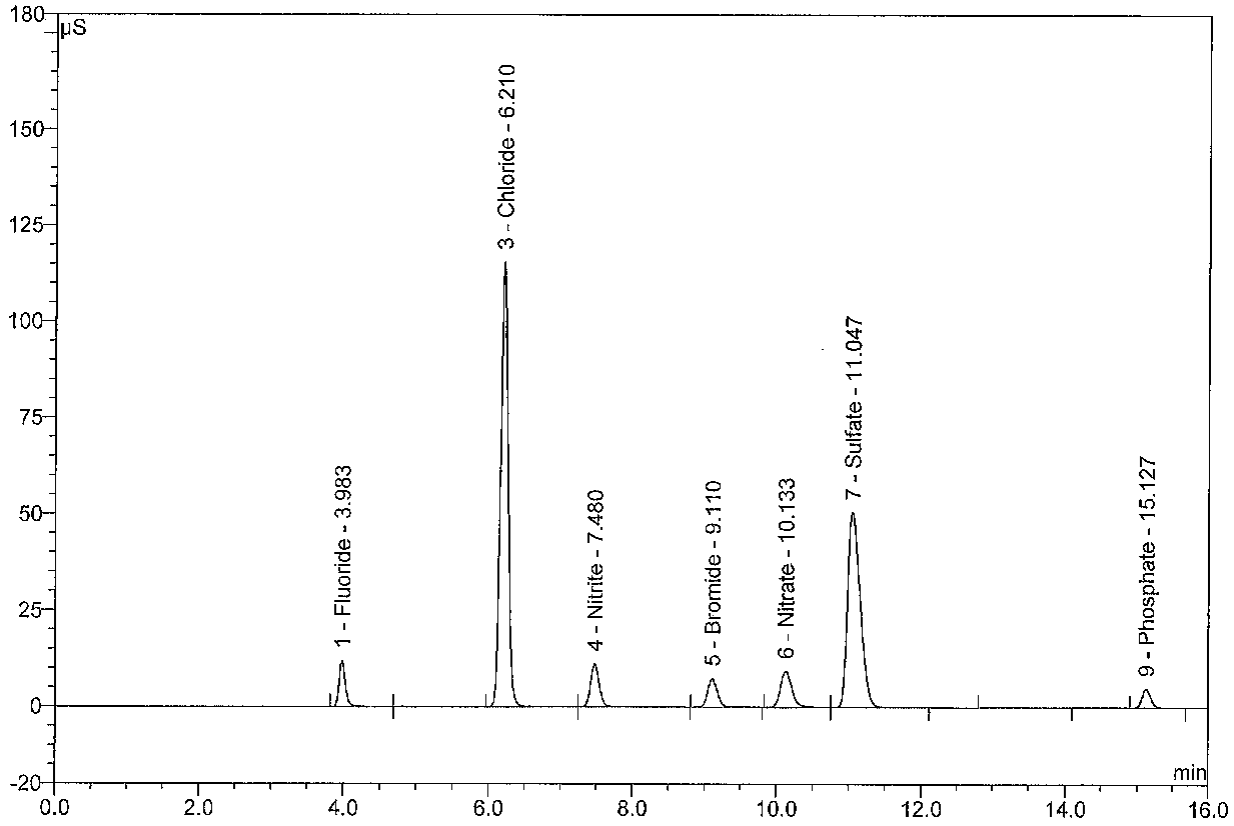
ICS-2100 / Integrion

	Concentration (mg/L)												
Analyte	**0.05**	**0.2**	**0.5**	**1**	**2**	**2.5**	**5**	**10**	**20**	**40**	**50**	**100**	**200**
F^-	3.98		3.98			3.98	3.99	3.99					
Cl^-				6.20				6.217			6.21	6.22	6.24
NO_2^-	7.49		7.50			7.49	7.48	7.47					
Br^-		9.14			9.14			9.12	9.10	9.08			
NO_3^-	10.18		10.17			10.15	10.12	10.07					
SO_4^{2-}				11.20				11.19			11.08	11.00	10.86

FIGURE 1

EXAMPLE ION CHROMATOGRAM

ICS-2100 and Integrion



Title: HEM / SGT-HEM BY SOLID PHASE EXTRACTION (SPE)

[Method: 1664A]

Approvals (Signature/Date):

Technology Specialist	02/22/18 Date	Health & Safety Coordinator	02/26/18 Date
Quality Assurance Officer	02/27/18 Date	Technical Director	03/01/18 Date

This SOP was previously identified as SOP No. NC-WC-091, Rev. 8, dated 2/16/17

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1. SCOPE AND APPLICATION

1.1. This method is used for the determination of n-hexane extractable material (HEM) and n-hexane extractable material that is not adsorbed by silica gel (SGT-HEM) in surface and saline waters and industrial and domestic wastewaters. Extractable materials that may be determined are relatively nonvolatile hydrocarbons (i.e., vegetable oils, animal fats, wastes, soaps, greases, and related materials).

1.2. This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act; the Resource Conservation and Recovery Act (RCRA); the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); and other EPA regulatory programs. "Oil and Grease" is a conventional pollutant defined in the Act and codified in 40 CFR 401.16. The term "n-hexane extractable material" reflects that this method can be applied to materials other than oils and greases. Similarly, the term "silica gel treated n-hexane extractable material" reflects that this method can be applied to materials other than aliphatic petroleum hydrocarbons that are not adsorbed by silica gel. This SOP is based on Method 1664A.

1.3. This method is not applicable to measurement of materials that volatilize at temperatures below approximately 85°C. Petroleum fuels from gasoline through #2 fuel oil may be partially lost in the solvent removal operation.

1.4. Some crude oils and heavy fuel oils contain a significant percentage of materials that are not soluble in n-hexane. Accordingly, recoveries of these materials may be low.

1.5. This method is capable of measuring HEM in the range of 5 to 1000 mg/L and SGT-HEM in the range of 5 to 1000 mg/L, and may be extended to higher levels by analysis of a smaller sample volume collected separately.

1.6. For HEM and SGT-HEM in this method, the method detection limit (MDL) is 1.4 mg/L or lower.

2. SUMMARY OF METHOD

2.1. A one-liter sample volume is acidified to a pH of less than two, and serially extracted three times with n-hexane by solid phase extraction. The extract is dried over sodium sulfate.

2.2. The solvent is evaporated from the extract and the HEM is weighed. If the HEM is to be used for determination of SGT-HEM, the HEM is reconstituted in n-hexane.

2.3. For SGT-HEM determination, an amount of silica gel proportionate to the amount of HEM is added to the solution containing the HEM to remove absorbable materials. The solution is filtered to remove the silica gel, the solvent is evaporated, and the SGT-HEM is weighed.

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3. DEFINITIONS

3.1. HEM (Hexane Extractable Material): The material that is extracted from a sample and determined by this method.

3.2. SGT-HEM (Silica Gel Treated - Hexane Extractable Material): HEM that is not absorbed by silica gel.

3.3. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QA Manual), current version.

4. INTERFERENCES

4.1. Solvents, reagents, glassware, and other sample processing hardware may yield artifacts that affect results. Specific selection of reagents and purification of solvents may be required.

4.2. All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running laboratory method blanks as described in Section 9.4.

4.3. Sodium sulfate and silica gel fines have the potential to inflate results for HEM and SGT-HEM by passing through the filter paper. If the filter paper specified in this method is inadequate for removal of these fines, use of a 0.45 - micron filter is recommended.

4.4. Interferences extracted from samples will vary considerably from source to source, depending upon the diversity of the site being sampled. For those instances in which samples are thought to consist of complex matrices containing substances (such as particulates or detergents) that may interfere with the extraction procedure, a smaller sample may need to be collected for analysis.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the Safety Data Sheet (SDS) for each of the materials listed in the table. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

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Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Hexadecane	Flammable Irritant	None established	Harmful or fatal if swallowed. Harmful if inhaled. Causes severe skin irritation. May cause eye and respiratory tract irritation. Prolonged exposure can cause narcotic effects.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Stearic Acid	Minor general health risk	Not available	May cause irritation to mucous membranes and upper respiratory tract. Can cause eye or skin irritation.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. n-Hexane has a flash point of –23ºC (-9ºF), has explosive limits in air in the range of 1–7 %, and poses a serious fire risk when heated or exposed to flame. n-Hexane can react vigorously with oxidizing materials. The laboratory should include procedures in its operations that address the safe handling of n-hexane.

5.6. The preparation of hazardous standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Analytical top-loading balance capable of weighing to 0.1 mg

6.2. Horizon SPE-DEX 3000 XL or equivalent

6.3. SPE disks and pre-filters

6.4. Nitrogen

6.5. Vacuum Pump

6.6. Waste collection flask

6.7. Speed Vap evaporation system or equivalent

6.8. Aluminum evaporation / weighing pans (Record “lot” number in analytical batch)

6.9. Filter paper: Whatman No. 4 to fit funnel (Record lot number in analytical batch)

6.10. Assorted laboratory glassware (i.e., funnels, volumetric flasks, pipettes, etc.)

6.11. Glass stirring rod or glass disposable pipette

7. REAGENTS AND STANDARDS

7.1. Reagent water:

7.1.1. Water in which HEM is not detected above the minimum level of this method. Bottled distilled water or water prepared by passage of tap water through activated carbon have been shown to be acceptable sources of reagent water.

7.2. Concentrated Hydrochloric Acid

7.3. Hydrochloric acid, 1:1

7.3.1. In a 500 mL volumetric flask containing ~ 200 mL of DI H_2O, **slowly** add 250 mL of concentrated hydrochloric acid. Bring to mark with DI H_2O. (Other volumes may be prepared as is convenient).

7.4. n-Hexane, 85% purity, 99.0 % min. saturated C_6 isomers, residue less than 1 mg/L.

7.5. Methanol: ACS

7.6. Acetone: ACS, residue less than 1 mg/L

7.7. Sodium sulfate: reagent grade, granular anhydrous. Dry at 200-250°C for 24-hour minimum, and store in a tightly sealed container until use. Record the drying time and date in the LIMS reagent module.

7.8. Silica gel: Anhydrous, 100- 200 mesh. Dry at 180- 250°C for 24 hour minimum and store in a desiccator or tightly sealed container. Determine the n-hexane soluble material content of the silica gel by extracting 30 g of silica gel with n-hexane and evaporating the n-hexane to dryness. The silica gel must contain less than 5 mg of n-hexane soluble material per 30 g (<0.17 mg/g). Test each lot and record the results when the reagent is logged. Record the drying time and date in the LIMS reagent module.

7.9. Hexadecane: 98% minimum purity.

7.10. Stearic Acid: 98% minimum purity.

7.11. Hexadecane/Stearic Acid (1:1) spiking solution: Prepare in acetone at a concentration of 4000 mg/L each.

7.11.1. Place 0.4g stearic acid and 0.4g hexadecane in a 200 mL volumetric flask, add about 200 mL acetone, dissolve the stearic acid and hexadecane and bring to volume with acetone. Transfer to a bottle with a Teflon® cap, mark the solution level on the bottle, and store in the dark at room temperature. Immediately prior to use, verify the level on the bottle and bring to volume with acetone, if required. Warm to re-dissolve all visible precipitate.

7.11.2. The hexadecane / stearic acid spiking solution must be replaced after one month or sooner if degradation is suspected. To check for degradation remove 10.0 +/- 0.1 mL with a volumetric pipette, place in a tared weighing pan, and evaporate to dryness. The weight must be 40 $\pm$ 1 mg.

7.11.3. A commercial premade LCS can also be substituted.

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8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. For aqueous samples, collect approximately one liter of representative sample in a glass bottle following conventional sampling practices, except that the bottle must not be pre-rinsed with sample before collection.

8.1.1. The sample must be preserved by adjusting the pH to < 2 with HCl or H_2SO_4 at the time of collection. Since the amount of HCl needed will vary depending on the waste stream, the bottles cannot be pre-preserved, and the volume of HCl required will need to be determined at the time of sampling.

8.1.2. If the sample is suspected to contain more than 1000 mg/L of extractable material, a proportionally smaller volume of sample should be collected.

8.2. Collect an additional two aliquots (1 L, additional smaller volume, or both) of a sample for each set of ten samples or less for the MS/MSD. Note that if the analysis is for compliance monitoring, an MS/MSD should be performed for each waste stream. The client is responsible for identifying samples for MS/MSD spiking. However, the TestAmerica Project Manager should attempt to inform the client of the regulatory requirements.

8.3. The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of oil and grease. Therefore samples must be collected as grab samples. If a composite measurement is required, individual grab samples collected at prescribed time intervals must be analyzed separately and the concentrations averaged.

8.4. All samples must be refrigerated at 4 ± 2^{o}C from the time of collection until extraction.

8.5. All samples must be analyzed within 28 days of the date of collection.

9. QUALITY CONTROL

9.1. QC Policy QA-003 document provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

9.2. Table I provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.3. Batch Definition

9.3.1. A batch is a group of no greater than 20 samples excluding QC samples (laboratory control sample (LCS), Method Blank (MD), Matrix Spike (MS), or Matrix Spike Duplicate (MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period

from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.4. Method Blank (MB)

9.4.1. One MB must be processed with each preparation batch. The MB consists of 1000 mL of reagent grade water that has been taken through the entire preparation and analytical process. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Analytes in the method blank must be below the reporting limit.

9.4.2. Corrective Action for MBs

9.4.2.1. If the level of HEM in the MB exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.4.2.2. If HEM is not present at a concentration greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.5. Laboratory Control Sample (LCS)

9.5.1. One LCS prepared from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS standard consists of 10 mL of the hexadecane/stearic acid spiking solution (Section 7.9) added to 1000 $\pm$ 50 mL reagent water. A commercial premade LCS may also be substituted.

9.5.2. The LCS control limits set by the method are 78-114% with 11% RPD for HEM and 64-132% with 28% RPD for SGT-HEM for waters.

9.5.3. Corrective Action for LCS

9.5.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.5.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the

batch is acceptable. **This must be addressed in the project narrative.**

9.5.3.3. Corrective action will be re-preparation and re-analysis of the batch, if additional sample is available, unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike (MS) or Matrix Spike/Matrix Spike Duplicate (MS/MSD):

9.6.1. An MS must be performed once per 20 analytical samples unless an MS/MSD is specified by a client, and sufficient sample volume is supplied. The client should identify samples for MS/MSD spiking. A MS/MSD is required for every 10 samples per site, or for compliance monitoring, per discharge. If the client does not identify at least one MS/MSD per analytical batch, the laboratory will choose one sample for spiking. Some client specific DQOs may require the use of un-spiked sample duplicates in place of or in addition to MS/MSDs. The MS and MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. The matrix spike concentration is normally the same as the LCS standard (i.e., 10 mL of the hexadecane/stearic acid spiking solution is added to 1000 mL of sample).

9.6.2. The MS/MSD control limits set by the method are 78-114% with 18% RPD for HEM and 64-132% with 34% RPD for SGT-HEM.

9.6.3. Calculate the relative percent difference between the two results (not the recoveries) using the following equation:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = Concentration of HEM or SGT-HEM in the matrix spike sample

D_2 = Concentration of HEM or SGT-HEM in the matrix spike duplicate sample

9.6.4. If the analyte recovery or Relative Percent Difference (RPD) falls outside the acceptance range, the results should be evaluated to determine the cause of the failure.

9.6.5. If laboratory error is suspected, consultation with the PM and the client is necessary to determine the impact on data usability. Re-preparation and /or re-analysis may be necessary.

9.6.6. If matrix interference is suspected, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted.

9.6.7. If the native analyte concentration in the MS/MSD exceeds 4x the spike level, the recovery data is reported and flagged with a "4". This indicates that the recovery and RPD were not calculated, because the native sample concentration was greater than four times the spike amount.

9.7. Control Limits

9.7.1. Control limits are determined as outlined in the method.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL checks are established by the laboratory as described in SOP NC-QA-021.

9.8.2. MDLs are easily accessible via the LIMs.

9.9. Nonconformance and Corrective Action

9.9.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration Verification of Balance: Check the calibration of the analytical balance before and after each analytical batch at 2 mg and 1000 mg using class "S" weights. If calibration is not verified after the measurements, re-tare the balance, ensure that the balance is level, and reweigh the batch. If the calibration verification fails again, notify group leader and QA, and tag out the balance.

10.1.1. Calibration measurements must be within ± 10% (i.e., 0.2 mg) at 2mg and ± 0.5% (i.e., 5 mg) at 1000 mg. If values are not within these limits, see section 10.1.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.2.1. The procedure as described below is based on preparation of a 1 L sample volume. If a smaller volume is collected for analysis, glassware and reagent quantities may be adjusted commensurably. This must be documented on the preparation bench sheet, but a nonconformance memo is not necessary.

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11.2.2. Glassware is cleaned by washing in hot water containing detergent, then rinsing with tap and distilled water.

11.3. Preparation of the analytical batch

11.3.1. Bring the analytical batch of samples, including the sample aliquots for the MS and MSD to room temperature.

11.3.2. Place approximately 1000 mL (950 - 1050 mL) of reagent water in a clean sample bottle to serve as the method blank.

11.3.3. Prepare the OPR/LCS (Section 9.5) using the hexadecane/stearic acid spiking solution (Section 7.9).

11.3.3.1. Place approximately 1000 mL of reagent water in a clean 1 L amber bottle.

11.3.3.2. Add 10 mL (± 0.05 mL) of the hexadecane/stearic acid spiking solution to the reagent water. A commercial premade LCS spike can also be substituted.

11.4. Weigh the sample bottles (including the MS/MSD) containing the samples and record on the electronic logsheet to the nearest gram.

11.5. Extraction Procedure

11.5.1. Verify that the pH of the sample is < 2 using the following procedure:

11.5.1.1. Open the sample bottle. With a glass rod or a disposable glass pipette, carefully dip the end in the sample. Place a drop of sample onto a pH paper strip. Using hexane, rinse the tip of the rod into the sample at the filtration stage.

11.5.2. If the sample does not have a pH <2 any additional containers provided will have their pH checked. If none of the containers meet the pH requirement then it will be narrated.

11.5.3. If none of the sample bottles meet the pH requirement and the sample is at neutral pH, add 5-6 mL HCl solution (Section 7.2) to the sample. If the sample is at high pH, use a proportionately larger amount of HCl solution.

11.5.4. Add the appropriate amount of HCl solution to the method blank, OPR/LCS.

11.5.5. Replace the cap and shake to mix thoroughly. Check the pH of the sample using the procedure in Section 11.5.2. If necessary, add more acid to the sample and repeat.

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11.5.6. Turn on the nitrogen, vacuum pump, and extractor controller. Allow the system to sit for a few minutes.

11.5.7. Attach the water sample inlet valve to the sample bottle, using the appropriate adapter

11.5.8. Place the support screen in the disk holder base. Place the SPE disk on the screen. Place a pre-filter over the SPE disk if needed.

11.5.9. Insert the riser into the disk holder base over the disk. Screw on the aluminum locking ring and load the disk holder on the extractor. Place the liquid sensor arm into the disk holder assembly.

11.5.10. Put a collection vessel in place to collect the extract. Ensure a tight seal is made and use a clamp if necessary.

11.5.11. Lower the sample holder arm on the extractor.

11.5.12. Load the sample bottles onto the unit. Be sure to cover the solvent injection port while inverting the sample. Ensure that there are no leaks.

11.5.13. Select the appropriate method for the extraction process according to disk size and sample type (see Appendix A). Load the method to each station that is being run.

11.5.14. Start the extraction

11.5.15. During the rinse portion of the extraction be sure to rinse the sample cap with a small portion of hexane and pour it onto the sample disk.

11.5.16. Determine the original sample volume in liters by weighing the empty sample bottle and cap, recording on the electronic logsheet and subtracting it from the weight of the sample bottle plus sample recorded earlier (Section 11.4).

11.5.17. If SGT-HEM only is to be determined, proceed to Section 11.7. This will not normally be the case, since generally HEM must be determined in order to ensure the correct amount of silica gel is added in the SGT-HEM procedure. SGT-HEM may be determined without determination of HEM only if HEM is known to be less than 100 mg in the volume of sample extracted.

11.6. Solvent Evaporation

11.6.1. Pour the hexane from the collection vessel into a pre-weighed, aluminum evaporation/weighing pan. Rinse the beaker with hexane to ensure complete sample transfer.

11.6.2. Turn on the Speed Vap evaporation system following the manufacturer's recommended procedure. Temperature should be 50°C; pressure should be at approximately 30 psi.

Note: Inspect and ensure the inside of the Speed VAP lid is clean and free of any oil residue.

11.6.3. Place the weighing pan with the hexane into the Speed Vap system and close the cover. Turn on the vacuum and evaporate to dryness.

11.6.4. Inspect the residue in the aluminum evaporation pan for crystals. Crystal formation is an indication that sodium sulfate may have dissolved and passed into the pan. This may happen when the drying capacity of the sodium sulfate is exceeded or if the sample was not adjusted to a low pH. If crystals are observed, dissolve the extract in warm hexane, filter through Na_2SO_4 into another weighed evaporation pan (rinsing thoroughly with hexane to ensure quantitative transfer), and repeat the evaporation procedure.

Note: Crystals of stearic acid are routinely observed for the OPR/LCS and matrix spikes. Analyst experience is valuable in distinguishing between stearic acid crystals and sodium sulfate crystals. If sodium sulfate crystals are observed, the sample is reconstituted with hexane and filtered through sodium sulfate.

11.6.5. When all of the hexane has been evaporated, remove the pan from the Speed Vap, place in a desiccator, and allow ample time (approximately 10 minutes) for cooling and then weigh to the nearest 0.1 mg. Repeat the desiccator/weight cycle until the weight loss is <4% of the previous weight or < 0.5 mg, whichever is less.

11.6.5.1. If the extract was from the HEM procedure, determine the HEM (W_h) by subtracting the weight of the aluminum evaporation pan from the total weight.

11.6.5.2. If the extract was from the SGT-HEM procedure, determine the SGT-HEM (W_s) by subtracting the weight of the SGT-HEM aluminum evaporation pan from total weight.

11.7. Silica Gel Treated - Hexane Extractable Material (SGT-HEM)

11.7.1. If HEM has been determined, and HEM is less than the SGT-HEM reporting limit, the analyst may report SGT-HEM as non-detect, generate an NCM, and stop at this point. If all SGT-HEM samples are reported as ND for a batch, no batch QC is reported. SGT-HEM should always be less than HEM.

11.7.2. Silica gel capacity: To ensure the capacity of the silica gel will not be exceeded, the amount of HEM must be known.

11.7.2.1. If it is known from historical data that the amount of HEM is less than 100 mg, the analyst may proceed with the determination of SGT-HEM per Section 11.7.3 without determination of HEM.

11.7.2.2. If, however, the amount of HEM is not known, HEM must first be determined using the procedure in Section 11.7.3

11.7.3. Extractable materials in silica gel: Because the capacity of silica gel is not known for all substances, it is presumed that 3 g will absorb 100 mg of all absorbable materials. The amount of silica gel that can be used for absorption in the SGT-HEM procedure below has been limited to 30 g because of concerns about possible extractable impurities in the silica gel. Therefore, if the extract contains more than 1000 mg of HEM, split the extract per the following procedure:

11.7.3.1. Add 85 - 90 mL of n-hexane to the evaporation pan to dissolve the HEM. If necessary, heat the solution to completely dissolve the HEM.

11.7.3.2. Allow to cool and transfer the extract to a 100 mL volumetric flask. Rinse the evaporation pan sequentially with 2-3 small portions of n-hexane and add to the volumetric flask. Dilute to mark with n-hexane.

11.7.3.3. Calculate the extract volume that contains 1000 mg of extractable material according to the following equation:

$$V_a = \frac{1000 V_t}{W_h}$$

where:

V_a = Volume of aliquot to be withdrawn (mL)

V_t = Total volume of solvent used in Section 11 (mL) (normally 100 mL)

W_h = Weight of extractable material HEM measurement (mg)

11.7.3.4. Using a calibrated Class A glass pipette, remove the volume to be withdrawn (V_a) and transfer to a clean glass beaker. Dilute to approximately 100 mL with n-hexane.

11.7.4. If the HEM is less than 1000 mg, dissolve it in hexane and transfer to a clean glass beaker. Rinse the evaporation pan with several aliquots of hexane. Make up to approximately 100 mL hexane in the beaker.

11.7.5. Adsorption with Silica Gel

11.7.5.1. Add 3.0 +/- 0.3 g of dried anhydrous silica gel (Section 7.6) to the beaker for every 100 mg of HEM, or fraction thereof proportionally, to a maximum of 30 g of silica gel.

11.7.6. Filter the solution through n-hexane moistened filter paper into a pre-weighed, aluminum evaporation pan. Rinse the beaker, silica gel and filter paper with several small amounts of n-hexane to complete the transfer.

11.7.7. Evaporate the solution and determine the weight of SGT-HEM per Section 11.6.

11.8. Analytical Documentation

11.8.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.8.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.8.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.8.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculate the concentration of HEM ("oil and grease") in the sample per the following equation:

$$\mathrm{HEM}(mg/L) = \frac{\mathrm{W_{HEM}}(mg)}{\mathrm{V_s}(L)}$$

Where:

W_{HEM} = Weight of hexane extractable material, Section 11.6.5

V_s = Sample volume in liters

12.2. Calculate the concentration of SGT-HEM ("petroleum hydrocarbons") in the sample per the equation in Section 13.2, substituting W_{SGT} for W_{HEM}. (W_{SGT} is the weight of Silica Gel Treated Hexane Extractable Material, Section 11.7). If the extract was split to decrease the total amount of material to 1,000 mg, determine the corrected total weight of SGT-HEM in the un-split extract (W_c) using the following equation:

$$W_c(\mathrm{mg}) = \frac{V_t}{V_a} W_d(\mathrm{mg})$$

Where:

W_c = SGT-HEM in the un-split sample
V_t = Volume of total extract (100 mL)
V_a = Volume of portion containing ≤ 1000 mg
W_d = Weight of the portion of the extract split for adsorption

12.3. Use the corrected total weight of SGT-HEM in the un-split extract (W_c) to determine the total SGT-HEM in the sample by substituting W_c for W_{HEM} in Equation 12.1.

13. METHOD PERFORMANCE

13.1. Initial Demonstration of Capability

13.1.1. Method Detection Limit (MDL). An MDL must be determined prior to analysis of any samples. The MDL is determined using seven replicates of reagent water spiked with the hexadecane/stearic acid standard that has been carried through the entire analytical procedure. MDLs must be determined on an annual basis. The result of the MDL determination must be below the TestAmerica reporting limit. Refer to SOPs NC-QA-021 and CA-Q-S-006 for details of the MDL procedure.

13.2. Initial Precision and Recovery (IPR): To establish the ability to generate acceptable precision and accuracy, each laboratory using this SOP shall perform the following operations:

13.2.1. Extract and evaporate four samples of the PAR standard (Section 9.6) according to the procedure beginning in Section 11.

13.2.2. Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation of the percent recovery(s) for HEM and for SGT-HEM (if determined). Use the following equation for calculation of the standard deviation of the percent recovery:

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

where: n = Number of samples
x = % recovery in each sample

13.2.3. Compare "s" and "x" with the corresponding limits for initial precision and recovery in Section 9.5.2. If "s" and "x" meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, "s" exceeds the precision limit or "x" falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem and repeat the test.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. Acidic waste generated by the analysis. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.1.2. Solvent waste: This waste is disposed of in a flammable liquid solvent container identified as "Flammable Solvent Waste".

15.2.1.3. Contaminated disposable glassware and contaminated filter paper generated in the laboratory. This waste is disposed in a solid waste container identified as "Solid Waste."

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Method 1664A: n-Hexane Extractable Material (HEM) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons). Office of Water, Engineering and Analysis Division, Washington, DC, 20460, EPA-821-R-98-002, February, 1999

16.1.2. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.3. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.4. Corporate Quality Management Plan (CQMP), current version

16.1.5. Revision History

Historical File:		Revision 1.0: 11/15/99		Revision 8: 02/16/17
(formerly CORP-WC-0003NC)		Revision 1.1: 08/28/01		
		Revision 1.2: 11/05/04		
		Revision 1.3: 07/16/07		
		Revision 0: 09/30/08 (NC-WC-091)		
		Revision 1: 11/07/08		
		Revision 2: 12/18/09		
		Revision 3: 01/26/11		
		Revision 4: 04/13/12		
		Revision 5: 03/29/13		
		Revision 6: 11/07/14		
		Revision 7: 12/10/15		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021

16.2.5. Standards and Reagents, NC-QA-017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications from reference method

17.1.1. This SOP does not mandate recovery of evaporated hexane. Individual laboratories may implement solvent recovery systems at their option.

17.1.2. In case of matrix problems, the laboratory will contact the Project Manager. The Project Manager will be responsible for contacting the client to discuss options regarding re-analysis or re-sampling. The laboratory will not make modifications to this method to compensate for matrix interferences.

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17.1.3. A performance based modification to the method requirement for 30 minutes in the desiccator has been implemented. A desiccation time study was performed to demonstrate that samples are generally stable after approximately 10 minutes in the desiccator.

TABLE 1.
SUMMARY OF QUALITY CONTROL REQUIREMENTS
(Refer to QA Policy, QA-003)

QC Samples	Frequency	Acceptance Criteria	Corrective Action
Initial Balance Check	Prior to and following sample weighing	+/- 0.2 mg for 2 mg and +/- 5 mg for 1000 mg	Recalibrate the balance and perform the balance checks
Method Blank	One per batch of samples	< Reporting Limit	Reprep and re-analyze (see Section 9.4.2.1)
OPR/LCS	One per batch of samples	Meets limits in Section 9.5.2. (or historical limits for soils)	Re-analyze or reprep all samples associated with unacceptable OPR/LCS
Matrix Spike samples (MS / MSD)	One MS / MSD pair per 20 samples	Meets limits in Section 9.6.2.	Supervisor's technical judgment

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Appendix A: Preprogrammed Methods For The Horizon SPE-DEX 3000XL

	Method 26	Method 27	Method 28	Method 29	Method 30
Disk Setup Size / Prefilter	**Pacific Premium 47 mm / None**	**Pacific Premium 47 mm / Prefilter**	**Pacific Premium 100 mm / None**	**Pacific Premium 100 mm / Prefilter**	**None / None**
PW Hexane					
Dispense	6 s	6 s	10 s	10 s	1 s
Saturate	1 s	1 s	1 s	1 s	0 s
Soak	30 s	30 s	1 min.	1 min.	0 s
Drain	30 s	30 s	1 min.	1 min.	5 s
PW Methanol					
Dispense	6 s	6 s	10 s	10 s	1 s
Saturate	1 s	1 s	1 s	1 s	0 s
Soak	30 s	30 s	1 min.	1 min.	0 s
Drain	3 s	30 s	3 s	3 s	5 s
Process Sample					
Air Dry	3 min.	5 min.	3 min.	8 min.	0 s
Hexane Rinse					
Rinse	4 s	4 s	8 s	8 s	
Soak	5 s	30 s	10 s	30 s	
Elute	15 s	15 s	15 s	15 s	
Hexane Rinse					
Rinse	2 s	3 s	7 s	7 s	
Soak	45 s	45 s	45 s	1 s	
Elute	44 s	45 s	45 s	45 s	
Hexane Rinse					
Rinse	2 s	3 s	7 s	7 s	
Soak	45 s	45 s	45 s	1 s	
Elute	30 s	45 s	30 s	30 s	
MeOH Discard					
Rinse	2 s	2 s	4 s	4 s	2 s
Soak	20 s	20 s	20 s	45 s	0 s
Elute	1 min.	1 min.	1 min.	1 min.	5 s
Hexane Rinse					
Rinse	2 s	2 s	4 s	4 s	**3 s**
Soak	45 s	45 s	45 s	45 s	**0 s**
Elute	45 s	45 s	45 s	45 s	**15 s**
Hexane Rinse					
Rinse	2 s	2 s	4 s	4 s	
Soak	45 s	45 s	45 s	45 s	
Elute	30 s	30 s	30 s	30 s	
Hexane Rinse					
Rinse	2 s	2 s	4 s	4 s	
Soak	45 s	45 s	45 s	45 s	
Elute	30 s	30 s	30 s	30 s	
Hexane Rinse					
Rinse	2 s	2 s	4 s	4 s	
Soak	45 s	45 s	45 s	45 s	
Elute	1 min.	1 min.	1 min	1 min.	

TITLE: DETERMINATION OF SOLIDS IN WATERS AND WASTES

[Methods: Standard Methods 2540B, 2540C, 2540D]

Approvals (Signature/Date):

Technology Specialist	07/20/17 Date	Health & Safety Coordinator	05/01/17 Date
Quality Assurance Manager	07/24/17 Date	Technical Director	07/20/17 Date

This SOP was previously identified as SOP No. NC-WC-092, Rev 6, dated 5/16/16

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1. SCOPE AND APPLICATION

1.1. This SOP is applicable to the determination of total solids, total suspended solids, and total dissolved solids using gravimetric techniques. This SOP is based on the residue methods contained in *Standard Methods for the Examination of Water and Wastewater* (SM).

1.2. This SOP is applicable to surface and saline waters and domestic and industrial wastes.

1.3. The Total Solids protocol is based on SM 2540B.

1.4. The Total Dissolved Solids protocol is based on SM 2540C.

1.5. The Total Suspended Solids protocol is based on SM 2540D.

1.6. The methods cover a practical range of 10 mg/L to 20,000 mg/L (TSS: 4 mg/L - 20,000 mg/L). As a practical matter, the final residue weight should be limited to about 200 mg.

1.7. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

2.1. Total Solids (TS): A well-mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105 °C. The increase in weight over that of the empty dish represents the total solids.

2.2. Total Dissolved Solids (TDS): A well-mixed sample is filtered through a glass fiber filter. The filtrate is quantitatively transferred into a pre-weighed evaporating dish and is evaporated to dryness and then dried to constant weight at 180 °C. The increase in weight over that of the empty dish represents the total dissolved solids. The filter from this procedure may also be used for TSS determination.

2.3. Total Suspended Solids (TSS): A well-mixed sample is filtered through a pre-weighed glass fiber filter. The residue on the filter is dried to constant weight at 103-105 °C. The increase in weight over that of the pre-weighed filter represents the TSS content. The filtrate from this procedure may be used for TDS determination.

3. DEFINITIONS

3.1. Total Solids (TS): The term applied to the residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at 103-105°C. Total solids includes “total suspended solids,” the portion of solids retained by a filter, and “total dissolved solids,” the portion that passes through the filter.

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3.2. Total Dissolved Solids (TDS): Those solids capable of passing through a glass fiber filter and dried to constant weight at 180 °C. TDS is also referred to as filterable residue.

3.3. Total Suspended Solids (TSS): Those solids which are retained by a glass fiber filter and dried to constant weight at 103-105 °C. TSS is also referred to as non-filterable residue.

3.4. Aliquot: A representative portion of a sample

3.5. Reagent Water: Deionized water which is free of the analyte(s) of interest

3.6. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of analysis by running method blanks.

4.2. Non-homogeneous samples may give erroneous results. Samples should be mixed as thoroughly as possible before removing an aliquot for analysis.

4.3. Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted in LIMS.

4.4. Samples containing large amounts of solids may filter slowly. Prolonged filtration times resulting from filter clogging may produce high TSS results due to increased colloidal materials captured on the clogged filter.

4.5. Oil and grease in the samples will cause unreliable results due to difficulty in drying to constant weight. Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

4.6. Filtration apparatus; filter material, pre-washing, post-washing, and drying temperatures are specified because these variables have been shown to affect the results.

4.7. The temperature at which the residue is dried has an important bearing on the results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

4.8. Each sample requires close attention to desiccation after drying. Minimize opening the desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

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4.9. Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic, and will require prolonged drying, desiccation and rapid weighing.

4.10. Samples containing high concentrations of bicarbonate may require careful and possibly prolonged drying to ensure that all the bicarbonate is converted to carbonate.

4.11. Too much residue in the drying vessel will crust over, entrapping water that will not be driven off during drying. Total residue should be limited to about 200 mg.

4.12. Some samples may have fine suspended solids, which will pass through the glass fiber filter causing high TDS results.

4.13. Aluminum pans should not be used for TS or TDS analyses. Components in some samples may react to form aluminum compounds, causing unreliable results.

4.14. For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material prior to TSS determination.

4.15. Static electricity, especially during colder months, can cause unstable balance readings. If static becomes an issue, the anti-static bracket should be used.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. There are no materials used in this method that have a significant or serious hazard rating. A complete list of materials used in the method can be found in the Reagents and Standards section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and Laboratory Supervisor.

5.6. If possible, place the oven under a canopy hood or vent in to a fume hood. Do not stand directly in front of an oven as the door is being opened. Stand behind the door to avoid breathing fumes that may be present.

5.7. Caution should be used when handling apparatus treated in the oven. Items will be hot. At a minimum, tongs must be used when placing material into or removing material from the oven.

5.8. Oily samples or those that contain volatile chemicals may ignite during this procedure. In the case of a fire, the oven should be turned off and allowed to cool before the sample can be removed and put under a hood.

6. EQUIPMENT AND SUPPLIES

6.1. Analytical balance capable of weighing to ± 0.0001 g

6.2. Vacuum filtration apparatus

6.3. Vacuum pump equipped with moisture trap

6.4. Glass fiber filter disks, 47 mm, without organic binder (Gelman Type A/E or equivalent)

Note: Commercially available pre-weighed filters may be used for TSS analyses.

6.5. Evaporating dishes, 100 mL, made of porcelain. These must be thoroughly cleaned, rinsed with deionized water, and baked at 180 ± 2 °C for at least one hour before use. Store in a desiccator.

Note: 150 mL glass beakers or StableWeigh vessels may also be used for TS or TDS determinations.

6.6. Desiccators providing sufficient space for storage of samples in process, separate from filters and evaporating dishes.

6.7. Desiccant containing a color indicator of moisture concentration or an instrumental indicator

6.8. Drying ovens set at 103-105 °C and 180 ± 2 °C. Separate ovens should be maintained at appropriate temperatures if possible.

6.9. Conductivity meter and associated apparatus

6.10. Graduated cylinders, assorted sizes, Class A

6.11. Volumetric flasks, Class A, assorted sizes

6.12. Aluminum weighing dishes large enough to hold a 47 mm filter

6.13. Forceps for handling filters

6.14. Crucible tongs

6.15. Zetex gloves or other gloves capable of providing protection at 180 °C

6.16. Anti-Static bracket

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent

7.2. LCS solution (500 mg/L TSS and TDS, 1000 mg/L TS): Place 500.0 mg of diatomaceous earth (infusorial earth or celite 545) and 500 mg sodium chloride into a 1000 mL volumetric flask and dilute to volume with deionized water. Mix well. Prepare fresh every three months.

Note: Commercially available reference materials may also be used. The concentration may vary per the vendor lot. The certified true value is used for calculation.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Samples should be collected in either plastic or glass bottles.

8.2. Samples must be stored at 4 °C ± 2 °C to minimize microbiological decomposition of solids. Bring samples to room temperature before analysis.

8.3. To achieve the reporting limits listed in Section 17, the lab will use the following volumes as maximums:

Parameter	Volume (mL)
TS	100
TDS	100
TSS	100

8.4. Holding times for solids determinations are as follows:

Parameter	Holding Time (days)
TS	7
TDS	7
TSS	7

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS and Method Blank) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank (MB)

9.2.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including filtration as applicable. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB should not contain any analyte of interest at or above the reporting limit.

9.2.2. Corrective Action for Blanks

9.2.2.1. If the analyte level in the method blank exceeds the RL for the analyte of interest in the sample, all associated samples are reprepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative**.

9.2.2.2. High blank results indicate contamination or could indicate an issue with the quality of the DI water. Make sure the glassware and filtering apparatus is clean.

9.2.2.3. Low blanks typically indicate that the balance was not operating correctly or the filter/weighing dish was not completely dry or sufficiently cooled when the initial weights were measured.

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9.2.2.4. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. An LCS is prepared and analyzed with each analytical batch of samples. Refer to Section 7.2 for instructions on how to prepare the LCS solution. The LCS volume is 100 mL.

9.3.3. Corrective Action for LCS

9.3.3.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.3.1.1. A control limit of 80-120% recovery must be applied until in-house control limits are established. If the result is outside established control limits, the system is out of control and corrective action must occur.

9.3.3.1.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.3.3.1.3. Corrective action includes re-preparation and re-analysis of the batch unless the client agrees that another corrective action is acceptable.

9.3.3.1.4. Poor LCS results are usually the result of contamination or poor mixing.

9.4. Sample Duplicate

9.4.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical

process. The sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.4.2. Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.4.3. Corrective Action for Duplicates

9.4.3.1. The failure of the sample duplicates to meet precision criteria **must be addressed in the project narrative**.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.5.3. Table I (Section 17) provides a summary of quality control requirements including type, frequency, acceptance criteria, and corrective action.

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.6.2. MDLs are easily accessible via the LIMs.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Since this method is based on gravimetric techniques, there is no calibration in the usual sense. Proper balance operation will be verified daily or prior to sample analysis by following SOP NC-QA-015. Analytical balance calibration must be performed daily (every 24 hours).

10.2. Oven temperature must be checked on each day of use and recorded in the LIMS batch information.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Proper sample identification is extremely important in any analytical procedure. Labeling of evaporating dishes and filters holders must be done in a manner to ensure connection with the proper sample.

11.4. If possible, analyze all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the Lab and Reporting group.

11.5. Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted in the LIMS.

11.6. If samples are visibly oily, this should be noted in the LIMS.

11.7. If there is limited sample volume or high solids content, smaller amounts of sample may need to be processed than detailed in the following sections. This occurrence must be noted in LIMS, and reporting limits must be adjusted appropriately.

11.8. Total Solids

11.8.1. Preparation of Evaporating Dish

11.8.1.1. If only total solids are to be measured, heat a clean dish or glass beaker to 103-105°C for one hour.

11.8.1.2. Cool and store the dish or glass beaker in the desiccator until it reaches room temperature or until needed.

11.8.1.3. Weigh the dish or glass beaker immediately before use to the nearest 0.1 mg. Record the weight on the worksheet in the LIMS.

11.8.2. Sample Analysis

11.8.2.1. Transfer a measured aliquot of well-mixed sample to the pre-weighed, labeled dish. Record the volume of sample (to the nearest mL) in LIMS.

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11.8.2.1.1. If the sample is known to contain > 2000 mg/L dissolved solids, it should be diluted. Prescreening is performed on all samples using a conductivity meter to determine the required sample volume or dilution. See Table 2 for conductivities and related sample volumes.

11.8.2.1.2. For the LCS, measure 100 mL of the LCS Solution (Section 7.2) and pour into the dish.

11.8.2.1.3. For the MB, measure 100 mL of reagent water and pour into the dish.

11.8.2.2. Evaporate the sample to dryness in a 103-105°C oven

11.8.2.3. Record the date, time, and oven temperature in the LIMS when the samples are initially placed in the oven and again when they are removed from the oven.

11.8.2.4. Using tongs remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

11.8.2.5. Weigh the dish to the nearest 0.1 mg. Record the weight on the worksheet in the LIMS.

11.8.2.6. Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, note this in the LIMs. After three cycles, the result is reported with a narrative. The laboratory does not repeat more than three weighings.

Note: When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation.

11.8.2.7. Calculate results according to the equation provided in Section 12.1. Use the lowest final weight achieved for calculating TS.

11.9. Total Dissolved Solids

11.9.1. Commercially available pre-washed, pre-weighed filters are used.

11.9.1.1. Preparation of Glass Fiber Filter Disc: **Note:** The steps outlined in Sections 11.10.1.1 through 11.10.1.7, must be used if prepared and pre-weighed filters are not available.

11.9.2. Preparation of Evaporating Dishes: **Note:** The following steps are not required when using pre-weighed StableWeigh Vessels.

11.9.2.1. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2 °C for one hour.

11.9.2.2. Store and cool dish in desiccator until dish reaches room temperature or until needed.

Note: Always transfer the dish with gloves or tongs to prevent added weight due to oil from fingerprints.

11.9.2.3. Weigh immediately before use to the nearest 0.1 mg. Record the weight of the dish on the worksheet in the LIMS.

11.9.3. Sample Analysis

11.9.3.1. Thoroughly rinse the entire filtration apparatus with reagent water before filtering each sample. Rinse each filter prior to filtering the sample.

11.9.3.2. Assemble the filtering apparatus, place a glass fiber filter in the apparatus, pre-wet the filter using reagent water, and begin suction.

Note: If the sample also requires TSS, use a pre-weighed, prepared filter and refer to Section 11.10 for additional guidance.

11.9.3.2.1. The conductance of each sample is used to determine the appropriate sample volume to process. See Table 2 for conductivities and related sample volumes.

11.9.3.3. Shake the sample vigorously and rapidly transfer 100 mL (or a smaller portion) to the funnel by means of a graduated cylinder. If more than 10 minutes are required to complete filtration, decrease sample size.

Note: Multiple filters may be used if performing only TDS analysis.

11.9.3.3.1. Record the volume of sample used (to the nearest mL) on the worksheet in the LIMS.

11.9.3.3.2. For the method blank, process 100 mL of reagent water as the sample.

11.9.3.3.3. For the LCS, process 100mL of the LCS Solution. Refer to Section 7.2 for instructions on how to prepare the LCS.

11.9.3.4. Filter the sample through the glass fiber filter.

11.9.3.5. Rinse the graduated cylinder, funnel walls, and filter with three successive 10 mL portions of reagent water and allow for complete drainage between washings. Continue to apply vacuum for about three minutes after filtration is complete to remove as much water as possible.

11.9.3.6. Transfer the filtrate (including the washings) to a pre-weighed evaporating dish. Rinse the receiving flask with 10-25 mL of reagent water and transfer washings into the dish to ensure complete transfer of the sample.

11.9.3.7. Evaporate the samples to dryness on a steam bath or in an oven set slightly below boiling. If filtrate volume exceeds dish capacity, add successive portions to the same dish after evaporation.

11.9.3.8. Dry the evaporated sample in an oven for at least one hour at 180 $\pm$ 2 °C.

11.9.3.9. Record the date, time, and oven temperature on the worksheet in the LIMS when the samples are initially placed in the oven and again when they are removed from the oven.

11.9.3.10. Using tongs remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

11.9.3.11. Weigh the dish to the nearest 0.1 mg. Record the combined weight of the dried residue and the dish on the worksheet in the LIMS.

11.9.3.12. Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. After three cycles, the result is reported

with a narrative. The laboratory does not repeat more than three weighings.

11.9.3.13. Calculate results according to the equation in Section 12.2. Use the lowest final weight achieved for calculating TDS.

11.10. Total Suspended Solids

11.10.1. Preparation of Glass Fiber Filter Disc

Note: As an alternative to the steps outlined in Sections 11.10.1.1 through 11.10.1.7, prepared and pre-weighed filters are purchased for use under this method.

11.10.1.1. Place the glass fiber filter discs, one at a time, on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up.

11.10.1.2. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water.

11.10.1.3. Remove all traces of water by continuing to apply vacuum after water has passed through and discard washings.

11.10.1.4. Remove the filter from the membrane filter apparatus, place in a labeled, aluminum weighing dish (or remove both the crucible and filter if a Gooch crucible is used), and dry in an oven at 103-105 °C for one hour.

11.10.1.5. Using tongs remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

11.10.1.6. Weigh the cooled filter using an analytical balance to the nearest 0.1 mg. Handle the filters or crucible/filter only with forceps. Record the weight and the dish identification number on the worksheet in the LIMS.

11.10.1.7. Repeat the drying, cooling, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg.

11.10.2. Selection of Sample Volume

11.10.2.1. For a 47 mm diameter filter, filter 100 mL of sample.

11.10.2.2. If during filtration of this initial volume, the filtration rate drops rapidly or if filtration time exceeds 5-10 minutes, a smaller volume of sample should be processed.

Note: If the sample has suspended particles or is cloudy, start with a sample volume < 100 mL.

11.10.3. Sample Analysis

11.10.3.1. Assemble the filtering apparatus, place the pre-weighed glass fiber filter in the apparatus, pre-wet the filter using reagent water and begin suction.

Note: Handle the filters or crucible/filter only with forceps.

11.10.3.2. Shake the sample vigorously and quantitatively transfer 100 mL (or an appropriate aliquot) of the sample to the filter using a graduated cylinder or pipette. A smaller amount should be filtered if the sample is high in TSS or is otherwise slow to filter. Filter 25 mL at a time until filtration slows. Record the volume of sample filtered (to the nearest mL) on the worksheet in the LIMS.

Note: If Total Dissolved Solids (TDS) is also required, the filtrate may be used. Refer to Section 11.10 for additional guidance.

11.10.3.3. Remove all traces of water by continuing to apply vacuum after the sample has passed through.

11.10.3.4. With suction on, rinse the graduated cylinder, filter, suspended solids residue, and filter funnel wall with three 10 mL portions of reagent water allowing complete drainage between washings.

11.10.3.5. Remove all traces of water by continuing to apply vacuum for about three minutes after the sample has passed through.

11.10.3.6. Carefully remove the filter from the filter support and transfer to an aluminum weighing dish. Alternatively, remove the crucible and filter from the crucible adapter.

11.10.3.7. Dry the filter at least one hour at 103-105 °C.

11.10.3.8. Record the date, time, and oven temperature on the worksheet in LIMS when the samples are initially placed in the oven and again when they are removed from the oven.

11.10.3.9. Using tongs remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

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11.10.3.10. Cool the samples in a desiccator, weigh (to the nearest 0.1 mg), and record the weight on the worksheet in the LIMS.

11.10.3.11. Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, note this on the worksheet in the LIMS. After three cycles, the result is reported with a narrative. The laboratory does not repeat more than three weighings.

11.10.3.12. Calculate the results using the formula given in Section 12.3. Use the lowest final weight achieved for calculating TSS.

11.11. Analytical Documentation

11.11.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.11.2. Record all standards and reagents in the LIMs reagents module. All standards and reagents are assigned a unique number for identification.

11.11.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.11.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculate **Total Solids** as follows:

$$\text{Total Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

12.2. Calculate **Total Dissolved Solids** as follows:

$$\text{Total Dissolved Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

12.3. Calculate **Total Suspended Solids** as follows:

$$\text{Total Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

where: A = weight of filter + residue (mg)
B = weight of filter (mg)
C = volume of sample filtered (mL)

12.4 The relative percent difference (RPD) of duplicates is calculated according to the following equation:

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

where: DU1 = Sample result
DU2 = Sample duplicate result

12.5 If multiple weighing cycles are required, the lowest final sample weight is used for calculating solids content.

12.6 If smaller or larger sample volumes are processed than are specified in the method, the reporting limit must be adjusted accordingly.

12.7 Sample results should be reported according to the following significant figure rules:

Significant Figures	Sample Result
2	< 10
3	≥ 10

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual, CW-E-M-001, for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced by this method.

15.2.1.1. Acidic sample waste generated by the analysis. This waste is disposed of in designated acid waste containers located in the laboratory.

15.2.1.2. Contaminated filter and filter residue generated by the analysis, aluminum weighing tins and filter residue generated by solid sample analysis. This waste is disposed of in solid waste and debris containers located in the laboratory.

16. REFERENCES

16.1. References

16.1.1. Standard Methods for the Examination of Water and Wastewater, 2540B, 2540C, and 2540D, 1997

16.1.2. Corporate Quality Management Plan (CQMP), current version

16.1.3. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.4. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.5. Revision History

Historical File:		Revision 0: 03/19/09		Revision 4: 12/19/13
		Revision 1: 04/22/10		Revision 5: 04/24/15
		Revision 2: 11/07/11		Revision 6: 05/16/16
		Revision 3: 11/30/12		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

16.2.5. Micropipette Calibration, NC-QA-004

16.2.6. Standards and Reagents, NC-QA-017

16.2.7. Equipment Monitoring and Thermometer Calibration, NC-QA-015

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The reporting limit is 10 mg/L for TS and TDS.

17.1.2. The reporting limit is 4 mg/L for TSS.

17.1.3. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Modifications/Interpretations from Reference Method

17.2.1. Samples are not taken through the drying, cooling, and weighing cycle more than three times. If the sample fails to reach constant weight within three cycles, the lowest final weight is used for the calculation. This is documented on the worksheet in the LIMS and an NCM is created.

17.2.2. The SM2540 methods specify that volume should be increased in order to get a minimum amount of residue. The lab will use a maximum of 100mL of sample for each analysis.

17.3. Tables

Table 1: Summary of Quality Control Requirements for Solids Determinations

QC Samples	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	1 per batch of up to 20 samples	< ± RL	Re-analyze all samples associated with unacceptable MB. If the MB fails high, associated samples that are below the reporting limit may be reported with narration.
Laboratory Control Sample (LCS)	1 per batch of up to 20 samples	80 - 120 % until in-house limits established	Re-analyze all samples associated with unacceptable LCS. If the LCS fails high, associated samples that are below the reporting limit may be reported with narration.
Duplicate (DU)	1 per 10 samples	≤ 20% RPD when results > 5x RL. For TSS, RPD must be ≤ 10%.	Narrate the results

Table 2: Conductivity and Sample Volume

Conductivity (umhos/cm)	mL of Sample Used
0-1500	100
1500-3000	50
3000-4500	25
4500-10000	20
10000-20000	10
Over Range	5 or 1 for brine samples

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Analysis of Organochlorine Pesticides and PCBs

Method: EPA Method 608

Approvals (Signature/Date):

11/27/2017	11/28/2017
Sharon Bacha Date	Steve Jackson Date
Organics Department Manager	Regional Safety Coordinator
11/23/2017	11/27/2017
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This SOP describes procedures to be used when 40 CFR 136 Appendix A, Method 608 is applied to the analysis of organochlorine pesticides and PCBs by GC/ECD. The PCBs are identified and quantitated as Aroclors. This SOP is applicable to extracts derived from any aqueous matrix that is prepared according to the appropriate TestAmerica sample extraction SOP (PT-OP-001).

1.1.1. Table 1 identifies compounds for which this method has been applied, along with expected Reporting Limits (RLs). Matrix interferences may result in higher RLs than those listed.

1.2. On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated in PT-QA-M-001, Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. This SOP presents conditions for the analysis of prepared extracts for organochlorine pesticides and PCBs. The extracts are analyzed by GC/ECD using a dual column injection and internal standard calibration techniques. Dual column analysis for PCBs is performed only upon client request.

2.2. See SOP PT-OP-001 for details on extraction procedures.

3. DEFINITIONS

3.1. TALS – TestAmerica Laboratory Information Management System

3.2. NCM – Non-Conformance Memo, a communication system for the laboratory to document anomalies or non-conformances encountered with samples and their analysis.

3.3. Please refer to the glossary of the Laboratory Quality Assurance Manual (PT-QA-M-001) current version, for additional definitions.

4. INTERFERENCES

4.1. Any compound that can give a measurable response on the electron capture detector is a potential interference.

4.1.1. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.1.2. Sulfur is a strong interferant.

4.2. Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Carryover may also occur with a positive or negative interferant as well as a target analyte. Any samples analyzed after a samples with high concentrations of target analytes, or high recovery of IS or surrogate compounds, which show the possible effects of carryover must re-analyzed.

4.3. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup, sulfur cleanup, carboprep cleanup and acid cleanup (PCBs only). These cleanup procedures are included in SOP # PT-OP-028.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste contains will be kept closed unless transfers are being made.

5.5. The preparation of standards, reagents, and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent Items should only be used when they result in an improvement in quality, efficiency, productivity or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1. Gas chromatographic system with dual columns and dual ECD (^{63}Ni) detectors, and a data system capable of measuring peak area and/or height. See Table 2 for instrument settings and column information.

6.2. Autosampler and vials with crimp caps with PTFE-faced septa.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the SDS prior to use of any reagent or standard.

7.1. Hexane: pesticide grade or equivalent

7.2. Standards

7.2.1. All standards are purchased as stock solutions, but may be optionally prepared from singles or neat. Secondary dilution standards (prepared from the stock) must be prepared every six months or sooner, if standards have degraded or concentrated. Refer to Table 3 for concentrations of working calibration standards. Refer to Tables 10 and 11 for preparation of the calibration standards.

7.2.2. Internal Standard Stock Standard

7.2.2.1. Stock - A commercially prepared stock standard solution is obtained that contains the internal standard compounds, 1-bromo-2-nitrobenzene and dibutylchlorendate, at concentrations of 1000 ug/ml and 200 ug/ml respectively. Follow manufacturer's instructions for expiration date and storage.

7.2.2.2. Pesticide Working IS - A working standard for the internal standard, 1-bromo-2-nitrobenzene and dibutylchlorendate, is prepared at a concentration of 1 ug/ml. This standard is added to all samples and standards to result in a final concentration of 0.1 ug/ml (20 ul of 1 ug/ml to 200 ul; 10 ul to 100 ul; etc.) after any cleanups or dilutions that may be necessary but before injection.

7.2.2.3. PCB Working IS - A working standard for the internal standard, 1-bromo-2-nitrobenzene and PCB-205, is prepared at a concentration of 10 ug/ml. This standard is added to all samples and standards to result in a final concentration of 0.1 ug/ml (2 ul of 1 ug/ml to 200 ul; 1

ul to 100 ul; etc.) after any cleanups or dilutions that may be necessary but before injection.

7.2.3. Refer to PT-GC-005 and PT-GC-006 for PCB and Pesticide standard (working standards, surrogates and ICV) concentrations, levels and preparation procedures.

7.2.4. A proprietary software database program is utilized for providing and managing all necessary detail regarding standards associated with this method. An example copy of a print out available from this database is provided in Figure 1.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT & STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Pesticide Waters	Amber glass	Cool >0.0 °C but ≤6.0°C	7 Days	40 Days from extraction	40 CFR Part 136.3
PCB Waters	Amber glass	Cool >0.0 °C but ≤6.0°C	1 year	1 year from extraction	40 CFR Part 136.3

9. QUALITY CONTROL

9.1. The TestAmerica-Pittsburgh QC Program document (PT-QA-021) provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required

9.2. A method blank (MB) must be extracted with each extraction batch and must be analyzed on at least one of the instruments on which associated samples are analyzed. A MB consists of laboratory reagent water, spiked with the surrogate and carried through the extraction, clean-up and analysis with samples. The method blank must be analyzed daily prior to sample analysis to ensure the chromatographic system is contaminant free.

9.2.1. The method blank must not contain any analyte of interest at or above the reporting. For analytes detected above the MDL, all associated results will be reported with B qualifiers. If the MB is found to be contaminated above the RL, the sample batch must be re-extracted / reanalyzed unless one of the following criteria is met:

- Evaluate the associated sample results. If sample results are non-detect for the compound of interest found in the MB, results may be reported using the "Method Blank – Report, ND" NCM.

- If the associated sample concentrations are >10x the MB concentration, results for these samples may be reported using the "Method Blank – Report, 10X" NCM.

- If neither of the above situations exists, and re-extraction is not possible due to limited sample volume or holding time, the lab must notify the Project Manager. Instructions must be sought from the client on how to proceed with reporting these results. Results that are reported must be properly qualified and an NCM created to document the situation for the case narrative. Re-extraction outside of the holding time must be approved by the client.

9.3. Laboratory Control Sample (LCS)

9.3.1. A LCS consists of laboratory reagent water, spiked with the surrogate and matrix spike and carried through the extraction, clean-up and analysis with samples. LCSs must be performed one for every 10 samples.

9.3.2. In order to be acceptable, a LCS must meet the recovery limits listed in Table 9.

9.3.3. If any analyte is outside the control limits in the LCS, the batch must be re-extracted / reanalyzed unless the following criterion is met:

- If the LCS recovery is above the upper control limit and sample results are non-detect, those associated sample results may be reported with the appropriate qualifier and using the "LCS/LCSD - %R High" NCM.

- If the above situation does not exists, and re-extraction is not possible due to limited sample volume or holding time, the lab must notify the Project Manager. Instructions must be sought from the client on how to proceed with reporting these results. Results that are reported must be properly qualified and an NCM created to document the situation for the case narrative.

9.4. A matrix spike (MS) must be analyzed every 10 samples. Client specifications or sample volume availability may override this frequency of analysis. The recoveries must be evaluated against the limits given in Table 9.

9.4.1. If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of analytical problems. This may indicate that the sample matrix itself has an adverse effect on recovering the analyte.

- If a matrix effect is suspected, the parent sample is qualified appropriately, and results are reported using the “MS/MSD - %R, LCS Pass” NCM.

- If the recovery for any component is outside control limits for both the MS and the LCS, the laboratory is out of control and corrective action must be taken.

- If an MS/MSD is not possible due to limited sample, then an LCS duplicate (LCSD) may be analyzed to monitor batch precision.

9.4.2. The MS/MSD must be analyzed at the same dilution level as the unspiked parent sample, unless the matrix spike components would then be above the calibration range. In this case, would require a dilution greater than the unspiked parent sample to bring the spiked compounds within the calibration range.

9.4.3. If the parent sample concentration is >4X, it may not be possible to accurately calculate %recoveries. Results will be reported with the “MS/MSD – High Targets” NCM.

9.5. Surrogates

9.5.1. Each field sample, QC sample, and calibration standard, is spiked with surrogate compounds decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). The surrogate spike solution is prepared as described in Section 7.2.3.

9.5.2. For field samples and batch QC, the surrogate recoveries must be within the established control limits, which are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. Surrogate recovery limits are maintained in TALS.

9.5.2.1. Surrogate recoveries for both DCB and TCMX in the MB and LCS both must pass on at least one column. If the recovery of the surrogates in MB or LCS's is outside of the control limits, check for calculation or instrument problems.

9.5.2.2. Surrogate recoveries (one or both) outside of control limits on both columns for the MB or LCS require re-preparation and reanalysis of the entire preparation batch.

9.5.2.3. For field samples, surrogate recovery is calculated and reported for both DCB and TCMX. At least one surrogate must pass on the one column from which compounds are identified and reported, and that column must have a passing CCV.

9.5.2.4. For CCV standards, surrogates must pass on the reporting column, for the data to be considered reportable.

9.5.2.5. If both surrogates fail on both columns for a sample, and matrix interference is not obvious from the initial analysis, it is only necessary to re-prepare and reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effects, as long as the extraction/instrument system is proven to be working properly according to the batch and instrument QC.

9.5.2.6. A re-extraction outside holding time must be approved. If reextraction is not possible, sample results should be evaluated for usability and appropriate comments made in the case narrative. In addition, a Nonconformance Memo must be completed.

9.5.3. For each sample and QC sample, the retention times of both surrogates must be within the appropriate retention time window. Any analyses that do not meet this requirement must be reanalyzed until this criterion is met.

9.6. Internal Standard Criteria

9.6.1. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration

standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

9.6.1.1. Any samples or standards that do not meet the internal standard criteria of > 50% and <200% of the response when compared back to the continuing calibration must be evaluated for validity. Samples that are reported with internal standard exceedances must have documentation supporting matrix effect. Where the matrix effect is well established it may be reported with narration, otherwise the samples must be reanalyzed to confirm matrix effect is required. If the internal standard exceedance is deemed to be due to an instrumental problem, instrument maintenance will be done and all affected samples must be reanalyzed after the problem is corrected.

9.6.1.2. Internal standard calibration involves the comparison of instrument responses from the samples to the responses from the target compounds in the calibration standards. The area (or height) of a peak and the area (or height) of the internal standard in a sample chromatogram is compared to the area (or height) of the peak and the area (or height) of the internal standard in the standard chromatograms that appears at the same retention time. The ratio of the detector response to the concentration of the target analyte in the calibration standard is defined as the response factor (RF) and is calculated as follows:

$$RF = \frac{Ax \times Cis}{Ais \times Cx}$$

Where:

Ax = Area (or height) of the peak to be measured

Ais = Area (or height) of the peak for the internal standard

Cis = Concentration of the internal standard

Cx = Concentration of the peak being measured

Note: It is also possible to use the concentration of the standard rather than the mass injected.

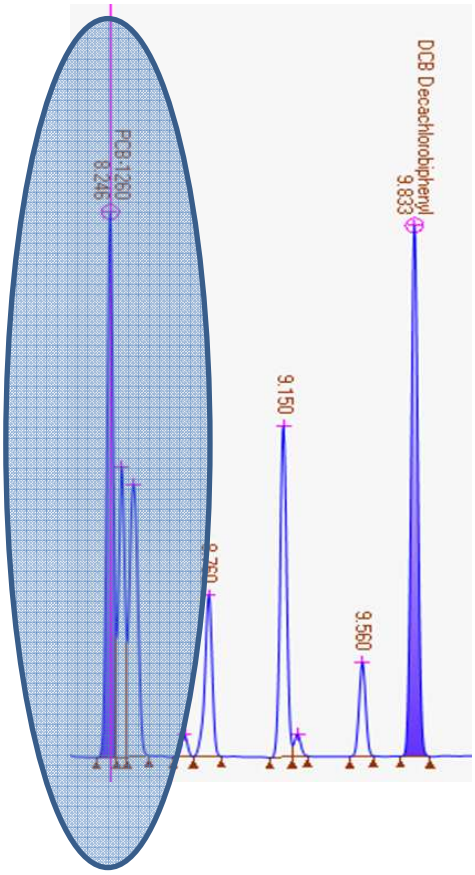
9.7. Resolution Check requirement for PCB's

9.7.1. The circled triplet of peaks in the figure below is observed towards the end of the 1260 pattern on columns such as CLP 1. Minimum resolution (degree of

overlap) requirement between peak 1 / 2 and peak 2 / 3 is <75%. This chromatogram shows overlap of about 50% between peak 2 and 3, and 30% between peak 1 and 2.

9.7.1.1. Resolution (degree of overlap) is calculated as follows:

[Height of the valley / (Sum of the two peak heights / 2)] x 100%



9.8. Retention Times

9.8.1. Absolute retention times are used for the identification of Pesticides and PCBs as Aroclors. However, in addition to retention times, peak patterns play a large role in the identification of Aroclors.

9.8.2. The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV (CCVIS) in the daily analytical sequence, whichever is more recent,.

9.8.3. Before establishing windows, make sure the GC system is within optimum operating conditions. Evaluate the deviation from expected RT for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours.

9.8.4 If three days of analytical data are not available, use a default RT window of 0.010 minutes. At the end of the batch, evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.

- Multiply the maximum deviation from the set by 1.5. This is the retention time window, unless the result is less than 0.010 minute, in which case the window is set at 0.010 minute.
- Determine the retention time (RT) windows for the 3-5 major peaks selected for each Aroclor, or multi-component Pesticide. The AR1016 windows will be used to establish retention time windows for PCBs AR1221, AR1016, AR1232, AR1242, and AR1248. The AR1260 windows will be used to establish retention time windows for PCBs AR1254, AR1260, AR1262, and AR1268.
- Retention time windows for analytes of interest must not overlap.

9.8.5 Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV (CCVIS) of the day. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the RT window, except as discussed below.

- Matrix spike analytes may fall outside the RT window if there is a large, non-target peak co-eluting, or overlapping, with the analyte in the matrix.

9.8.6 If any analyte falls outside the RT window in CCV, LCS of matrix spike (except as discussed above for matrix spikes), then the RT window for that analyte shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

9.8.7 Retention time windows should be reliably narrower than +/- 0.03 minute. If RT windows wider than this are necessary, the instrument should be evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained and the foregoing requirements.

9.8.8 The laboratory must calculate retention time windows for each analyte on each GC column and whenever a new type of GC column is installed. The data must be retained by the laboratory and available for review.

10 PROCEDURE

10.1 CALIBRATION AND STANDARDIZATION

Internal standard calibration will be used. Prepare standards containing each analyte of interest at a minimum of three concentration levels (typically five levels). The low-level standard must be less than or equal to the RLs in Table 1. The other standards define the working range of the detector. Recommended calibration levels are given in Table 3.

10.1.1 A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns and any changes in instrument operation parameters, including gas flow, detector temperatures, oven temperatures, etc. Initial Calibration will be performed at least every 6 months.

10.1.2 With the exception of Section 10.1.3 below, it is not acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve and the reporting limit and/or linear range is adjusted accordingly. In any event, at least 3 points must be included in the calibration curve.

10.1.3 A level other than the lowest or highest may only be removed from the calibration if an injection or instrument problem confined to that point can be clearly documented (see examples below). If a point is removed for documented valid reason, it must be removed for all compounds. A minimum of three levels must remain in the calibration. The documentation must be retained with the initial calibration.

10.1.3.1 One of the following conditions must be documented to allow removal or replacement of a calibration point:

- The data file is corrupted and unusable, or the run is interrupted before completion.

- The analyst observes problem such as broken vial, leaking purge vessel, or autosampler failure during that standard injection.

- All internal standard responses, where applicable, are <70% or >130% of the responses in all other calibration standards, indicating an improperly prepared standard or bad injection.

- All analyte responses are <70% or >130% of expected for that level, indicating an improperly prepared standard or bad injection.

10.1.3.2 The excluded point may be reanalyzed and the reanalysis used for the calibration if it is performed within 24 hours and before any samples are analyzed using the calibration. All initial calibration points must be analyzed without any changes to instrument conditions. The ICV must be analyzed after the replacement standard is analyzed.

10.1.3.3 The reason for the removal/replacement of a calibration point must be clearly and completely documented in the run log.

10.1.3.4 If the calibration does not meet acceptance criteria with the removal/ replacement of the documented poor point, the whole calibration must be re-analyzed.

10.1.4 The PCBs are analyzed separately from the pesticides. The surrogate curve is calculated from the Aroclor 1016/1260 Mix. Surrogates in the other calibration standards are used only as retention time markers.

10.1.5 For multi-component pesticides (Toxaphene and technical chlordane) a multi-point calibration (minimum of 3 points) is analyzed. For PCB's a single point calibration is used for all PCB's except Aroclors 1016 and 1260, where a multi-point calibration curve is analyzed. If an Aroclor other than 1016/1260 is detected the sample(s) are reanalyzed following an acceptable multi-point (minimum of 3 points) calibration for that Aroclor(s).

10.1.6 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors (CF) or as linear regression curves, using a systematic approach to select the optimum calibration

function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until calibration acceptance criteria are met. For additional calibration details, see TestAmerica Calibration Policy, CA-Q-P-003.

10.1.7 Calibration Using Average Response Factor

For each analyte in each calibration standard, calculate the response factor (RF) relative to the response of the assigned internal standard. The RSD of the tabulated response factors is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

Calculate the Response Factor:

$$\textit{Response Factor (RF)} = \frac{(R_S * C_{IS})}{(R_{IS} * C_S)}$$

Where:

R_S = Instrument response (peak height or peak area) of Standard

R_{IS} = Response of Internal Standard

C_S = Concentration of Standard

C_{IS} = Concentration of Internal Standard

Calculate the average response factor**:**

$$Average\ \mathrm{Re}sponseFactor = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where:

RF_i = Response factor for the i^{th} calibration level

n = number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{RF}} \times 100\%$$

Where SD is the standard deviation of the average RF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}}$$

10.1.8 Evaluation of the Average Response Factor

Use of the average response factor assumes that the calibration is linear through the origin. A minimum of 5 points is required. Plot the calibration curve using the average RF as the slope of a line that passes through the origin. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the lowest and highest points, and if the residual values are relatively large, a linear regression should be considered.

Acceptance Criteria: The RSD must be ≤10%. If the RSD exceeds the limit, linearity through the origin cannot be assumed, and an alternative curve fit must be considered.

NOTE: The RSD criteria must be met for each individual peak for PCB Aroclors and multi-component pesticide compounds,

10.1.9 Calibration Using Linear Regression

A linear regression is a mathematical calculation of a straight line over two axes. The response factor is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit of the regression line to the data points. If linear regression is used, a minimum of 5 points are required. For linear least-squares, the weighting used is the reciprocal of the square of the standard deviation. Linear regression produces the slope and intercept terms for a linear equation in the following form:

$$y = ax + b$$

Where:

y = Response factor

x = Concentration of the target analyte in the calibration standard

a = Slope of the line

b = The y-intercept of the line

To calculate the concentration in an unknown sample extract, the regression equation is solved for concentration, resulting in the following equation, where C_s is now C_e, the concentration of the target analyte in the unknown sample extract, and R_s is now R_e, the response of the target analyte in the sample extract.

$$C_e = \frac{R_e * C_{IS}}{AvgRF * R_{IS}}$$

10.1.10 Evaluation of the Linear Calibration Function

- With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting, or least-squares, regression of the linear function is recommended to optimize the accuracy at low concentrations.

- Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than reporting limit (RL), and preferably less than the MDL.

- The correlation coefficient (r) or coefficient of determination (r2) must be ≥ 0.990. This criteria must be met for each individual peak for PCB Aroclors and multi-component pesticide compounds,

- Corrective Action: If the correlation coefficient falls below the acceptance limit, the linear regression is unacceptable and the calibration should be repeated since a higher order regression is not allowed for this method.

NOTE: Due to the stability of the PCB and Pesticide compounds, non-linear calibration curves (quadratic) are not acceptable for these analyses.

10.1.11 Removal of calibration points and/or levels

Certain analytes that have particularly high or low sensitivity may need to have the high or low calibration points removed in order to optimize the calibration curve. Removal of high or low calibration points is allowed, but the working range of the calibration must be adjusted accordingly. The reporting limit must be supported by the lowest point remaining in the calibration and any samples with

concentrations above the highest point in the calibration must be diluted and reanalyzed.

Points for individual compounds from the interior levels of the calibration may not be removed. A complete level may be removed if the laboratory can document a clear reason for incorrect response in the standard (see section 10.1.3 above for details).

10.1.12 Calibration Point Read-back Criteria

Whichever calibration model above is selected, it should be subjected to an additional check to establish the representativeness of the data that were used to produce it. This check is the refitting of each calibration point response back to the calibration model, or the comparison of the calculated amount of the standard against the expected amount.

- CHROM software provides an Initial Calibration %Drift report which shows the % Error for each calibration point. This report must be reviewed in addition to the %RSD / Linear Response Factor.
- The absolute value of the % Error for each calibration point should be $\leq$ 30%. For the lowest calibration point, the % Error may be $\leq$ 50%.

- If this readback criteria fails for any analyte, sample detects should be reanalyzed under passing criteria. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.
- For non-detects, if the readback failed with high recovery, reanalysis is not required, and flagging is not required. If the readback failed low, samples should be reanalyzed. If reanalysis is not possible, the result must be flagged as estimate, or the situation described in the narrative.

10.1.13 Column Degradation Evaluation

The column evaluation mix must be injected before each initial or daily calibration (see Table 4 for standard concentrations). The degradation of DDT and endrin must be calculated (see equations 15 and 16) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.1.14 Calibration Verification:

Initial Calibration Verification (ICV): The working calibration curve or average response factor must be verified with second source standards of all single peak pesticides and all PCB Aroclors. The ICV must be analyzed prior to the analysis of any samples. The result for the target analyte(s) in the ICV Pesticide standard must be within ± 15% of the expected value. The result for the target analyte(s) in the ICV PCB standard must be within ± 20% of the expected value. This criteria must be met for each individual peak for PCB Aroclors and multi-component pesticide compounds

10.1.14.1 Continuing Calibration Verification (CCVIS): The working calibration curve or average response factor must be verified by the analysis of a mid-point continuing calibration standard at the beginning of every analytical batch. An analytical batch consists of up to 20 samples (all injections except solvent blanks count as samples) or every 12 hours, whichever is more frequent.

10.1.14.2 The result for each target analyte in the CCV standard must be within ± 15% of the expected value.

10.1.15 It is not necessary to run a continuing calibration standard at the beginning of the sequence if the first 20 samples are analyzed immediately after the completion of an acceptable initial calibration and ICV.

10.1.16 If an Internal standard is used, it is not necessary to close each analytical batch with an ending calibration verification.

10.1.17 Percent Difference/Drift (%D) Calculation:

$$\%\ Drift = \frac{Calculated\ Conc. - Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.1.18 Corrective Actions for Continuing Calibration: If the percent difference for any analyte is >15%, or any individual peak for multi-component analytes, corrective action must be taken. This may include clipping the column, changing the injection port liner or other minor instrument adjustments, followed by reanalyzing the standard. If the response for any analyte still varies by more than 15%, a new calibration curve must be prepared.

10.1.19 Corrective Action for Samples: Any samples injected after the standard exceeding the continuing calibration criteria must be reanalyzed, unless the

CCV recovery is above the control limits and the sample results are non-detect for the affected compound.

10.2 ANALYTICAL PROCEDURE

10.2.13 Extraction - Extraction procedures are referenced in SOP PT-OP-001.

10.2.14 Cleanup - Cleanup procedures are referenced in SOP PT-OP-028.

10.2.15 Chromatography - Suggested chromatographic conditions are presented in Table 2.

10.2.16 Sample Introduction – Sample analysis is initiated by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

10.2.17 Analytical Sequence - An analytical sequence starts with an initial calibration or daily calibration verification. Refer to Table 8 for an example of an analytical sequence.

10.3 Upon completion of the analytical sequence, transfer the raw chromatography data to CHROM for further processing and review.

10.3.1 Review chromatograms online and determine whether manual data manipulations are necessary. All manual integrations must be justified and documented. See CA-Q-S-002 for requirements for manual integration.

10.3.2 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD.

10.3.3 Perform a level 1 data review and document the review on the data review checklist (GC Data Review Checklist).

10.3.4 Submit the data package and review checklist to the peer reviewer for the Level 2 review process. The data review process is explained in SOP PT-QA-018.

11 CALCULATIONS/DATA REDUCTION

11.1 Dual Column Quantitation and Reporting:

11.1.1 Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if estimated results ("J" qualified) are required. Normally confirmation is required on a second column, but if the sample matrix is well enough defined, single column analysis may be adequate, if permitted by the project. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (or MDL if estimated results are required).

11.1.2 Each sample is analyzed on two different columns at the same time. The laboratory designates a primary column based on optimal separation of the compounds of interest and other desirable chromatographic characteristics. The higher of the two results is normally reported if the percent difference between the responses of the two columns or detectors is within 40%. The result from the secondary (confirmatory) column is reported if any of the following is true:

- There is obvious chromatographic interference on the primary column.
- The difference between the result for the primary column and the result for the secondary column is > 40% and chromatographic interference is evident.
- The continuing calibration verification, bracketing standard, or surrogate recovery fails on the primary column, but is acceptable on the secondary column. However, if the difference between the primary column result and the secondary column result is > 40% and the primary column calibration fails, then the sample must be evaluated for reanalysis.

11.1.3 Dual Column Results with > 40% RPD

- If the Percent Difference (%D) between the response on the two columns or detectors is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. If the CCV % D is within ± 15% for one column and > 15% for the other column and the %D between the two columns is within 40%, the data is reported from the column with the CCV within ± 15%.

11.1.4 Multiresponse Analytes: For multiresponse analytes, the analyst should use the retention time windows, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

11.1.5 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

11.2 Calibration Range: If concentrations of any analytes exceed the working range as defined by the calibration standard, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50 percent of the high-level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

11.3 Dilutions: Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20 percent of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50 percent of the calibration range.

11.3.1 Guidance for Dilutions Due to Matrix: If the sample is initially run at a dilution and the baseline rise is less than half the height of the peaks in the mid-level calibration standard, then the sample should be reanalyzed at a more concentrated dilution.

11.3.2 Reporting Dilutions: The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Interferences: If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

11.5 Calculations: Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in the appendix attached to this document.

11.5.1 Sample Results

(using average Response Factor)

$$\text{Concentration } (\mu\text{g/L}) = \frac{(\text{As x Is}) \text{ x DF}}{(\text{Ais x RF x Vo})}$$

Where:
A_s = Response for the analyte in the sample.
I_s = Amount of internal standard added to each extract, µg.
DF = Dilution factor.
A_{is} = Response for the internal standard
V_o = Volume of sample extracted, mL

RF = Average Response factor, area or height/ng
A = Intercept of Linear calibration line

If linear regression curve is used, the above equation is used with the following exceptions:
A_s = Concentration in the extract from the curve, ng.
RF = Does not apply (can be assumed to be 1).

(using Linear Regression)

$$\text{Concentration } (\mu\text{g/L}) = \text{A} + \text{B}\frac{(\text{As x Is}) \text{ x DF}}{(\text{Ais})}$$

11.6 LCS Recovery

Concentrations of each compound in the LCS are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. LCS recoveries are calculated using the following equation:

$$\%\ \text{Recovery} = \frac{\textit{Concentration (or amount) found}}{\textit{Concentration (or amount) spiked}} \times 100$$

11.7 MS/MSD Recovery and RPD

Concentrations of each compound in the MS and MSD are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. The MS and MSD recoveries and the RPD between the MS and MSD are calculated using the following equations:

$$\%\ Spike\ Recovery\ (\%R) = \frac{SSR - SR}{SA}\ x\ 100$$

Where: SSR=Spiked Sample Result
SR=Sample Result
SA=Spike Added

$$RPD = \frac{|Conc.\ 1 - Conc.\ 2|}{(Conc.\ 1 + Conc.\ 2)/2} \times 100$$

Where: Conc. 1=MS Concentration
Conc. 2=MSD Concentration

11.8 Surrogate Recovery: Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equations:

$$\%Recovery = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}}\ \text{x } 100$$

11.9 Calculation of Column Degradation/% Breakdown (%B)

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}}\ x\ 100$$

Where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_E} x\ 100$$

Where:

A_{EK}, A_{EA}, and A_E = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

12 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

13 POLLUTION CONTROL

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2 This method does not contain any specific modifications that serve to minimize or prevent pollution.

14 WASTE MANAGEMENT

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.2 Waste's collected in this procedure are vials and extracts containing hexane that go into waste stream #7. PCB standards waste will go into waste stream #8.

14.3 Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator should be contacted if additional information is required.

15 REFERENCES

15.1 40 CFR Part 136, Appendix A, United States Environmental Protection Agency. 1984, Methods 608

15.2 Part III, Environmental Protection Agency, 40 CFR Part 122, 136, et al. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Final Rule, March 12, 2007. Table II, Required Containers, Preservation Technique and Holding Time.

15.3 Corporate SOP CA-Q-S-002, Acceptable Manual Integration Practices

15.4 Corporate Policy CA-Q-P-003, Calibration Curves and the Selection of Calibration Points

15.5 Pittsburgh Laboratory Quality Assurance Manual, PT-QA-M-001

15.6 SOP PT-OP-001, Extraction of Organic Compounds from Waters Based on SW-846 3500 and EPA 600 Series Methods

15.7 SOP PT-QA-007, Detection Limits

15.8 SOP PT-QA-016, Nonconformance & Corrective Action System

15.9 SOP PT-QA-018, Technical Data Review Requirements

15.10 SOP PT-QA-021, Quality Assurance Program

15.11 SOP PT-QA-031, Internal Chain of Custody

15.12 PT-HS-001, Pittsburgh Facility Addendum EH&S Manual (PT-HS-001) to the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.13 PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

16 METHOD MODIFICATIONS

16.1 None

17 ATTACHMENTS

17.1 Table 1 – Standard Analyte List and Reporting Limits

17.2 Table 2 – Suggested Instrument Conditions

17.3 Table 3-A – Pesticide Calibration Levels

17.4 Table 3-B – PCB Calibration Levels

17.5 Table 4 - Column Degradation Evaluation Mix

17.6 Table 5 - Full Analyte Pesticide Matrix Spike

17.7 Table 6 - PCB Matrix Spike

17.8 Table 7 - Surrogate Spike

17.9 Table 8 - Suggested Analytical Sequence

17.10 Table 9 – Performance Limits: Initial Demonstration of Capability (IDOC), LCS, and MS Acceptance Limits

17.11 Table 10 - Preparation of Pesticide Calibration Standards

17.12 Table 11 - Preparation of PCB Calibration Standards

18 REVISION HISTORY

18.1 Revision 2, 1/7/2008
18.2 Revision 3, 1/16/2009
18.3 Revision 4, 8/18/2011
18.4 Revision 5, 5/22/2012
18.5 Revision 6, 6/22/2014

18.6 Revision 7, 8/17/2016
18.7 Revision 8, 5/26/17
18.6 Changes to current revision

SOP section	Change from	Change to	Reason
2.2		Added reference to SOP PT-OP-001 for extraction	Clarification
4.2		Added discussion of carryover interference	Correction for PA DEP audit finding
9.2 & 9.3.1		Added matrix for MB and carried through all with samples to MB and LCS	Clarification
10.1.8, 10.1.10, 10.1.14, 10.1.18		Added that calibration and verification criteria apply to each individual peak for PCB arochlors and multicomponent pesticides	Correction for PA DEP audit finding
10.3		Section added for manual integration and data review	Correction

TABLE 1
STANDARD ANALYTE LIST AND REPORTING LIMITS

COMPOUND	CAS #	REPORTING LIMIT, µg/L WATER
Aldrin	309-00-2	0.0013
alpha-BHC	319-84-6	0.0013
beta-BHC	319-85-7	0.0013
delta-BHC	319-86-8	0.0013
gamma-BHC (Lindane)	58-89-9	0.0013
alpha-Chlordane	5103-71-9	0.0013
Gamma-Chlordane	5103-74-2	0.0013
4,4'-DDD	72-54-8	0.0013
4,4'-DDE	72-55-9	0.0013
4,4'-DDT	50-29-3	0.0013
Dieldrin	60-57-1	0.0013
Endosulfan I	959-98-8	0.0013
Endosulfan II	33213-65-9	0.0013
Endosulfan sulfate	1031-07-8	0.0013
Endrin	72-20-8	0.0013
Endrin aldehyde	7421-93-4	0.0013
Endrin ketone	53494-70-5	0.0013
Heptachlor	76-44-8	0.0013
Heptachlor epoxide	1024-57-3	0.0013
Methoxychlor	72-43-5	0.0013
Toxaphene	8001-35-2	0.05
Aroclor-1016	12674-11-2	0.01
Aroclor-1221	11104-28-2	0.01
Aroclor-1232	11141-16-5	0.01
Aroclor-1242	53469-21-9	0.01
Aroclor-1248	12672-29-6	0.01
Aroclor-1254	11097-69-1	0.01
Aroclor-1260	11096-82-5	0.01
Technical Chlordane	57-74-9	0.0125

The following concentration factors are assumed in calculating the reporting limits:

	EXTRACTION VOL.	FINAL VOL.
Aqueous	1000 mL	1.0 mL

TABLE 2
SUGGESTED INSTRUMENT CONDITIONS

Organochlorine Pesticides	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	100°C for 0.5 min, 35°C/min to 220°C, 20 °C/min to 300 °C, 4.071 min hold
Column 1	MR1, 30m X 0.53 mm id, 0.50µm
Column 2	MR-2, 30m X 0.53 mm id, 0.50µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

PCBs	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	CLP1,30m x 0.53 mm id, 0.50µm
Column 2	CLP2, 30m X 0.53 mm id, 0.50µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Dual towers are used and not a Y splitter

Table 3-A PESTICIDE CALIBRATION LEVELS (ng/mL)						
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6[2]**
Individual Mix A and B[1]						
Aldrin	1	5	25	50	100	200
g-BHC (Lindane)	1	5	25	50	100	200
Heptachlor	1	5	25	50	100	200
Methoxychlor	1	5	25	50	100	200
Dieldrin	1	5	25	50	100	200
Endosulfan I	1	5	25	50	100	200
Endosulfan II	1	5	25	50	100	200
4,4'-DDT	1	5	25	50	100	200
Endrin Aldehyde	1	5	25	50	100	200
Endrin Ketone	1	5	25	50	100	200
β-BHC	1	5	25	50	100	200
δ-BHC	1	5	25	50	100	200
α-BHC	1	5	25	50	100	200
4,4'-DDD	1	5	25	50	100	200
4,4'-DDE	1	5	25	50	100	200
Endosulfan Sulfate	1	5	25	50	100	200
Endrin	1	5	25	50	100	200
α-Chlordane [3]	1	5	25	50	100	200
γ-Chlordane [3]	1	5	25	50	100	200
Multicomponent Standards						
Chlordane (Technical)	5	25	250[4]	1250	2500	
Toxaphene	20	200	1000[5]	2500	5000	

Table 3-A PESTICIDE CALIBRATION LEVELS (ng/mL)						
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6[2]**
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	1	5	25	50	100	200
Decachlorobiphenyl	1	5	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.
[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.
[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.

Table 3-B PCB CALIBRATION LEVELS (ng/mL)							
	Level 1	**Level 2**	**Level 3**	**Level 4**	**Level 5**	**Level 6**	**Level 7[1]**
Aroclor 1016/1260	10	50	200	500	1000	2000	4000
Aroclor 1242/1268[2]				500			
Aroclor 1221 +1254[2]				500			
Aroclor 1232/1262[2]				500			
Aroclor 1248[2]				500			
Surrogates are included with all the calibration mixes at the following levels:							
Tetrachloro-m-xylene	0.5	2.5	10	25	50	100	200
Decachlorobiphenyl	0.5	2.5	10	25	50	100	200

[1] Level 7 is optional and should only be used if linearity can be maintained on the instrument to this level.
[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

TABLE 4
COLUMN DEGRADATION EVALUATION MIX
ng/mL

COMPONENT	CONCENTRATION
4,4'-DDT	50
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

TABLE 5
FULL ANALYTE PESTICIDE MATRIX SPIKE
µg/L

COMPONENT	CONCENTRATION
Alpha-BHC	0.025
Gamma-BHC	0.025
Beta-BHC	0.025
Delta-BHC	0.025
Heptachlor	0.025
Aldrin	0.025
Heptachlor Epoxide	0.025
Endosulfan I	0.025
Gamma-Chlordane	0.025
Alpha-Chlordane	0.025
Endosulfan II	0.025
Dieldrin	0.025
4,4'-DDE	0.025
Endrin	0.025
4,4'-DDD	0.025
4-4'-DDT	0.025
Endosulfan Sulfate	0.025
Endrin Aldehyde	0.025
Endrin Ketone	0.025
Methoxychlor	0.025

TABLE 6
PCB MATRIX SPIKE
µg/L

COMPONENT	CONCENTRATION
Aroclor 1016	1.0
Aroclor 1260	1.0

TABLE 7
SURROGATE SPIKE
µg/L

COMPONENT	CONCENTRATION
Tetrachloro-m-xylene	0.02
Decachlorobiphenyl	0.02

TABLE 8
SUGGESTED ANALYTICAL SEQUENCE

Organochlorine Pesticides

With Initial Calibration:

Solvent blank (optional)
Breakdown Mix
Toxaphene All Levels
Technical Chlordane All Levels
Pesticide Mix All Levels
ICV (all single component analytes)
MB
LCS
Up to 20 samples
Solvent blank (optional)
Individual mix A and B Mid level (Continuing calibration)
Up to 20 samples
Solvent blank (optional)
Individual mix A and B Mid level (Continuing calibration)
Etc.

With Daily Calibration:

Solvent blank (optional)
Breakdown mix
Pesticide Mix Mid level (Continuing calibration)
Up to 20 samples
Solvent blank (optional)
Pesticide Mix Mid level (Continuing calibration)
Etc.

PCBs

With Initial Calibration:

Solvent blank (optional)
Aroclor 1221/1254 Level 4
Aroclor 1232/1262 Level 4
Aroclor 1242/1268 Level 4
Aroclor 1248 Level 4
Aroclor 1016/1260 Level 1
Aroclor 1016/1260 Level 2
Aroclor 1016/1260 Level 3
Aroclor 1016/1260 Level 4
Aroclor 1016/1260 Level 5
Aroclor 1016/1260 Level 6
Aroclor 1016/1260 Level 7
ICVs (second source standard of all Aroclors)
MB
LCS
Up to 10 samples
Solvent blank (optional)
Aroclor 1016/1260 Level 4
Etc.

With Daily Calibration:

Solvent blank (optional)
Aroclor 1221/1254 Level 4
Aroclor 1232/1262 Level 4
Aroclor 1242/1268 Level 4
Aroclor 1248 Level 4
Aroclor 1016/1260 Level 4
Up to 10 samples
Solvent blank (optional)
Aroclor 1016/1260 Level 4
Etc.

Table 9		
Performance Limits Initial Demonstration of Capability (IDOC), LCS, and MS Acceptance Limits		
Compound	IDOC, LCS, and MS recovery limits[1]	IDOC RSD limits *
Aldrin	42 - 122	21
alpha-BHC	37 - 134	24
beta-BHC	17 - 147	32
delta-BHC	19 - 140	36[2]
gamma-BHC	32 - 127	23
Chlordane	45 - 119	20
4,4'-DDD	31 - 141	28
4,4'-DDE	30 - 145	27
4,4'-DDT	25 - 160[2]	36[2]
Dieldrin	36 - 146	38[2]
Endosulfan I	45 - 153[2]	24
Endosulfan II	D - 202[2]	61[2]
Endosulfan Sulfate	26 - 144	27
Endrin	30 - 147	37[2]
Heptachlor	34 - 111	20
Heptachlor Epoxide	37 - 142	20
Toxaphene	41 - 126	25
Aroclor 1016	50 - 114	20
Aroclor 1221	15 - 178[2]	48[2]
Aroclor 1232	10 - 215[2]	35[2]
Aroclor 1242	39 - 150	24
Aroclor 1248	38 - 158[2]	31
Aroclor 1254	29 - 131	27
Aroclor 1260	8 – 127[2]	20

* If a MS/MSD pair is analyzed, these are the RPD limits between the MS and MSD.

[1] Minimum and maximum recovery limits given in method 608. (Tighter limits may be applied if statistically determined.) The notation "D" in the column indicates that a detected concentration, above the MDL, must be achieved.

[2] Method limits exceed the TestAmerica minimum or maximum recovery limits of 10-150%, or maximum %RPD limit of 35%, therefore the control limits for this compound have been narrowed in TALS to meet TestAmerica criteria in practice.

Table 10
Preparation of Pesticide Calibration Standards

Calibration Level	Intermediate Pesticide Mix AB (uL)	Toxaphene Stock (uL)	Chlordane Stock (uL)
Level 1	4		
Level 2	20		
Level 3	250	400	100
Level 4	200		
Level 5	400		
Level 6	800		

The single peak pesticide stock standards are purchased as certified standards in one solution in 50%hexane/50% toluene. The AB Mix stock includes alpha-BHC, Dieldrin, Endosulfan I, Endrin, gamma-BHC, Heptachlor, 4,4'-DDD, 4,4'-DDT, Aldrin, alpha-Chlordane, beta-BHC, delta-BHC, Endosulfan II, Endosulfan sulfate, Endrin aldehyde, Endrin ketone, gamma-Chlordane, Heptachlor epoxide, and 4,4'-DDE, Methoxychlor, Decachlorobiphenyl (surrogate) and Tetrachloro-m-xylene (surrogate) at 100 ug/mL. An intermediate AB Pesticide stock standard is prepared by diluting 1.0 mL of the stock mix to 10.0 mL in hexane. The intermediate AB mix concentrations are 10 ug/mL for all compounds except methoxychlor which is 20 ug/mL. The working standards are prepared by diluting the volume noted in Table 10 to a 40.0 mL final volume in hexane except for the Level 3 standard, which is taken to a 100 mL final volume in hexane.

Toxaphene and Technical Chlordane stock standards are purchased certified solutions at 100 ug/mL. The mid level (Level 3) Toxaphene calibration standard is prepared by diluting 0.40 mL of the stock standard mix to 40 mL in hexane. The mid level (Level 3) Technical Chlordane calibration standard is prepared by diluting 0.10 mL of the stock standard mix to 40 mL in hexane.

Table 11 Preparation of PCB Calibration Standards					
Calibration Level	**1016/1260 Intermediate (uL)**	**1221 + 1254 Stock (uL)**	**1232 + 1262 Stock (uL)**	**1242 + 1268 Stock (uL)**	**1248 Stock (uL)**
Level 1	4				
Level 2	20				
Level 3	80				
Level 4	1000	250	250	250	250
Level 5	400				
Level 6	800				
Level 7	1600				

The surrogate stock is purchased (Decachlorobiphenyl and Tetrachloro-m-xylene) at 200 ug/mL.

The Aroclor 1016 and 1260 stock standards are purchased as certified standards in isooctane at 1000 ug/mL. The other five Aroclor stock standards are purchased at 200 ug/mL.

For Aroclors 1016 and 1260, an intermediate standard is prepared by diluting 1.0 mL of each of the stock standards and 0.25 mL of the surrogate stock standard to 10.0 mL in hexane. The intermediate Aroclor 1016/1260 standard concentrations are 100 ug/mL for each Aroclor and 5 ug/mL for each surrogate.

The Aroclor 1016/1260 calibration standards are prepared by diluting the volumes noted in Table 11 to a 40.0 mL final volume in hexane except for the Level 4 standard, which is taken to a 200 mL final volume in hexane.

The mid level (Level 4) calibration standards for each of the other sevenAroclors (1221, 1232, 1242, 1248, 1254, 1262 and 1268) are prepared by diluting 0.25 mL of the appropriate stock standard to a final volume of 100 mL in hexane. Aroclors 1221 and 1254, Aroclors 1232 and 1262, and Aroclors 1242 and 1268 are combined into one standard and Aroclor 1248is prepared individually.

Title: Polychlorinated Biphenyls (PCBs) and PCBs as Congeners by GC/ECD

Method: SW-846 8082 and 8082A

Approvals (Signature/Date):

11/15/2017	11/15/2017
Sharon Bacha Date	Steve Jackson Date
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11/28/2017	11/27/2017
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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedure for the determination of concentrations of polychlorinated biphenyls (PCB) as Aroclors and as individual Congeners (see Appendix A) using the methodology prescribed in EPA SW-846 Methods 8082 and 8082A.

1.2 This procedure is applicable to the analysis of aqueous, solid, sediment, biological, and waste/oil samples. When utilized for the analysis of waste/oils, additional cleanup procedures may be required.

1.3 This SOP does not include the procedures for extracting environmental samples. Refer to TestAmerica SOPs PT-OP-001 for aqueous and PT-OP-026 for solid and waste sample preparation procedures.

1.4 Table 1 at the end of this document lists the specific Aroclors that are determined using this procedure and their associated reporting limits (RLs).

1.5 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 Preparation

The extraction procedure is detailed in SOP PT-OP-001 for aqueous samples and PT-OP-026 for solids matrices and wipes.

Extract clean-up procedures are addressed in SOP PT-OP-028.

2.2 Analysis

Samples are analyzed using a gas chromatograph with dual electron capture detectors (ECDs). Specific Aroclor mixtures are identified by the pattern of peaks compared to chromatograms of reference standards. The concentrations of Aroclors in the sample extract are determined using an internal standard calibration.

3.0 DEFINITIONS

3.1 Polychlorinated biphenyls (PCBs): PCBs are a class of organic compounds with 1 to 10 chlorine atoms attached to biphenyl, with a general chemical formula of $C_{12}H_{10-x}Cl_x$. There are 209 possible congeners.

3.2 Aroclor: PCBs were produced as technical mixtures by the chlorination of biphenyl. Production processes were designed to produce mixtures with characteristic chlorine contents. In the United States, most of the PCBs in the environment are in the form of Aroclors, which were produced by Monsanto from the 1930s through 1977. Each Aroclor mixture is identified by a four-digit number, the first two digits of which indicate the number of carbons in the biphenyl ring, i.e., 12, and the second two of which indicate the weight percent of chlorine. For example, Aroclor 1254 has 12 carbons and 54% by weight chlorine. The exception is Aroclor 1016, which has 12 carbons and 41% by weight chlorine.

Each specific Aroclor produces a characteristic gas chromatographic pattern that represents the relative amounts of PCB congeners in the formulation. The formulation of the mixtures from batch to batch was fairly consistent, but never exactly the same. In almost all cases, the gas chromatogram can be used as a fingerprint to identify the specific Aroclor. Exceptions occurred for Aroclors 1254 and 1221. In each case, at least one batch was produced under different conditions, which resulted in an Aroclor mixture with the same approximate chlorine content, but with a significantly different distribution of congeners. These odd batches of 1254 and 1221 produce chromatographic patterns that are very different from the typical formulations. Standards for these odd batch Aroclors can be used to aid in the qualitative identification of Aroclors in environmental samples.

3.3 TALS: TestAmerica Laboratory Information Management System

3.4 NCM: Non-Conformance Memo – a system within TALS for documenting and communicating QC failures or anomalies encountered during sample receipt, preparation or analysis.

3.5 Please see the glossary of the TestAmerica Pittsburgh Quality Assurance Manual (PT-QA-M-001) for additional definitions.

4.0 INTERFERENCES

4.1 Hydrocarbons can co-elute and thereby mask the Aroclor pattern. The laboratory uses acid cleanup with concentrated sulfuric acid to remove hydrocarbons from solid and oil sample extracts, and for water samples when extracts have noticeable color or whenever there is clear evidence of interferences in the initial sample chromatograms. Acid cleanup removes low-to-medium molecular weight polar organic interferences from sample extracts. Detailed instructions for performing acid cleanup are provided in SOP PT-OP-028.

4.2 Sulfur will interfere and can be removed using procedures described in SOP PT-OP-028.

4.3 Carboprep 90 Cleanup – This method may be performed to remove potential interference prior to analysis if the sample extract is colored.

NOTE: When the Carboprep Cartridge Clean-up Method is used, the recovery of the TCMX surrogate is poor.

4.3.1 Cartridge Method

4.3.1.1 Place approximately 2 ml of sample extract into a test tube and mark the sample volume on the tube.

4.3.1.2 Condition the cartridge by adding 2 ml of methylene chloride and allowing it to drip through the cartridge. Do not allow the cartridge packing to go dry in this or any subsequent step, until the final rinse has been completed.

4.3.1.3 Add 2 ml of hexane/methylene chloride (80%/20%) mixture and allow it to drip through the cartridge until almost empty.

4.3.1.4 Add the sample extract to the cartridge and place the test tube

under the cartridge to collect the liquid as it drips through.

4.3.1.5 Rinse 3 times with 2 ml aliquots of hexane/methylene chloride (80%/20%) mixture, while not allowing the cartridge to go dry. After the final rinse, use a pipette bulb to force out all of the remaining liquid in the cartridge.

4.3.1.6 Concentrate the sample extract back down to the original volume according to the mark on the test tube. The extract is now ready for analysis.

4.3.2 Quick Method

4.3.2.1 Add a half scoop of Carboprep 90 to approximately 2 ml of sample extract. Swirl for about one minute and allow the extract to settle.

4.3.2.2 Add a half scoop of Copper Granules to 1 mL of sample or a whole scoop to 2 mL of sample, cap the vial and shake vigorously for 2 minutes.

4.3.2.3 Pipette out an aliquot of extract and filter through a 0.45 µm syringe filter. The extract is now ready for analysis.

4.4 Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Carryover may also occur with a positive or negative interferent as well as a target analyte. Any samples analyzed after a sample with high concentration of target analytes, or high recovery of IS or surrogate compounds, which show the possible effects of carryover must re-analyzed.

4.5 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use.

5.2 It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns and Requirements

5.3.1 Eye protection that protects against splash, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.3.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.3.4 All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the TestAmerica Denver Radiation Safety Officer and the TestAmerica Corporate EH&S Director shall be immediately notified and a letter sent to the Colorado Department of Public Health and Environment.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	**Hazards**	**Exposure Limit** (2)	**Signs and Symptoms of Exposure**
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Methylene Chloride	Carcinogen Irritant	25 ppm (TWA) 125 ppm (STEL)	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Hydrogen Gas	Explosive	None	The main hazard is flammability. Exposure to moderate concentrations may cause dizziness, headache, nausea, and unconsciousness. Exposures to atmospheres less than 8 to 10% oxygen will bring about sudden unconsciousness, leaving individuals unable to protect themselves. Lack of sufficient oxygen may cause serious injury or death.

(1) Always add acid to water to prevent violent reactions.

(2) Exposure limit refers to the OSHA regulatory exposure limit.

6.0 EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Instrumentation

6.1.1 A gas chromatographic system with dual columns and dual ECD (^{63}Ni) detectors, and a data system capable of measuring peak area and/or height.

6.2 Supplies

6.2.1 Columns

- Primary Column: RTX-CLP1, 30 m x 0.53 mm id, 0.5 µm coating.
- Secondary Column: RTX-CLP2, 30 m x 0.53 mm id, 0.42 µm coating.
- Additional columns that can be used for confirmation include 30m x 0.53mm id MR1, MR2, RTX5, RTX50 or RTX-1701.

6.3 Autosampler vials, crimp caps with PTFE-faced septa

6.4 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution

7.0 REAGENTS AND STANDARDS

7.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

7.2 Reagents

7.2.1 Acetone, 99.4% for organic residue analysis

7.2.2 Hexane, pesticide grade.

7.2.3 Carrier Gas: ≥ 99.99999% pure hydrogen

7.2.4 Make-up Gas: ≥ 99.99980% pure nitrogen

7.3 Standards

7.3.1 Stock Standards

7.3.1.1 All standards must be refrigerated at >0.0 ºC but ≤6.0 ºC. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.3.1.2 Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced annually from the date of receipt or earlier if the vendor indicates an earlier date.

7.3.1.3 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. The standards must be replaced at least every six months, or sooner, if comparison with check standards indicates a problem.

7.3.2 PCB, Surrogate and Internal Standard Stock Calibration Standards

7.3.2.1 Stock A

For each of the Aroclors listed in Table 1, a commercially prepared stock standard solution is obtained. Each stock standard contains the specific Aroclor in isooctane at a concentration of 1,000 µg/mL. (Note: At times, specific Aroclor stock standards may also be purchased at various concentration levels, for example 2nd source stock standards are purchased at 200 ug/mL concentration.)

7.3.2.2 Surrogate Stock B

A commercially prepared stock standard solution is obtained that contains the surrogate compounds tetrachloro-m-xylene (TCMX) and decachlorobiphenyl (DCB) in acetone, each at a concentration of 200 µg/mL.

7.3.2.3 Internal Standard Stock Standard

A commercially prepared stock standard solution is obtained that contains the internal standard compound, 1-bromo-2-nitrobenzene, at a concentration of 1000 ug/mL.

7.3.3 Intermediate and Working Level Calibration Standard Solutions

7.3.3.1 Stock C (Level 7 Calibration) Standard Solutions

A Stock C standard solution is prepared for the various Aroclors or combination of Aroclors as summarized in the following table. In each case, the Stock C standard solution is also the highest concentration (i.e., Level 7) calibration standard.

Stock C	Recipe	Conc. (µg/mL)	Final Volume (mL)	Final Concentrations (µg/mL)	
AR1660	0.1 mL of Aroclor 1016 Stock A 0.1 mL of Aroclor 1260 Stock A	100	10	Aroclor 1016 Aroclor 1260	4.0 4.0
		200	10	TCMX	0.2
	0.2 mL of surrogate Stock B	200	10	DCB	0.2
AR2154	0.125 mL of Aroclor 1221 Stock A	1000	250	Aroclor 1221	0.5
	0.125 mL of Aroclor 1254 Stock A	1000	250	Aroclor 1254	0.5
AR3262	0.125 mL of Aroclor 1232 Stock A	1000	250	Aroclor 1232	0.5
	0.125 mL of Aroclor 1262 Stock A	1000	250	Aroclor 1262	0.5
AR4268	0.125 mL of Aroclor 1242 Stock A	1000	250	Aroclor 1242	0.5
	0.125 mL of Aroclor 1268 Stock A	1000	250	Aroclor 1268	0.5
AR1248	0.125 mL of Aroclor 1248 Stock A	1000	250	Aroclor 1248	0.5

7.3.4 AR1660 Calibration Levels

7.3.4.1 A total of 7 calibration standards are prepared for AR1660 as summarized in the following table. As needed, the following table can be used to prepare calibration standards for any of the Aroclors, but only the AR1660 calibration standards include the surrogates. In all cases, measured volumes of the Stock C standard are diluted using pesticide-grade hexane to the final volume indicated in the following table.

Level	Volume of Stock C Used (mL)	Final Volume (mL)	Final PCB Conc (µg/mL)	Final Surrogate Conc (µg/mL)*
1	0.01	100	0.01	0.0004
2	0.05	100	0.05	0.002
3	0.20	100	0.20	0.008
4 (CCV)	1.0	200	0.50	0.020
5	2.0	200	1.0	0.040
6	2.0	100	2.0	0.080
7	4.0	100	4.0	0.160
*Surrogates are in the AR1660 calibration solutions only. None of the other Aroclor calibration solutions contain the surrogate compounds.				

7.3.5 Working Single-Point PCB Calibration Standards

The Level 4 standard in the table above is used for single-point calibrations of the individual Aroclors. These standards are also used as pattern recognition standards.

7.4 Second-Source Standards for Initial Calibration Verification (ICV)

These standards are purchased from a vendor different from the one that supplied the stock calibration standards.

7.4.1 Second-Source Stock A Aroclor Standard Solutions

Commercially prepared solutions in pesticide-grade hexane (or isooctane) are routinely obtained for Aroclors 1016 and 1260. The Aroclor concentration in each solution is 200 µg/mL. Additionally, a second source standard is obtained for all other Aroclors.

7.4.2 Second-Source Working Level Standards

The working level second-source ICV standard is prepared by combining 0.5 mL of Aroclor 1016 Stock A' and 0.5 mL of Aroclor 1260 Stock A' diluting to a final volume of 200 mL with pesticide-grade hexane. This results in a concentration of 0.5 µg/mL for each of the Aroclors. Note: Surrogates are not added to any 2nd source working level standards.

7.5 Continuing Calibration Verification Standard (CCV), 0.5 µg/mL

The working CCV solution is the same as the Level 4 initial calibration standard, as shown in the table in Section 7.3.4.1.

7.6 Laboratory Control Standard (LCS) Spiking Solution (AR1660)

7.6.1 The LCS/MS spiking solution is prepared and used as part of the scope of the organic preparation SOP PT-OP-001. The following information is provided for reference only.

7.6.2 The working LCS spike solution is prepared in a volumetric flask by combining 1 mL of the Aroclor 1016 Stock standard (10,000 ug/ml) and 1 mL of the Aroclor 1260 Stock standard (10,000 ug/ml), and diluting to a 250 mL final volume with acetone. The final concentration of each Aroclor is 40.0 µg/mL.

7.7 Matrix Spike (MS) Spiking Solution:

The working matrix spike solution is the same as the LCS spike solution. The MS duplicate (MSD) is prepared in the same way using a third aliquot of the selected sample.

Matrix Spike and LCS Solutions		
Analyte Group	Matrix spike Solution ID	Volume added in mL
AR1660	40 ug/mL PCB Spike	1.0 - waters
		0.5 - soils
		0.025 - low-level waters
		0.025 – low-level soils
		1.0 – tissues (40 mL F.V.)
		0.5 – tissues (20 mL F.V.)

7.8 Surrogate Spike Solution

7.8.1 Stock Surrogate Spike Solution: A commercially prepared solution containing 200 µg/mL each of decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX) in acetone is purchased.

7.8.2 Working Surrogate Spike Solution: Samples are spiked with the surrogate compounds during sample preparation, which is described in the organic preparation SOP. The following information is provided for reference only.

7.8.3 The working surrogate spike solution is prepared in a volumetric flask by adding 1.6 mL of the DCB (1000 ug/mL) stock surrogate spike solution, 0.80 mL of the TCMX (2000 ug/mL) stock surrogate spike solution and diluting to a final volume of 2000 mL with acetone. The surrogate compounds are added to all field and QC samples as follows:

Surrogate Spiking Solutions		
Analyte Group	**Surrogate Spike Solution ID**	**Volume added in mL**
PCB Aroclors	0.8 ug/mL DCB/TCMX	1.0 - Waters
		1.0 - Tissues (40 mL F.V.)
		0.5 - Tissues (20 mL F.V.)
		0.5 - Solids
	0.2 ug/mL DCB/TCMX	0.1 - low-level waters
		0.1 - low-level soils

7.9 Internal standard

7.9.1 Stock - A commercially prepared stock standard solution is obtained that contains the internal standard compounds, 1-bromo-2-nitrobenzene and BZ-205, at concentrations of 1000 ug/ml and 100 ug/ml respectively.

7.9.2 A working standard for the internal standard, 1-bromo-2-nitrobenzene and BZ-205, is prepared at a concentration of 10 ug/ml. This standard is added to all samples and standards to result in a final concentration of 0.1 ug/ml (20 ul of 1 ug/ml to 200 ul; 10 ul to 100 ul; etc.) after any cleanups or dilutions that may be necessary but before injection.

7.10 Aroclor mixes

The following Aroclors can be analyzed together for calibration and calibration verification: 1016/1260, 1221/1254, 1232/1262, 1242/1268. If standards are mixed together, concentrations need to be taken into account (initial concentrations and final volumes). A calibration curve will be analyzed for 1660 and midpoint standards will be analyzed for all other Aroclors.

7.11 RT standard

It is an option to make a multi Aroclor standard for the purposes of the daily RT update.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Water samples are collected in pre-cleaned amber glass bottles fitted with a Teflon-lined caps. To achieve routine reporting limits, a full one liter of sample is required for regular level extraction and 250mL for LVI extraction*. Because the entire sample volume is used for extraction, additional bottles are needed to satisfy the requirements for matrix spike and matrix spike duplicate analyses.

8.2 Soil samples are collected in 8-ounce, wide-mouth jars with a Teflon-lined lid.

Matrix	Sample Container	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	Cool >0.0 but ≤6.0°C	1 year	1 year from extraction	40 CFR Part 136.3
Soils	Glass	Cool >0.0 but ≤6.0°C	14[1] Days	40[1] Days from extraction	N/A
Tissues	Borosilicate glass, PTFE, quartz, aluminum foil	Freeze at < - 10°C can be stored this way for 1 year prior to extraction	14 Days from date of thawing	40 Days from extraction	PSEP [2]

[1] Some states will accept a 1 year holding time from sampling to extraction and from extraction to analysis for Solid samples. Consult the Project Manager or the QA Department for specific project requirements before exceeding 14/40 days.

[2]This maximum holding time is also recommended by the PSEP (1990). The California Department of Fish and Game (1990), and the USGS National Water Quality Assessment Program (Crawford and Luoma, 1993) recommend a more conservative maximum holding time of 1 year at < -10℃ for dioxins/furans. NOAA recommends a maximum holding time of 3 months.

*NOTE: LVI cannot be used for samples from South Carolina. The 1 Liter bottles must be used for sampling.

9.0 QUALITY CONTROL

9.1 Refer to the TestAmerica Pittsburgh QC program document (PT-QA-021) for

further details on criteria and corrective actions. Refer to "project checklist" for project specific requirements. More stringent project-specific requirements will supersede the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via special instructions in the LIMS.

9.2 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP PT-QA-016. This is in addition to the corrective actions described in the following sections.

9.3 If dual column reporting is required, the choice of which column to report the QC from is made in the same manner as for the associated samples.

9.4 The following Quality Controls are required:

Quality Controls	Frequency	Acceptance Limits
Initial Calibration: Minimum 5 points for 1016/1260, One point for all other Aroclors Minimum 6 points for Congeners	Every 6 months, or more often as needed	Average RF: ≤ 20%RSD Linear Regression: Linear Correlation Coefficient ≥0.990 and intercept <1/2 RL
ICV (second source)	After each ICAL	≤ 20%D (80-120% recovery)
CCV[1]	Beginning of run and every 20 samples	8082 ≤ 15%D (85-115% recovery) 8082A ≤ 20%D (80-120% recovery)
RT Windows	With each ICAL (mid-point updated daily with CCVIS)	± 3X SD / ± 0.01 min
Internal Standard (IS)	All standards, samples, and QC	50 – 150% of the response in mid-level calibration standard
Method Blank (MB)	1 per preparation batch	<RL
Laboratory Control Sample (LCS)	1 per preparation batch	Statistical control limits are maintained in TALS.
Matrix Spike (MS)	1 per preparation batch	Statistical control limits are maintained in TALS. MS is not used for batch control.

Quality Controls	Frequency	Acceptance Limits
Matrix Spike Duplicate (MSD)	1 per preparation batch	Statistical control limits are maintained in TALS. MSD is not used for batch control.
Surrogates	All samples and QC	Statistical control limits are maintained in TALS.
Dual column agreement	All positive results	40% RPD (see section 11.4 for reporting instructions)

[1]If the analysis includes the use of internal standards, a closing CCV is not required at the end of the analytical run.

9.5 Method blank

9.5.1 A method blank (MB) is prepared and analyzed with each batch of 20 or fewer samples. The method blank consists of reagent water for aqueous sample batches, or 50:50 sodium sulfate : magnesium sulfate mixture for solid sample batches, to which the surrogate compounds are added (see SOP PT-OP-001 or PT-OP-026 for details). The method blank is subject to the entire extraction, cleanup and analysis process. The method blank must be analyzed daily prior to sample analysis to demonstrate that the chromatographic system is contaminant free.

9.5.2 The method blank must not contain any analyte of interest at or above the reporting limit (RL). For analytes detected above the MDL, all associated results will be reported with B qualifiers. If the MB is found to be contaminated above the RL, the sample batch must be re-extracted / reanalyzed unless one of the following criteria is met:

- Evaluate the associated sample results. If sample results are non-detect for the Aroclor found in the MB, results may be reported using the “Method Blank – Report, ND” NCM.
- If the associated sample concentrations are >10x the MB concentration, results for these samples may be reported using the “Method Blank – Report, 10X” NCM.
- If neither of the above situations exists, and re-extraction is not possible due to limited sample volume or holding time, the lab must notify the Project Manager. Instructions must be sought from the client on how to proceed with reporting these results. Results that are reported must be properly qualified and an NCM created to document the situation for the case narrative.

9.6 Laboratory Control Sample (LCS)

9.6.1 One LCS is prepared and analyzed with each batch of 20 or fewer samples. The LCS is prepared as described in Section 7.6, using the same clean matrix as for the MB. The LCS is subject to the entire extraction, cleanup and analysis process.

9.6.2 The LCS recovery must be within the established control limits. The laboratory's standard control limits are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. Current control limits are maintained in the LIMS. Unless otherwise requested by the client, the PCB LCS contains only Aroclors 1016 and 1260.

9.6.3 For batches that include samples from South Carolina, the LCS control limits are static at 70-130%.

9.6.4 Laboratory generated Control Limits are maintained in TALS and can be provided upon request.

9.6.5 If any analyte is outside the control limits in the LCS, the batch must be re-extracted / reanalyzed unless the following criterion is met:

- If the LCS recovery is above the upper control limit and sample results are non-detect, those associated sample results may be reported with the appropriate qualifier and using the “LCS/LCSD - %R High” NCM.
- If the above situation does not exist, and re-extraction is not possible due to limited sample volume or holding time, the lab must notify the Project Manager. Instructions must be sought from the client on how to proceed with reporting these results. Results that are reported must be properly qualified and an NCM created to document the situation for the case narrative.

9.7 Matrix Spike (MS) and Matrix Spike Duplicate Samples (MSD)

9.7.1 One MS/MSD pair is required with each analytical batch of 20 or fewer samples. Note that some programs (e.g., North Carolina and South Carolina) require preparation and analysis of an MS/MSD pair at a 10% frequency. This shall be noted in the project when required. Preparation of the MS is described in Section 7.7. The MSD is another aliquot of the sample selected for the MS that is spiked in the same manner as the MS.

9.7.2 The MS and MSD recoveries must fall within the established LCS control limits. The relative percent difference (RPD) between the MS and MSD must be less than the established limit, which is based on statistical analysis of past results, unless otherwise dictated by project requirements. Current control limits are maintained in the LIMS.

Laboratory generated Control Limits are maintained in TALS and can be provided upon request.

9.7.3 If analyte recovery or RPD falls outside the acceptance range, but the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, then there is no evidence of

analytical problems. This may indicate that the sample matrix itself has an adverse effect on recovering the analyte.

- If a matrix effect is suspected, the parent sample is qualified appropriately, and results are reported using the "MS/MSD - %R, LCS Pass" NCM.
- If the recovery for any component is outside control limits for both the MS and the LCS, the laboratory is out of control and corrective action must be taken. Refer to section 9.6.4.
- If an MS/MSD is not possible due to limited sample, then an LCS duplicate (LCSD) may be analyzed to monitor batch precision.

9.7.4 The MS/MSD must be analyzed at the same dilution level as the parent sample, unless the matrix spike components would then be above the calibration range. In this case, would require a dilution greater than the parent sample to bring the spiked compounds within the calibration range.

9.7.4.1 For PCB analysis, the matrix spike added is diluted to concentrations below the RL at a dilution of 40X. MS/MSD that are diluted above 40X must be reported with a "D" qualifier on the spiked compounds to indicate that recovery is not able to be accurately calculated.

9.7.4.2 If the parent sample concentration is >4X, it may not be possible to accurately calculate %recoveries. Results will be reported with the "MS/MSD – High Targets" NCM.

9.8 Surrogates

9.8.1 Each field sample, QC sample, and calibration standard, is spiked with surrogate compounds decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). The surrogate spike solution is prepared as described in Section 7.8.

9.8.2 For field samples and batch QC, the surrogate recoveries must be within the established control limits, which are set at ± 3 standard deviations around the historical mean, unless project requirements dictate otherwise. Surrogate recovery limits are maintained in TALS.

9.8.2.1 Surrogate recoveries for both DCB and TCMX in the MB and LCS <u>both must pass</u> on at least one column. If the recovery of the surrogates in MB or LCS's is outside of the control limits, check for calculation or instrument problems.

- Surrogate recoveries (one or both) outside of control limits on both columns for the MB or LCS require re-preparation and reanalysis of the entire preparation batch.

9.8.2.2 For field samples, surrogate recovery is calculated and reported for

both DCB and TCMX. At least one surrogate must pass on the one column from which Aroclors are identified and reported, and that column must have a passing CCV.

9.8.2.3 For CCV standards, Aroclors 1016 and1260 and surrogates must pass on the reporting column, for the data to be considered reportable.

9.8.2.4 If both surrogates fail on both columns for a sample, and matrix interference is not obvious from the initial analysis, it is only necessary to re-prepare and reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effects, as long as the extraction/instrument system is proven to be working properly according to the batch and instrument QC.

9.8.2.5 For PCB analysis, the surrogate spike added is diluted to concentrations below the RL at a dilution of 40X. Samples that are diluted above 40X must be reported with a "D" qualifier on the surrogates to indicate that recovery is not able to be accurately calculated.

9.9 Initial Calibration

9.9.1 See section 10.3 below for initial calibration options and evaluation requirements.

9.9.2 A full calibration (minimum 5 points) is required on both columns for Aroclor 1016 and 1260 and the two surrogates plus internal standards. A single point is used for all other Aroclors.

9.9.3 Each peak in the Aroclor (a minimum of 5 peaks is required for all Aroclors, except 1221, which requires a minimum of 3 peaks) is intergrated using peak height.

9.9.4 The calibration must be verified by the analysis of a second source standard (ICV) near the mid-point of the calibration range. The %Drift/Difference for this standard must be $\leq$ 20% from the ICAL. The response for each individual peak for the aroclors in the ICV standard must be within ± 20.0% of the expected value.

If the ICV response does not meet this limit, repeat the ICV analysis once with a freshly made standard. If failure repeats, the initial calibration and ICV standards must be prepared fresh and calibration repeated.

9.10 Continuing Calibration Verification (CCVIS)

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration and ICV.

9.10.1 A mid-level calibration standard of 1016/1260 is analyzed as the continuing calibration verification (CCVIS) standard at the beginning of the analytical sequence, and after every 20 samples (all injections except solvent blanks count as samples), or every 12 hours, whichever is more frequent. Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns. If 12 hours elapsed since the last CCV was analyzed, a new sequence is started with a fresh CCV.

9.10.2 A mid-range CCV standard of each Aroclor must be analyzed at least every 24 hours, for retention time updating.

9.10.3 If Aroclors other than 1016 or 1260 are detected in any sample, a CCV of the associated Aroclor(s) must be analyzed within 12 hours of the sample and pass criteria in order for the sample data to be reported. If a CCV is not run within 12 hours of the sample, or if the CCV does not meet the method CCV criteria, the sample must be re-analyzed along with a passing CCV for that compound. CCV's of other Aroclors may be run every 20 samples/12 hours along with the 1016/1260 CCVs in a routine analysis sequence to meet this requirement. If the analysis includes the use of internal standards, a closing CCV is not required at the end of the analytical run.

9.10.4 Acceptance criteria for CCVs is < 15%D for method 8082 and <20%D for 8082A. All Aroclors (each individual peak) and surrogates must meet these recovery limits on both columns, unless only reporting from one column. If a CCV does not meet the acceptance criteria explained above, associated samples must be re-analyzed unless one of the following conditions is met:

- If the CCV %D fails high, >15.0% for 8082 or >20.0% for 8082A, and the sample results are ND for that compound, the data may be reported with the appropriate qualifier and the "CCV - %D, High, Samples ND" NCM.
- If the CCV % D fails low, and samples results are ND, then a low level standard can be analyzed to prove that the instrument is sensitive enough to call the sample "Not Detected" and the sample can be reported. This low level standard must be analyzed prior to the samples. Results may be reported with proper qualification and using the "CCV – Low Biased, ND, RL Check Passes" NCM.
- If the CCV fails on the non-reporting, or confirmation, column, and that failure does not exceed 40%D, results may be reported without qualification.
- If a continuing batch CCV fails, and there is evidence that the sample matrix has affected the column performance, samples must be rerun once to confirm this affect. Results may be reported from the first or second analysis, with proper qualification and using the "CCV - %D, Capping, RR Confirms" NCM.

9.11 Retention Time (RT) Windows

9.11.1 Absolute retention times are used for the identification of PCBs as Aroclors. However, in addition to retention times, peak patterns play a large role in the identification of Aroclors.

9.11.2 The center of the retention time (RT) window shall be updated based on the middle level in the initial calibration or the first CCV (CCVIS) in the daily analytical sequence, whichever is more recent,.

9.11.3 Before establishing windows, make sure the GC system is within optimum operating conditions. Evaluate the deviation from expected RT for each analyte in at least three CCV and/or LCS samples spread over at least 72 hours.

- If three days of analytical data are not available, use a default RT window of 0.010 minutes. At the end of the batch, evaluate all CCVs and LCS in the batch. If necessary, widen the window such that all analytes fall within the RT window. Reprocess the batch using the new RT windows.
- Multiply the maximum deviation from the set by 1.5. This is the retention time window, unless the result is less than 0.010 minute, in which case the window is set at 0.010 minute.
- Determine the retention time (RT) windows for the 3-5 major peaks selected for each Aroclor. The AR1016 windows will be used to establish retention time windows for PCBs AR1221, AR1016, AR1232, AR1242, and AR1248. The AR1260 windows will be used to establish retention time windows for PCBs AR1254, AR1260, AR1262, and AR1268.
- Retention time windows for analytes of interest must not overlap.

9.11.4 Evaluate the retention time windows on an ongoing basis. The center of the RT window is updated on the first CCV (CCVIS) of the day. All analytes for all subsequent CCVs, LCS and matrix spikes must fall within the RT window, except as discussed below.

- Matrix spike analytes may fall outside the RT window if there is a large, non-target peak co-eluting, or overlapping, with the analyte in the matrix.

9.11.5 If any analyte falls outside the RT window in CCV, LCS or matrix spike (except as discussed above for matrix spikes), then the RT window for that analyte shall be widened to the minimum degree required for the analyte to fall within the RT window. All samples in the batch shall be reprocessed with the new RT window, and the wider RT window shall remain in place for subsequent batches.

9.11.6 Retention time windows should be reliably narrower than +/- 0.03 minute. If RT windows wider than this are necessary, the instrument should be

evaluated and maintenance performed as needed. Subsequent to maintenance, RT windows shall be narrowed to the extent that is consistent with the data obtained and the foregoing requirements.

9.11.7 The laboratory must calculate retention time windows for each analyte on each GC column and whenever a new type of GC column is installed. The data must be retained by the laboratory and available for review.

9.12 Control Limits: In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be reviewed at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy PT-QA-021 for more details.

9.12.1 Surrogate and matrix spike recoveries will be reported unless the dilution is more than 40X.

9.13 Percent Moisture

9.13.1 Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined on a separate portion of the sample if results will be reported based on dry weight.

9.14 Internal Standard Criteria

9.14.1 If the internal standard response in the continuing calibration is more than 150% or less than 50% of the response in the mid-level calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Reanalysis of samples analyzed while the system was malfunctioning is required.

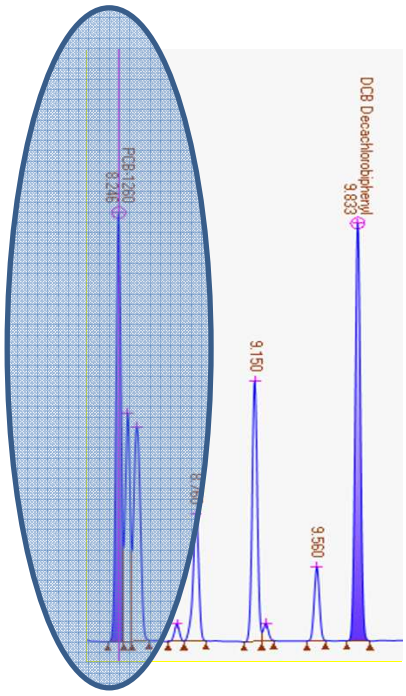
9.14.2 Any samples or standards that do not meet the internal standard criteria of > 50% and <150% of the response of the mid-level calibration standard must be evaluated for validity. Samples that are reported with internal standard exceedances must have documentation supporting matrix effect. Where the matrix effect is well established it may be reported with narration, otherwise the samples must be reanalyzed to confirm matrix effect is required. If the internal standard exceedance is deemed to be due to an instrumental problem, instrument maintenance will be done and all affected samples must be reanalyzed after the problem is corrected.

9.15 Resolution Check requirement

9.15.1 The circled triplet of peaks in the figure below is observed towards the end of the 1260 pattern on columns such as CLP 1. Minimum resolution (degree of overlap) requirement between peak 1 / 2 and peak 2 / 3 is <75%. This chromatogram shows overlap of about 50% between peak 2 and 3, and 30% between peak 1 and 2.

9.15.2 Resolution (degree of overlap) is calculated as follows:

[Height of the valley / (Sum of the two peak heights / 2)] x 100%



9.16 Procedural Variations

9.16.1 Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 Samples are extracted and prepared for analysis as described in SOPs PT-OP-001 and PT-OP-026. Allow extracts to warm to room temperature before injecting.

10.1.2 If needed, extracts are cleaned up using the procedure in section 4.3 of this SOP or one of the clean-up procedures in SOP PT-OP-028. Any clean-up

performed is documented either within the method chain or using an NCM.

10.1.3 Internal standard is added to each extract prior to loading the extract on the instrument for analysis. Add 1µL of Internal Standard Spike (7.9) per 100µL of extract or standard.

10.2 Calibration

Instrument conditions for this method are presented in Table 2.

10.2.1 Use the ChemStation interface to establish instrument operating conditions for the GC.

10.2.2 Raw data obtained by the ChemStation software is transferred to the CHROM DB(database) for further processing. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the CHROM DB software.

10.2.3 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.2.4 Unprocessed calibration data are transferred to the CHROM DB database for processing. After processing the calibration data, print the calibration report and review it using the calibration review checklist (GC and HPLC Data Review Checklist - ICAL). Submit the calibration report to a qualified peer or the group leader for final review. The completed calibration reports are scanned and stored as Adobe Acrobat files on the Public Drive.

10.2.5 A new calibration curve must be generated initially, after major changes to the system, or when continuing calibration criteria cannot be met. Major changes include installation of new type of column and replacing the ECD detector. Initial Calibration will be performed at least every 6 months.

10.3 Initial Calibration (ICAL)

10.3.1 An initial standard calibration using seven concentration levels of the AR1660 mixture is routinely performed. (At least five calibration levels are required.) Table 3 provides concentration levels for Aroclor 1016, Aroclor 1260, and the surrogate compounds DCB and TCMX.

10.3.2 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.3.3 The calibration curves for Aroclors 1016 and 1260 and the surrogate compounds, relative to the internal standard response, are modeled either as average response factors (RF) or as calibration curves using a systematic approach to selecting the optimum calibration function. PCB's are well established linear responding compounds and an average curve fit should be the norm. Use of linear regression is acceptable, however the individual points should be evaluated to determine if there has been a change in the instrument sensitivity or if there is a potential issue with the standards.

10.3.4 The calibration for each of the other Aroclors (see Tables 1 & 3) is initially determined using a single, mid-level calibration standard. As needed, the laboratory may generate a multi-point calibration for other commonly detected Aroclors, such as 1221, 1254, and 1248. When additional multi-point calibrations are developed for the other Aroclors, a second-source ICV standard is also analyzed, see section 9.9.

NOTE: Samples from sites known to be contaminated with specific Aroclors should be analyzed using a multi-point calibration curve for the identified Aroclors. This information is provided to the analyst through special instructions in the LIMS.

NOTE: Generally, it is NOT acceptable to remove points from a calibration for the purposes of meeting calibration criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or the linear range is adjusted accordingly. A minimum of five levels must remain in the calibration for a linear regression. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration.

10.3.5 The high and low standard for the initial calibration of the AR1660 mixture defines the acceptable quantitation range for all of the Aroclors. If a sample extract contains any Aroclor at a concentration that exceeds the upper range of the calibration, then the extract must be diluted and reanalyzed.

10.3.6 Select 5 major peaks (at least 25% peak height of the largest peak in the aroclor) in the analyte pattern (only 3 peaks are usable for Aroclor 1221). The response factors or curves will be generated for each of these major peaks for each Aroclor. The results are based off of an average of the calculated concentrations of these major peaks.

NOTE: A minimum of five accurate peaks must be used to quantify an Aroclor (three peaks for Aroclor 1221).

10.4 Internal Standard Calibration

10.4.1 Internal standard calibration involves the comparison of instrument responses from the samples to the responses from the target compounds in the calibration standards. The area (or height) of a peak and the area (or height) of the internal standard in a sample chromatogram is compared to the area (or height) of the peak and the area (or height) of the internal standard in the standard chromatograms that appears at the same retention time. The ratio of the detector response to the concentration of the target analyte in the calibration standard is defined as the response factor (RF) and is calculated as follows:

$$RF = \frac{Ax \times Cis}{Ais \times Cx}$$

Where:

A_x = Area (or height) of the peak to be measured

A_{is} = Area (or height) of the peak for the internal standard

C_{is} = Concentration of the internal standard

C_x = Concentration of the peak being measured

NOTE: It is also possible to use the concentration of the standard rather than the mass injected.

10.5 Establishing the Calibration Function

10.5.1 Calibrations are modeled either as average response factors (RF) or as linear regression curves, using a systematic approach to select the optimum calibration function. Start with the simplest model, i.e., average RF, and progress through the other options until calibration acceptance criteria are met. PCB's are well established linear responding compounds and an average curve fit should be the norm. If linear regression is utilized, it is acceptable, however the individual points should be evaluated to determine if there has been a change in the instrument sensitivity or if there is a potential issue with the standards. Different calibration models can be applied to each of the major peaks chosen to represent the Aroclor.

NOTE: Each individual peak used for each Aroclor must meet the calibration acceptance criteria.

10.5.2 Linear Calibration Using Average Response Factor (RF)

The response factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected.

When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

The average response factor is calculated as follows:

$$\text{Average RF} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where:

RF_i = The response factor for the i^{th} calibration level.

n = The number of calibration levels.

The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{RF}} \times 100\%$$

Where SD is the standard deviation of the average RF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}}$$

10.5.3 Evaluation of the Average Response Factor:

Plot the calibration curve using the average RF as the slope of a line that passes through the origin. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

- The RSD for each peak chosen to represent the aroclor must be ≤ 20.0% for both 8082 and 8082A.
- If the %RSD is <20.0% (8082/8082A), alternative curve fits may still be considered.
- If the RSD exceeds the limit, linearity through the origin cannot be assumed, and alternative curve fits must be considered.

10.5.4 Linear Calibration Using Least-Squares Regression (weighted) - Evaluation of the Linear Least-Squares Regression Calibration Function

With an unweighted linear regression, points at the lower end of the

calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum "Clarification Regarding Use of SW-846 Methods", Attachment 2, Page 9, includes the statement "The Agency further recommends the use of this for weighted regression over the use of an unweighted regression."

- To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than reporting limit (RL), and preferably less than the MDL.
- Also examine the residuals, but with particular attention to the residuals at the bottom of the curve. If the intercept or the residuals are large, the calibration should be repeated since a higher order regression is not allowed for this method.
- If weighted linear regression is used 1/(Amt) or 1/(Amt)2 a minimum of 5 points are required. The coefficient of determination (r2) must be > 0.990. If the correlation of determination falls below the acceptance limit, linear regression cannot be used and a second-order regression should be attempted.
- If the correlation coefficient falls below the acceptance limit, the linear regression is unacceptable and the calibration should be repeated since a higher order regression is not allowed for this method.
    - For non-detects, reanalysis is not required, and flagging is not required.

10.5.5 Other curve types

Due to the stability of the compounds, non-linear calibration curves (quadratic) and unweighted linear regression curves are not applicable for this method.

10.5.6 Calibration point read-back criteria

Whichever calibration mode above is selected, it should be subjected to an additional check to establish the representativeness of the data that were used to produce it. This check is the refitting of each calibration point response back to the calibration model, or the comparison of the calculated amount of the standard against the expected amount.

- CHROM software provides an Initial Calibration %Drift report which shows the % Error for each calibration point. This report must be reviewed in addition to the %RSD / Linear Response Factor.
- The absolute value of the % Error for each calibration point should be $\leq$ 30%. For the lowest calibration point, the % Error may be $\leq$ 50%.

10.5.7 Removal of calibration points and/or levels

10.5.7.1 Certain analytes that have particularly high or low sensitivity may need to have the high or low calibration points removed in order to optimize the calibration curve. Removal of high or low calibration points is allowed, but the working range of the calibration must be adjusted accordingly. The reporting limit must be supported by the lowest point remaining in the calibration and any samples with concentrations above the highest point in the calibration must be diluted and reanalyzed.

10.5.7.2 Points for individual compounds from the interior levels of the calibration may not be removed. A complete level may be removed if the laboratory can document a clear reason for incorrect response in the standard (for example, analysis of the incorrect level, failure to add internal standards or instrument malfunction).

10.6 Second-Source Initial Calibration Verification (ICV)

10.6.1 Second-source ICV standards are analyzed for all Aroclors. The stock standards are obtained from a source different than that of the standards used for the calibration. The ICV standards are analyzed immediately following the initial calibration. Refer to section 9.9.4 for acceptance criteria.

10.7 Sample Analysis

10.7.1 An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract.

10.7.2 Samples, standards, and QC samples must be introduced using the same procedure.

10.7.3 All extracts and standards are allowed to warm to room temperature before injection.

10.7.4 Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

10.8 Analytical Sequence

10.8.1 An analytical sequence starts with a minimum five-level initial calibration (ICAL) or a daily calibration verification. The daily run sequence is generated electronically using the ChemStation software.

The following is the typical analytical sequence for routine sample analysis:

Suggested Analytical Sequence		
Initial Calibration	(not required daily)	
Injection No.		
1	Solvent Blank (optional)	
2	Aroclor 2154	Level 4
3	Aroclor 3262	Level 4
4	Aroclor 4268	Level 4
5	Aroclor 1248	Level 4
6	Aroclor 1016/1260	Level 1
7	Aroclor 1016/1260	Level 2
8	Aroclor 1016/1260	Level 3
9	Aroclor 1016/1260	Level 4
10	Aroclor 1016/1260	Level 5
11	Aroclor 1016/1260	Level 6
12	Aroclor 1016/1260	Level 7
13-17	ICV's (2^{nd} source standard of all Aroclors)	
18	Method Blank	
19-38	Sample 1-20 (or 12 hours)	
39	Aroclor 1016/1260	Level 4
At least every 24 hours, counting from the start of the initial calibration or from the start of the last daily calibration, the retention time windows must be updated. CCVs for 1016/1260 must be run every 20 samples or 12 hours, whichever is more frequent. Mid-level standards of any other Aroclors expected to be present in the samples are also injected. For sequences without an initial calibration, start with CCVIS 1660 and CCVs for 1248 and 2154, method blank plus 19 samples, then CCVIS 1660 and CCVs for 3262 and 4268, method blank plus 19 samples. This way all standards are run within 24 hours for RT's and samples with detections other than 1660 have CCVs within 12 hours.		

10.9 When a sample result exceeds the upper calibration range, then that sample extract is diluted to obtain a result in the upper half of the calibration range and reanalyzed. Any samples that were analyzed immediately following the high sample are evaluated for carryover. If the samples had target analyte detections at or above the RL, the samples must be reanalyzed to rule out carryover.

10.10 Upon completion of the analytical sequence, transfer the raw chromatography data to the CHROM DB database for further processing. Review chromatograms online and determine whether manual data manipulations are necessary. All manual integrations must be justified and documented. See CA-Q-S-002 for requirements for manual integration.

10.11 Manual integrations may be processed using an automated macro, which prints the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature. Alternatively, the manual integration may be processed manually. In the latter case, print both the both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration.

10.12 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD. Perform a level 1 data review and document the review on the data review checklist (GC Data Review Checklist). Submit the data package and review checklist to a peer analyst for the level 2 review. The data review process is explained in SOP PT-QA-018.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Qualitative Identification of Aroclors

Retention time windows are used for identification of Aroclors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram. If there are any anomalies in the pattern due to the presence of multiple PCBs or weathering of peaks the analyst should discuss this with another analyst or technical director to come to a consensus about which PCB(s) should be identified. An NCM should be completed indicating the rationale behind the decision made. Sometimes Aroclors 1262 and 1268 are not requested as target analytes. If these patterns are observed, an NCM should be completed informing the project manager of possible PCB detection.

11.2 Quantitation of Aroclors

Quantitation of Aroclors is accomplished using 5 major peaks. The peaks must be within the established retention time windows. If there is an interference that affects the accuracy of results, the analyst must use 5 major peaks (3 peaks for Aroclor 1221). The same peaks that are used for sample quantitation must be used for standards and QC quantitation. The concentrations of each of the major peak are averaged for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be co-eluting with contaminant peaks from the quantitation (i.e. peaks that are significantly larger than would be expected from the rest of the pattern or peaks that have been significantly

weathered and are smaller than would be expected). This should be done if there are peaks that differ from the others by a factor of 2 to 5 depending on where the results fall within the calibration curve.

11.3 Second column confirmation of Aroclors is always performed and is reported when requested by the client.

11.4 Dual Column Quantitation

11.4.1 Dual column quantitation is routinely performed for PCB analysis and reported as such when requested by the client.

11.4.2 When reporting the analytical results for field samples of dual column analysis, the higher of the two results is normally reported. The result from the second column confirmation is reported if any of the following is true:

- There is obvious chromatographic interference on the initial quantitation column.
- The difference between the result on the initial quantitation column and the result on the second column is > 40% and chromatographic interference is evident.
- A continuing or bracketing standard fails on the initial quantitation column, but is acceptable on the second column. However, if the difference between the initial quantitation column and second column results is > 40% and the initial quantitation column calibration verification fails, then the sample must be evaluated for reanalysis.

11.4.3 Dual Column Results with > 40% RPD:

- If the relative percent difference (RPD) between the responses on the two columns is greater than 40%, the lower of the two results is reported unless there is obvious interference documented on the chromatogram. If the result is < the RL it will be reported as estimated with a “J” flag.
- If there is visible positive interference, e.g., co-eluting peaks, elevated baseline, etc., for one column and not the other, then report the results from the column without the interference with the appropriate data qualifier flag, footnote, and/or narrative comment in the final report.
- If there is visible positive interference for both columns, then report the lower of the two results with the appropriate flag, footnote, and/or narrative comment in the final report.
- If the relative percent difference (RPD) between the results on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. The RPD is calculated as follows:

$$\%RPD = \frac{|R_1 - R_2|}{1/2(R_1 + R_2)} \times 100\%$$

Where:

R_1 = initial quantitation column result

R_2 = second column result

11.5 Calibration Range and Sample Dilutions

11.5.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for any analyte, they must be reanalyzed to rule out carryover. It may also be necessary to dilute samples because of matrix interferences.

11.5.2 If the initial diluted run has no hits or hits below 20% of the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample should be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.5.3 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

11.5.4 Reporting Dilutions

Some programs (e.g., South Carolina) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported. If results are reported from a diluted run, the cause for the dilution should be narrated in an NCM. For dilutions greater than 40X report the surrogates diluted out (“D”).

11.6 Interferences in Observed in Samples

11.6.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

11.6.2 Suspected Negative Interferences: If peak detection is prevented by interferences, further cleanup should be attempted. Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

11.7 Concentration of Analyte in Sample Extract

11.7.1 Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10 for details on establishing the calibration function):

Average Response Factor: $C_{ex} = \frac{R_x C_{is}}{R_{is} RF}$

Linear Regression: $C_{ex} = A + B\frac{(R_x C_{is})}{R_{is}}$

Where:

Cex = Concentration in the extract, µg/mL

Rx = Response for the analyte

Ris = Response for the internal standard

Cis = Concentration of the internal standard

A = Intercept of linear calibration line

RF = Average response factor

B=Slope of linear calibration line Conc. of Analyte in Original Sample

11.7.2 The concentration of the analyte in the original sample is calculated as follows:

$$C_{sample} = \frac{C_e}{1000\frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF$$

Where:

C_{sample} = Concentration of analyte in original sample (µg/L or µg/kg).

C_e = Concentration of analyte in sample extract injected in GC (ng/mL).

$1000\frac{ng}{\mu g}$ = Factor to convert ng/mL to µg/mL.

V_e = Volume of sample extract (mL).
V_s = Volume (or weight) of original sample (L or kg).
DF = Dilution Factor (post extraction dilutions)

11.7.3 Spike Recovery Calculation

$$\%\text{Recovery} = \frac{\text{Measured Concentration}}{\text{Spiked Concentration}} \times 100\%$$

11.7.4 MS/MSD RPD Calculation

$$RPD = \frac{|MS - MSD|}{1/2(MS + MSD)} \times 100\%$$

12.0 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual and SOP PT-QA-007, must be performed initially, annually and any time a significant change is made to the analytical system.

12.4 Lower Limit of Quantitation Verification – The lowest calibration standard analyzed establishes the LLOQ or Reporting Limit. The capability to reliably detect this concentration through the preparation, clean-up and analytical procedure is verified through the annual analysis of a standard at the LLOQ/RL. The LLOQ verification shall also be performed whenever significant changes are made to the preparation and/or analytical procedure.

12.4.1 The LLOQ verification standard shall be prepared at a concentration 0.5-2 times the LLOQ/RL, and be taken through all preparation and clean-up methods which samples would be.

12.4.2 The LLOQ verification standard for aqueous matrix shall be prepared using laboratory deionized water and for the solid matrix using clean Ottawa

sand. Other clean matrices may be used in addition, for project specific requirements.

12.4.3 The LLOQ shall be verified annually on each instrument used for client sample analysis.

12.4.4 Recovery of each analyte must meet the laboratory established LCS recovery limits ± 20%. (For example, if the LCS recovery limits are 70-130%, the LLOQ verification must meet recovery limits of 50-150%.) Once sufficient points have been generated, LLOQ based statistical limits may be used in place of limits based on LCS recovery.

NOTE: The lower recovery limit for the LLOQ can be no lower than 10%.

12.4.5 If the LLOQ cannot be verified, it will be necessary to raise the RL to a concentration level that can be carried through the preparation and clean-up steps to meet recovery limits.

13.0 POLLUTION CONTROL

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

14.0 WASTE MANAGEMENT

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.2 Methylene Chloride in vials. This waste is placed in waste container identified as "Vials & Extracts", Waste #7.

14.3 Flammable solvents in vials. This waste is placed in waste container identified as "Vials & Extracts", Waste #7.

14.4 Waste flammable solvents. This waste is collected in a waste container identified as "Mixed Flammable Solvent Waste", Waste #3.

14.5 Expired primary and working PCB standards. This waste is placed in a waste container identified as "PCB Standard Waste", Waste #8.

14.6 Samples containing polychlorinated biphenyls (PCB's) at concentrations ≥50 ppm are regulated under the Toxic Substance Control Act (TSCA) and must be segregated from all other waste streams. Analysts are responsible for contacting the Group Leader, Sample Control, and the Health and Safety Coordinator immediately if a sample falls into the TSCA category.

15.0 REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Method 8082, Polychlorinated Biphenyls (PCBs) by Gas Chromatograph, Revision 0, December, 1996

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Method 8082A, Polychlorinated Biphenyls (PCBs) by Gas Chromatograph, Revision 1, February, 2007

15.3 SW 846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Update V, Method 8000D, Determinative Chromatographic Separations, Revision 4, October 2012.

15.4 SOP PT-OP-001, Extraction of Organic Compounds from Waters, SW-846 3500 Series and EPA 600 Series Methods

15.5 SOP PT-OP-026, Extraction of Organic Compounds from Solids, Sediments, Tissues, and Wipes, SW-846 3500 Series Methods

15.6 SOP PT-OP-028, Clean-up of Organic Extracts by SW-846 3600 Series Methods

15.7 SOP PT-QA-001, Employee Orientation and Training

15.8 SOP PT-QA-007, Detection Limits

15.9 SOP PT-QA-016, Nonconformance & Corrective Action System

15.10 SOP PT-QA-018, Technical Data Review Requirements

15.11 SOP PT-QA-021, Quality Control Program

15.12 SOP PT-QA-031, Internal Chain of Custody

15.13 PT-QA-M-001, Pittsburgh Laboratory Quality Assurance Manual

15.14 Corporate SOP CA-Q-S-002, Manual Integration

15.15 Corporate Quality Memorandum No. CA-Q-QM-003, Technical Guidance on Reporting of Multicomponent Organochlorine Analytes, September 24, 2009

15.16 Corporate Policy No. CA-T-P-003, Revision 2, Reporting Results for Methods that Require 2nd Column Confirmation, January 2, 2013

15.17 SOP PT-HS-001, Pittsburgh Facility Addendum EH&S Manual, to the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

16.0 METHOD MODIFICATIONS

16.1 None

17.0 ATTACHMENTS

17.1 Table 1 - Analyte List and Standard Reporting Limits
17.2 Table 2 - Typical Instrument Conditions
17.3 Table 3 - Calibration Levels (µg/mL)
17.4 Table 4 - LCS/Matrix Spike and Surrogate Spike Levels (µg/L)
17.5 Table 5 - Preparation of Calibration Standards
17.6 Appendix A – Analysis of PCB Congeners

18.0 REVISION HISTORY

18.1 Revision 1, 7/27/2009
18.2 Revision 2, 8/5/2011
18.3 Revision 3, 7/24/2011
18.4 Revision 4, 10/16/2012
18.5 Revision 5, 4/25/2014
18.6 Revision 6, 9/28/2015
18.7 Revision 7, 7/19/2016
18.8 Revision 8, 12/12/2016
18.9 Revision 9, 3/10/2017
18.10 Changes to current revision

SOP section	Change from	Change to	Reason
2.1	Removed prep details	Referenced OP SOPs	Clarification
4.4		Expanded carryover interference to include IS and surrogates	Correction for PADEP audit finding
7.9.1	Dibutylchlorendate at 200 ug/mL	BZ205 at 100 ug/mL	Correction
7.9.2	Dibutylchlorendate at 1 ug/mL	BZ205 at 10 ug/mL	Correction
9.4 Table, 9.14.1 and 9.14.2		Added “for 8082A and 50-150% of the response in the mid-level ICAL standard for 8082.”	Correction for PADEP audit finding
9.5.1	Sodium sulfate	50:50 sodium sulfate:magnesium sulfate mixure	Correction
9.9.4	“The result for the average value of peaks chosen… must be within ±20%”	“The response for each individual peak …must be within ±20%”	Correction for PADEP audit finding
9.10.4	“All Aroclors and surrogates…” Bullet 4 deleted	. “All Aroclor peaks and surrogates…”	Correction for PADEP audit finding
10.2	Chromatographic	Instrument	Correction
10.5.1		Added note that each individual peak must meet calibration criteria	Correction for PADEP audit finding

10.5.7.3	Deleted – redundant to 10.5.1		Redundant text
11.8	Deleted – redundant to 10.12		Redundant text
12.3, 15.8		Added reference to SOP PT-QA-007	Clarification

Table 1				
Standard Analyte List and Reporting Limits				
Compound	**CAS #**	**Reporting Limit, µg/L, µg/wipe or µg/kg**		
		Water/Wipe Regular/ Low Level	**Soil/ Tissue Regular/Low Level**	**Waste**
Aroclor 1016	12674-11-2	0.4/0.01	16.67/0.833	500
Aroclor 1221	11104-28-2	0.4/0.01	16.67/0.833	500
Aroclor 1232	11141-16-5	0.4/0.01	16.67/0.833	500
Aroclor 1242	53469-21-9	0.4/0.01	16.67/0.833	500
Aroclor 1248	12672-29-6	0.4/0.01	16.67/0.833	500
Aroclor 1254	11097-69-1	0.4/0.01	16.67/0.833	500
Aroclor 1260	11096-82-5	0.4/0.01	16.67/0.833	500
Optional Compounds:				
Aroclor 1262	37324-23-5	0.4/0.01	16.67/0.833	500
Aroclor 1268	11100-14-4	0.4/0.01	16.67/0.833	500

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	**Final Vol.**	**Low Level Vol.**
Groundwater	1000 mL	40 mL	1 mL
Wipe	1 wipe	40 mL	NA
Low-Level Soil	30 g / 15 g	40 mL / 20 mL	1 mL
High-Level Soil/Waste	1 g	40 mL	NA
Tissue	6 g	2 mL (1 mL with GPC clean-up)	NA

Table 2	
Typical Instrument Conditions	
Parameter	Recommended Conditions
Injection Port Temperature:	220 °C
Detector Temperature:	325 °C
Temperature Program:	120 °C for 0.75 minute 18 °C/min to 260 °C 1 minute hold 20 °C/min to 300 °C, 1.5 minute hold
Column 1:	RTX-CLP1, 30 m x 0.53 mm id, 0.5 µm
Column 2:	RTX-CLP2, 30 m x 0.53 mm id, 0.42 µm
Injection:	1 or 2 µL
Carrier Gas:	Hydrogen or Helium
Make-up Gas:	Nitrogen

Table 3							
Calibration Levels ng/mL							
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7[1]
AR1660	10	50	200	500	1000	2000	4000
AR1242[2]				500			
AR2154[2]				500			
AR1232[2]				500			
AR1248[2]				500			
Surrogates are included with all the calibration mixes at the following levels:							
TCMX	0.5	2.5	10	25	50	100	200
DCB	0.5	2.5	10	25	50	100	200

[1] Level 7 is optional and should only be used if linearity can be maintained on the instrument to this level.

[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000 ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table 4			
LCS/Matrix Spike and Surrogate Spike Levels for Aroclor Analysis µg/L, µg/wipe or µg/kg			
	Aqueous/Wipe	Soil/Tissue	Waste
Aroclor 1016/1260	10	333	10,000
TCMX (surrogate)	0.20	6.67	200
DCB (surrogate)	0.20	6.67	200

Table 5					
Preparation of Calibration Standards					
Calibration Level	1016/1260 Intermediate (µL)	1221 + 1254 Stock (µL)	1232 Stock (µL)	1242 Stock (µL)	1248 Stock (µL)
Level 1	4				
Level 2	20				
Level 3	80				
Level 4	1000	250	250	250	250
Level 5	400				
Level 6	800				
Level 7	1600				

The surrogate stock is purchased (Decachlorobiphenyl and Tetrachloro-m-xylene) at 200 ug/mL.

The Aroclor 1016 and 1260 stock standards are purchased as certified standards in isooctane at 1000 ug/mL. The other five Aroclor stock standards are purchased at 200 ug/mL.

For Aroclors 1016 and 1260, an intermediate standard is prepared by diluting 1.0 mL of each of the stock standards and 0.25 mL of the surrogate stock standard to 10.0 mL in hexane. The intermediate Aroclor 1016/1260 standard concentrations are 100 ug/mL for each Aroclor and 5 ug/mL for each surrogate.

The Aroclor 1016/1260 calibration standards are prepared by diluting the volumes noted in Table C-6 to a 40.0 mL final volume in hexane except for the Level 3 standard, which is taken to a 200mL final volume in hexane.

The mid-level (Level 3) calibration standards for each of the other five Aroclors (1221, 1232, 1242, 1248, 1254) are prepared by diluting 0.25 mL of the appropriate stock standard to a final volume of 100 mL in hexane. Aroclors 1221 and 1254 are combined into one standard and Aroclors 1232, 1242, and 1248 are prepared individually.

Appendix A

Analysis of PCB Congeners Based on Method 8082A

1.0 SCOPE OF METHOD

1.1 This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) congeners by GC/ECD. This Appendix is to be applied when SW-846 Method 8082A is requested, and is applicable to extracts derived from any matrix, which are prepared according to the appropriate TestAmerica sample extraction SOP (PT-OP-001 or PT-OP-026). The PCBs are determined and quantitated as individual PCB congeners.

1.2 Table A-1 lists the congeners, which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2.0 SUMMARY OF METHOD

2.1 This method presents conditions for the analysis of prepared extracts for PCB congeners. The PCBs are injected onto the GC column(s) and separated and detected by electron capture detection. Quantitation is by the external standard method.

3.0 DEFINITIONS

3.1 Refer to Section 3 of the main body of this SOP for definitions.

4.0 INTERFERENCES

4.1 Refer to Section 4 of the main body of this SOP for information regarding chromatographic interferences.

5.0 SAFETY

5.1 Refer to Section 5 of the main body of this SOP for general safety requirements.

5.2 PCB congeners have been classified as a potential carcinogen under OSHA. Concentrated solutions of PCB congeners must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

6.0 EQUIPMENT AND SUPPLIES

6.1 Refer to Section 6 of the main body of this SOP for equipment and supplies.

6.2 Refer to Table A-2 for analytical column requirements

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Acetone, 99.4% for organic residue analysis.

7.1.2 Hexane, pesticide grade.

7.1.3 Carrier Gas: ≥ 99.99999% pure hydrogen.

7.1.4 Make-up Gas: ≥ 99.99980% pure nitrogen.

7.2 Standards

7.2.1 Stock Standards

7.2.1.1 All standards must be refrigerated at >0.0˚C but ≤6.0℃. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before use.

7.2.1.2 Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced annually or earlier if the vendor indicates an earlier date.

7.2.1.3 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. The standards must be replaced at least every six months, or sooner, if comparison with check standards indicates a problem.

7.2.2 PCB Congener and Surrogate Stock Standards

7.2.2.1 PCB Congener Stock Mix 1: For the PCB Congeners listed in Table A-1, except BZ-205 (surrogate), a commercially prepared stock standard solution is obtained. The concentration of the PCB Congeners contained in Mix 1 is 4.0 ug/mL and the concentration of the TCMX (surrogate) is 6.6 ug/mL PCB Congener Stock Add-on Mix: This stock standard is prepared by adding 400 uL of 100 ug/mL of the following individual congener standards brought to a final volume of 10 mL with Hexane and resulting in a final concentration of 4 ug/mL: BZ-205 (surrogate).

7.2.2.2 TCMX (2000 ug/mL) and BZ-205 (100 ug/mL) Surrogate Stock Standards are commercially purchased standards.

7.2.2.3 PCB Congener Matrix Spike Stock Standard is a commercially purchased standard containing BZ-8, BZ-18, BZ-28, BZ-44, BZ-52, BZ-66, BZ-77, BZ-101, BZ-105, BZ-118, BZ-126, BZ-128, BZ-138, BZ-153, BZ-170, BZ-180, BZ-187, BZ-195 and BZ-206 at a concentration of 100 ug/mL. (NOTE: BZ-49, BZ-81, BZ-87, BZ-114, BZ-123, BZ-156, BZ-157, BZ-167, BZ-169, BZ-187 and BZ-189 are also used as needed, however these are separate commercially purchased stock solutions also at a concentration of 100 ug/mL).

7.2.3 Calibration Curve Standard Solutions

The calibration standards are prepared as follows:

Calibration Level	Recipe	Stock Concentration (ug/mL)	Final Volume (ml of Hexane)
1	5 uL of PCB Congener Stock Mix 1 and 5 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
2	10 uL of PCB Congener Stock Mix 1 and 10 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
3	25 uL of PCB Congener Stock Mix 1 and 25 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
4	50 uL of PCB Congener Stock Mix 1 and 50 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
5	100 uL of PCB Congener Stock Mix 1 and 100 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40
6	200 uL of PCB Congener Stock Mix 1 and 200 uL of PCB Congener Stock Add-on Mix	4 ug/mL (TCMX 6.6 ug/mL)	40

7.2.3.1 Refer to Table A-3 for details of calibration standard concentrations.

7.2.4 Surrogate Standards

7.2.4.1 The Working Surrogate Solution is made as follows: 2.5 uL of the 2000 ug/mL commercially purchased TCMX stock and 50 uL of the 100 ug/mL commercially purchased BZ-205 stock brought to a final volume of 20 mL with Acetone (see section 7.2.2.3). The final concentration of the Working Surrogate Solution is 0.025 ug/mL. Refer to Table A-3 for details of surrogate standard concentrations in the calibration standards.

NOTE: The Working Surrogate Solution is prepared and used as part of the scope of the organic preparation SOP PT-OP-001 and PT-OP-026. The preceding information is provided for reference only.

7.2.5 Laboratory Control Standard (LCS) and Matrix Spiking (MS) Solution

The working LCS/MS spiking solution is prepared by combining 1mL of the PCB Congener Matrix Spike Stock Standard and 1 mL each, as needed, of the BZ-49, BZ-81, BZ-87, BZ-114, BZ-123, BZ-156, BZ-157, BZ-167, BZ-169, BZ-187 and BZ-189 stock standards brought to a 100 mL final volume with Acetone. The final concentration of the working LCS/MS spiking solution is 1.0 ug/mL.

NOTE: The LCS/MS spiking solution is prepared and used as part of the scope of the organic preparation SOP SOP PT-OP-001 and PT-OP-026. The following information is provided for reference only.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Refer to Section 8 of the main body of this SOP.

9.0 QUALITY CONTROL

9.1 Refer to Section 9 of the main body of this SOP.

10.0 PROCEDURE

10.1 Calibration and Standardization

10.1.1 PCB Congeners uses an External Standard Calibration as follows:

External standard calibration involves the comparison of instrument responses from the samples to the responses from the target compounds in the calibration standards. The area (or height) of a peak in a sample chromatogram is compared to the area (or height) of the peak in the standard chromatograms that appears at the same retention time. The ratio of the detector response to the concentration of the target analyte in the calibration standard is defined as the calibration factor (CF) and is calculated as follows:

$$CF = \frac{Area\ or\ Height\ of\ Peak}{Mass\ Injected}$$

Note: It is also possible to use the concentration of the standard rather than the mass injected.

10.1.2 Refer to Section 10 of the main body of this SOP for the other general calibration requirements.

10.2 Initial Calibration

10.2.1 Refer to Table A-5 for the initial calibration analytical sequence.

10.2.2 The response for each PCB congener will be calculated by the procedures described in the general method for 8082A analysis, with the following modifications.

- A minimum five-point calibration of each of the individual congeners mixes is generated. At least 2 separate mixes are prepared to ensure that there is complete resolution of all congeners in the mixes. Calibration levels are listed in Table A-3. Refer to Table A-6 for preparation of calibration levels.

10.3 Initial Calibration Verification

10.3.1 The ICV will consist of second source standards of all congeners of interest. The ICV is prepared from a second source stock standard of a concentration of 4ppm for all congeners of interest. 25 uL of the ICV stock standard is added to Hexane and brought to a final volume of 40 mL for a concentration of 0.0025 ppm.

10.3.2 Refer to section 9.9.4 in the main body of this SOP for acceptance criteria and corrective actions for failures.

10.3.3 12 hour Calibration

The 12-hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12-hour calibration.

The retention time windows for any analytes included in the daily calibration are updated.

For this method, samples must be bracketed with successful calibration verification runs.

10.3.4 Calibration Verification

10.3.4.1 A mid-level calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples or 12 hours, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.3.4.2 The daily CCV analysis at a concentration other than the mid-level (to meet NELAC requirements) will consist of all of the congeners of interest. All other CCVs will be mid-level calibration standards.

10.3.5 Procedure - Refer to Section 10 of the main body of this SOP for general procedural requirements.

10.3.6 Suggested gas chromatographic conditions are given in Table A-2.

10.3.7 The suggested analytical sequence is given in Table A-5.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Identification of Congeners

Retention time windows are used for identification of PCB congeners. Second column confirmation must be performed.

11.2 Refer to section 11 of the main body of this SOP for calculation details.

12.0 METHOD PERFORMANCE

12.1 Refer to section 12.3 for initial demonstration of capability requirements under Section 12 of the main body of this SOP. The LCS spiking level is used for IDOC.

13.0 POLLUTION CONTROL

13.1 Refer to Section 13 of the main body of this SOP.

14.0 WASTE MANAGEMENT

14.1 Refer to Section 14 of the main body of this SOP.

15.0 REFERENCES

15.1 Refer to Section 15 of the main body of this SOP.

16.0 METHOD MODIFICATIONS

16.1 Refer to Section 16 of the main body of this SOP.

17.0 ATTACHMENTS

17.1 Table A-1: Standard Analyte List and Reporting Limits
17.2 Table A-2: Recommended GC Operating Conditions
17.3 Table A-3: Calibration Levels
17.4 Table A-4: LCS/Matrix Spike and Surrogate Spike Levels
17.5 Table A-5: Suggested Analytical Sequence

18.0 REVISION HISTORY

18.1 See section 18 of the Main Body of this SOP.

Table A-1
Standard Analyte List and Reporting Limits

Compound *	CAS #	Reporting Limit			
		Water ng/L	Soil/Sediment/Tissue ug/kg	Wipe ng/wipe	Waste ug/kg
BZ-8	34883-43-7	1.0	1.0	1.0	10
BZ-18	37680-65-2	1.0	1.0	1.0	10
BZ-28	7012-37-5	1.0	1.0	1.0	10
BZ-44	41464-39-5	1.0	1.0	1.0	10
BZ-49	41464-40-8	1.0	1.0	1.0	10
BZ-52	35693-99-3	1.0	1.0	1.0	10
BZ-66	32598-10-0	1.0	1.0	1.0	10
BZ-77	32598-13-3	1.0	1.0	1.0	10
BZ-81	70362-50-4	1.0	1.0	1.0	10
BZ-87	38380-02-8	1.0	1.0	1.0	10
BZ-101	37680-73-2	1.0	1.0	1.0	10
BZ-105	32598-14-4	1.0	1.0	1.0	10
BZ-114	74472-37-0	1.0	1.0	1.0	10
BZ-118	31508-00-6	1.0	1.0	1.0	10
BZ-123	65510-44-3	1.0	1.0	1.0	10
BZ-126	57465-28-8	1.0	1.0	1.0	10
BZ-128	38380-07-3	1.0	1.0	1.0	10
BZ-138	35065-28-2	1.0	1.0	1.0	10
BZ-153	35065-27-1	1.0	1.0	1.0	10
BZ-156	38380-08-4	1.0	1.0	1.0	10
BZ-157	69782-90-7	1.0	1.0	1.0	10
BZ-167	52663-72-6	1.0	1.0	1.0	10
BZ-169	32774-16-6	1.0	1.0	1.0	10
BZ-170	35065-30-6	1.0	1.0	1.0	10
BZ-180	35065-29-3	1.0	1.0	1.0	10
BZ-183	52663-69-1	1.0	1.0	1.0	10
BZ-184	74472-48-3	1.0	1.0	1.0	10
BZ-187	52663-68-0	1.0	1.0	1.0	10
BZ-189	39635-31-9	1.0	1.0	1.0	10
BZ-195	52663-78-2	1.0	1.0	1.0	10
BZ-206	40186-72-9	1.0	1.0	1.0	10
BZ-209	2051-24-3	1.0	1.0	1.0	10

* The congener identifications are consistent with the short-hand identifications recommended by Ballschmiter and Zell (1980).

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Volume	Dilution Factor
Groundwater	1000 mL	2 mL	1
Soil/Tissue/Sediment	10 g	20 mL	1
Waste	1 g	20 mL	1
Wipe	1 wipe	2 mL	1

Table A-2	
Parameter	**Recommended Conditions**
Injection port temp	225°C
Detector temp	325°C
Temperature program	80°C ramping 30°C/min to 190°C, then 20°C/min to 230°C, then 4°C/min to 270°C and finally 20°C/min to 300°C holding for 5 minutes (22 minute run-time)
Column 1	ZB 50, 30 m, 0.25 mm id, 0.25 µm FT
Column 2	ZB 1701, 30 m, 0.25 mm id, 0.25 µm FT
Injection	1-2µL
Carrier gas	Hydrogen
Make up gas	Nitrogen

Table A-3						
Calibration Levels ug/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
BZ-8	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-18	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-28	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-44	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-49	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-52	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-66	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-77	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-81	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-87	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-101	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-105	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-114	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-118	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-123	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-126	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-128	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-138	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-153	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-156	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-157	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-167	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-169	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-170	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-180	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-183	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-184	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-187	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-189	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-195	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-206	0.0005	0.001	0.0025	0.0050	0.010	0.020
BZ-209	0.0005	0.001	0.0025	0.0050	0.010	0.020
SURROGATES						
TCMX	0.000825	0.00165	0.004125	0.00825	0.0165	0.033
BZ-205	0.0005	0.001	0.0025	0.0050	0.010	0.020

Table A-4				
LCS/Matrix Spike and Surrogate Spike Levels for Congener Analysis[1]				
ng/L, ng/wipe or ug/kg				
Compound	Aqueous	Soil/Sediment/Tissue	Wipe	Waste
BZ-8	20	20	20	200
BZ-18	20	20	20	200
BZ-28	20	20	20	200
BZ-44	20	20	20	200
BZ-49	20	20	20	200
BZ-52	20	20	20	200
BZ-66	20	20	20	200
BZ-77	20	20	20	200
BZ-81	20	20	20	200
BZ-87	20	20	20	200
BZ-101	20	20	20	200
BZ-105	20	20	20	200
BZ-114	20	20	20	200
BZ-118	20	20	20	200
BZ-126	20	20	20	200
BZ-123	20	20	20	200
BZ-128	20	20	20	200
BZ-138	20	20	20	200
BZ-153	20	20	20	200
BZ-156	20	20	20	200
BZ-157	20	20	20	200
BZ-167	20	20	20	200
BZ-169	20	20	20	200
BZ-170	20	20	20	200
BZ-180	20	20	20	200
BZ-183	20	20	20	200
BZ-184	20	20	20	200
BZ-187	20	20	20	200
BZ-189	20	20	20	200
BZ-195	20	20	20	200
BZ-206	20	20	20	200
BZ-209	20	20	20	200
Surrogates				
TCMX	5	5	5	50
BZ-205	5	5	5	50

[1]Individual Congeners are spiked as needed.

Table A-5		
Suggested Analytical Sequence		
Initial Calibration		
Injection #		
Solvent blank (optional)		
PCB Congener Mix 1	5-point	6-point
ICV (second source standard(s) of all congeners of interest)		
Samples 1-20 (or 12 hours, whichever is more frequent)		
Solvent blank (optional)		
PCB Congener Mix 1		Level 3
After 12 hours:		
PCB Congener Mix 1		Level 3
Samples 1-20 (or 12 hours)		
Solvent blank (optional)		
PCB Congener Mix 1		Level 3
12 hour Calibration		

At least every 24 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated.

Title: Extraction of Organic Compounds from Waters

Method(s): SW846 3500 Series and EPA 600 Series Methods

Approvals (Signature/Date):

10/12/2017	10/13/2017
Sharon Bacha Date	Steve Jackson Date
Organics Department Manager	Regional Safety Coordinator
10/12/2017	10/23/2017
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes extraction procedures for the preparation of semivolatile organic analytes in aqueous and TCLP leachate matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.2 Extraction procedures 608, 625, 3510C, and 3520C for the following determinative methods are covered:

608, 625, 8081A, 8081B, 8082, 8082A 8141A, 8141B, 8270C, and 8270D.

1.3 The extraction procedures discussed here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.4 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated the Quality Assurance Manual (PT-QA-M-001).

2.0 SUMMARY OF METHOD

2.1 Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2 Continuous Liquid/Liquid Extraction (CLLE)

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3 Concentration

Extracts are concentrated to specific final volumes by evaporation of the solvent under controlled conditions.

3.0 DEFINITIONS

3.1 Definitions of terms used in this SOP may be found in the glossary of the Pittsburgh Quality Assurance Manual (PT-QA-M-001).

3.2 TALS – TestAmerica Laboratory Information Management System

3.3 NCM – Non-Conformance Memo – a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch, or a QC failure.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

4.3 Residual Chlorine from water treatment must be removed from samples prior to extraction for 625 analysis and for 608 analysis when Aldrin is included in the compound list.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001), and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 Samples containing or suspected to contain cyanide or sulfide concentrations at or greater than 250 ppm or 500 ppm, respectively, shall be processed in a fume hood.

5.3 The use of separatory funnels to extract aqueous samples with Methylene Chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when it is performed.

5.4 Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP, and should not be used.

5.5 During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints, which can become stuck. Technicians must use Kevlar or other cut/puncture resistant gloves when separating stuck joints.

5.6 Care must be used when separating glass parts of extraction and concentration setups. Protective gloves must be used when separating stuck glass joints.

5.7 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit[i]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Sulfuric Acid[ii]	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.

[i] Exposure limit refers to the OSHA regulatory exposure limit.
[ii] Always add acid to water to prevent violent reactions.

5.8 Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.9 The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible.

5.10 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6.0 EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2 Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Separatory funnel	CLLE	Conc
Separatory Funnel: 2 L	X		
Separatory Funnel Rack	X		
Balance: >1400 g capacity, accurate ±1 g	X	X	
pH indicator paper, wide-range: covers extraction pH	X	X	
Graduated cylinder: 1 liter. (other sizes may be used)	X	X	
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	X		
Solvent Dispenser Pump or 100 mL Graduated Cylinder	X		
Continuous Liquid/Liquid Extractor		X	
Round or flat Bottom: 250, 500 mL or 1 L		X	
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		X	X
Cooling Condensers		X	
Heating Mantle: Rheostat controlled		X	
Auto-timer for heating mantle		X	
Kuderna-Danish (K-D) Apparatus: 500 mL			X
Concentrator Tube: 10 mL, attached to K-D with clips			X
Snyder Column: Three-ball macro			X
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5℃) up to 95℃. The bat h must be used in a hood or with a solvent recovery system.			X
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap			X
Nitrogen Blowdown Apparatus			X
Nitrogen: reagent grade.			X
Culture tubes: 10 mL, 16 mmx100 mm			X
Syringe: 1 mL	X	X	
Phase Separation Paper	X	X	
Glass Wool	X	X	
Glass Funnel: 75 X 75 mm	X	X	X
Disposable Pipettes	X	X	X
Potassium Iodide-Starch Indicator Paper	X	X	
Aluminum foil	X	X	X
Paper Towels	X	X	X

7.0 REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

7.1 Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Separatory funnel	CLLE	Conc.
Sodium hydroxide (NaOH), Pellets: Reagent Grade	X	X	
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	X	X	
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade	X	X	
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	X	X	
Organic free reagent water.	X	X	
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400℃ a minimum of two hours.	X	X	
Extraction/Exchange Solvents: Methylene chloride, hexane, acetone, pesticide quality or equivalent	X	X	X
Acetone: Used for cleaning	X	X	X
Sodium Thiosulfate, granular	X	X	

7.2 Standards

7.2.1 Stock Standards

Stock standards are purchased as certified solutions or prepared from neat. Semivolatile stock standards are stored at > 0.0ºC but ≤ 6.0°C. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.2.2 Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Work Instruction PT-OP-WI-001. Surrogate spiking standards are prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.3 Matrix Spiking and Laboratory Control Spiking Standards

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Work Instruction PT-OP-WI-001. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

8.0 SAMPLE COLLECTION PRESERVATION, SHIPMENT AND STORAGE

Matrix	Sample Container	Min. Sample Size	Preservation	Leachate Extraction Holding Time	Extraction Holding Time
Waters	1 liter amber	1 Liter	Cool, > 0.0ºC but ≤ 6.0ºC	NA	7 Days
Waters for PCB Analysis (608 or 8082)	1 liter amber	1 Liter	Cool, > 0.0ºC but ≤ 6.0ºC	NA	1 year
WI Waters for 608 analysis to include Aldrin	1 liter amber	1 Liter	Cool, > 0.0ºC but ≤ 6.0ºC; Add 0.008% Sodium Thiosulfate	NA	1 year
Leachates	4oz Jar	100 grams	Cool, > 0.0ºC but ≤ 6.0ºC	14 Days	7 Days

9.0 QUALITY CONTROL

9.1 Extraction batches are composed of twenty or fewer samples, of similar matrix, plus the required batch QC. Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count.

9.2 If insufficient sample is available to process a MS/MSD, then an LCS Duplicate may be processed to evaluate batch extraction precision. Use of a LCS/LCSD pair in place of a MS/MSD due to insufficient sample volume must be documented using the "Insufficient Volume" NCM. Because subsamples cannot be taken from a wipe sample for MS/MSD analyses, wipe samples should be processed with a LCS/LCSD.

9.3 The extraction of at least a Matrix Spike is required for all methods. If double sample volume is not provided for any samples in the batch, document this with the "Insufficient Volume" NCM.

9.4 The following quality control samples are prepared with each batch of samples. For QC control limits, refer to the individual analytical method SOPs and TALS.

Quality Controls	Frequency
Method Blank (MB)	1 per preparation batch[1]
Laboratory Control Sample (LCS)	1 per preparation batch[1]
Matrix Spike (MS)[2,3]	1 per preparation batch[1]
Matrix Spike Duplicate (MSD)[2,3]	1 per preparation batch[1]
Surrogates	All samples and QC

[1]A preparation batch is limited to 20 samples, except for 608 and a batch is limited 10 samples.
[2]The sample used for MS/MSD is randomly selected, unless specifically requested by a client.
[3]An MS should be performed without an MSD if there is insufficient volume for both.

9.5 Method Blank

A method blank with all reagents added the same as to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.5.1 Aqueous Method Blanks use 1000 mL (or the same target volume as the samples) of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2 TCLP Leachate Blanks (LB) use 200 mL of leachate fluid for GC/MS Semivolatiles and 100 mL for organochlorine pesticides. The leachate blank may optionally be diluted to 1000 mL with reagent water. Once the organic prep group receives the TCLP samples and leachate blank they will extract all using the appropriate method and QC, including an extracted method blank. The method blank and leachate blank go through the entire analytical procedure, including any cleanup steps.

9.6 Laboratory Control Sample (LCS)

Laboratory Control Samples are clean matrix, known concentration, laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with the list of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.1 The LCS is made up in the same way as the method blank (See sections 9.5.1 - 9.5.2) but spiked with the LCS standard as well as the surrogates.

9.6.2 For the 600 series methods (608 and 625), the LCS is equivalent to the QC Check Sample specified in the reference methods.

9.7 Surrogates

9.7.1 Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.7.2 Each sample, blank, LCS and MS/MSD is spiked with surrogate standards prior to the extraction process. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.8.1 A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample, which is spiked prior to the beginning of the extraction process and prepared and analyzed along with the sample and matrix spike. Matrix spike analysis is required for every 20 samples, except for method 608, which is every 10 samples.

9.8.2 If sufficient volume is not received for both and MS and MSD, at least an MS should be extracted along with the batch to meet method QC requirements.

10.0 PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (10.1), continuous liquid/liquid extraction (10.2), and extract concentration (10.3) are presented in this section.

10.1 Separatory Funnel Liquid/Liquid Extraction of Water Samples:

Refer to Figure 1 – Separatory Funnel Extraction flowchart.

10.1.1 Remove surrogate and matrix spiking solutions from refrigerator and allow them to warm to room temperature.

10.1.2 Mark the meniscus of the sample volume on the sample bottle.

10.1.3 Measure the initial sample pH with wide-range pH paper and record on the TALS worksheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, Note on the benchsheet if there is any discrepancy.

10.1.3.1 Refer to Table 1 for the required extraction pH for each method. If required, sample pH is adjusted in the sample bottle if possible, to the pH range as indicated in Table 1. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary to adjust the pH into the required range. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record the adjusted pH on the TALS worksheet.

Note: If the sample bottle is completely full, it may be difficult to adjust the pH in the bottle. In this case, transfer the sample to the separatory funnel and then adjust the pH prior to adding any methylene chloride.

10.1.4 For 625 samples, and 608 samples when the compound list includes Aldrin, check samples for residual chlorine by adding a few drops of sample from a pipette or glass stirring rod onto a piece of potassium iodide (KI) - starch paper that has been moistened with reagent water.

10.1.4.1 If the paper turns blue, treat the entire sample volume by adding a small scoop of granular sodium thiosulfate. Check the sample again with KI-starch paper. Continue treating and checking the sample until the paper no longer turns blue.

10.1.4.2 If the residual chlorine cannot be removed after 4 additions of sodium thiosulfate, contact the PM to obtain the client's instructions on whether to proceed with the extraction.

10.1.4.3 Document any samples that have been treated to remove residual chlorine using the "Residual Chlorine" NCM.

10.1.5 The normal sample volume is approximately 1 liter. Clients may send bottles that have not been completely filled. The entire volume in the bottle is extracted, and the exact volume used is documented in the TALS batch.

10.1.5.1 Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples. Unusual volumes must be documented in an NCM.

10.1.6 Spike all samples in the bottle with surrogate solution. Also spike the MS and MSD aliquots with Matrix Spike solution (Refer to Work Instruction PT-OP-WI-001). Replace the cap and mix well. Record the spike volumes and standard numbers on the TALS worksheet. Return spiking solutions to the refrigerator as soon as possible.

Note: If the sample bottle is completely full, it may be difficult to add the spike solutions to the bottle. In this case, transfer the sample to the separatory funnel and then add the spike prior to adding any methylene chloride.

10.1.7 Transfer the entire sample to the separatory funnel. Add 60 mL of methylene chloride to the bottle. Cap and shake for approximately 30 seconds to rinse all inner surfaces. Transfer the methylene chloride to the separatory funnel.

10.1.8 The sample volume is determined by filling the sample bottle with reagent water up to the marked meniscus or to the top of the sample bottle if the bottle is completely full and measuring that volume in a graduated cylinder. Record the volume to the nearest 10 mLs.

10.1.8.1 If the entire sample bottle will not be used (i.e., for smaller sample aliquots such as TCLP), mix the sample in the bottle and measure out the desired volume in a graduated cylinder. Spike the surrogate, and MS solution, where appropriate, and adjust initial sample pH in the cylinder. Transfer the aliquot to the separatory funnel.

10.1.8.2 Rinse the cylinder with 60 mL of methylene chloride and transfer to the separatory funnel.

10.1.9 Prepare a method blank, LCS, MS and MSD for each batch as specified in section 9 of this SOP. The LCS and MS/MSD are spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates (see Work Instruction PT-OP-WI-001 for spike volumes).

10.1.10 Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

Warning: Methylene chloride creates excessive pressure very rapidly. Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

10.1.11 Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation.

- The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.
- If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous liquid-liquid extractor (CLLE) and proceed as described in continuous liquid-liquid extraction (Section 10.2). If this is done, the sample must be extracted as part of a valid CLLE batch, with all associated QC.

Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

10.1.12 Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

10.1.13 Use a second 60 mL portion of methylene chloride to rinse the bottle and transfer it to the separatory funnel. Repeat the extraction process, filtering the extract through the same filter funnel into the same collection vessel. Repeat the extraction process a third time using a fresh 60 mL portion of solvent. Combine all three solvent extractions in the collection container.

10.1.14 If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the TALS worksheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps 10.1.10 to 10.1.12. Collect these three extracts in the same container used for the initial pH fraction.

Note: Alternatively, the acid and base fractions may be kept separate. Separate analysis of the acid and base fractions may be required for method 625. Individual client requirements must be checked before starting the extraction.

10.1.15 Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

10.1.16 Dispose of water remaining in the separatory funnel into the appropriate waste container.

10.1.17 Cover the collection container with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.3 for concentration.

10.2 Continuous Liquid/Liquid Extraction from Water Samples:

Refer to Figure 2 – Continuous Liquid/Liquid Extraction flowchart.

10.2.1 Remove surrogate and matrix spiking solutions from refrigerator and allow them to warm to room temperature.

10.2.2 Assemble the apparatus. Add 200-300 mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

10.2.3 Mark the meniscus of the sample volume on the sample bottle.

10.2.4 Measure the initial sample pH with wide-range pH paper and record on the extraction TALS worksheet. If sample is a leachate (e.g. TCLP), compare the current pH against the leachate log. Note on the benchsheet if there is any discrepancy.

10.2.4.1 Refer to Table 1 for the required extraction pH for each method. If required, sample pH is adjusted in the sample bottle if possible, to the

pH range as indicated in Table 1, for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary to adjust the pH into the required range. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record the adjusted pH on the TALS worksheet.

Note: If the sample bottle is completely full, it may be difficult to adjust the pH in the bottle. In this case, transfer the sample to the extractor and then adjust the pH prior to adding any methylene chloride.

10.2.5 See section 10.1.4 above for checking and treating residual chlorine in 625 and 608 samples.

10.2.6 Spike all samples in the bottle with surrogate solution. Also spike the MS and MSD aliquots with Matrix Spike solution (see Work Instruction PT-OP-WI-001 for spike volumes). Mix well. Record the spike volumes and standard numbers on the TALS worksheet. Return spiking solutions to the refrigerator as soon as possible.

Note: If the sample bottle is completely full, it may be difficult to add the spike solutions to the bottle. In this case, transfer the sample to the extractor and then add the spike prior to adding any methylene chloride.

10.2.7 Transfer the entire sample to the liquid-liquid extractor. Add 60 mL of methylene chloride to the bottle. Cap and shake for approximately 30 seconds to rinse all inner surfaces. Transfer the methylene chloride to the liquid-liquid extractor.

10.2.7.1 Repeat the sample bottle rinse with an additional 50-100mL portion of methylene chloride and add the rinse to the extractor.

10.2.8 The sample volume is determined by filling the sample bottle with reagent water up to the marked meniscus or to the top of the sample bottle if the bottle is completely full and measuring that volume in a graduated cylinder. Record the volume to the nearest 10 mLs.

10.2.8.1 If the entire sample bottle will not be used (i.e., for smaller sample aliquots such as TCLP), mix the sample in the bottle and measure out the desired volume in a graduated cylinder. Spike the surrogate, and MS solution, where appropriate, and adjust initial sample pH in the cylinder. Transfer the aliquot to the liquid-liquid extractor.

10.2.8.2 Rinse the cylinder with 60 mL of methylene chloride and transfer to the liquid-liquid extractor.

10.2.9 Prepare a method blank and LCS for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions. Note that different spiking solutions are used for methods 625, 8270 and TCLP (see Tables 3 and 4 for spike volumes).

10.2.10 Use 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate may be made up to 1 L in volume with reagent water.

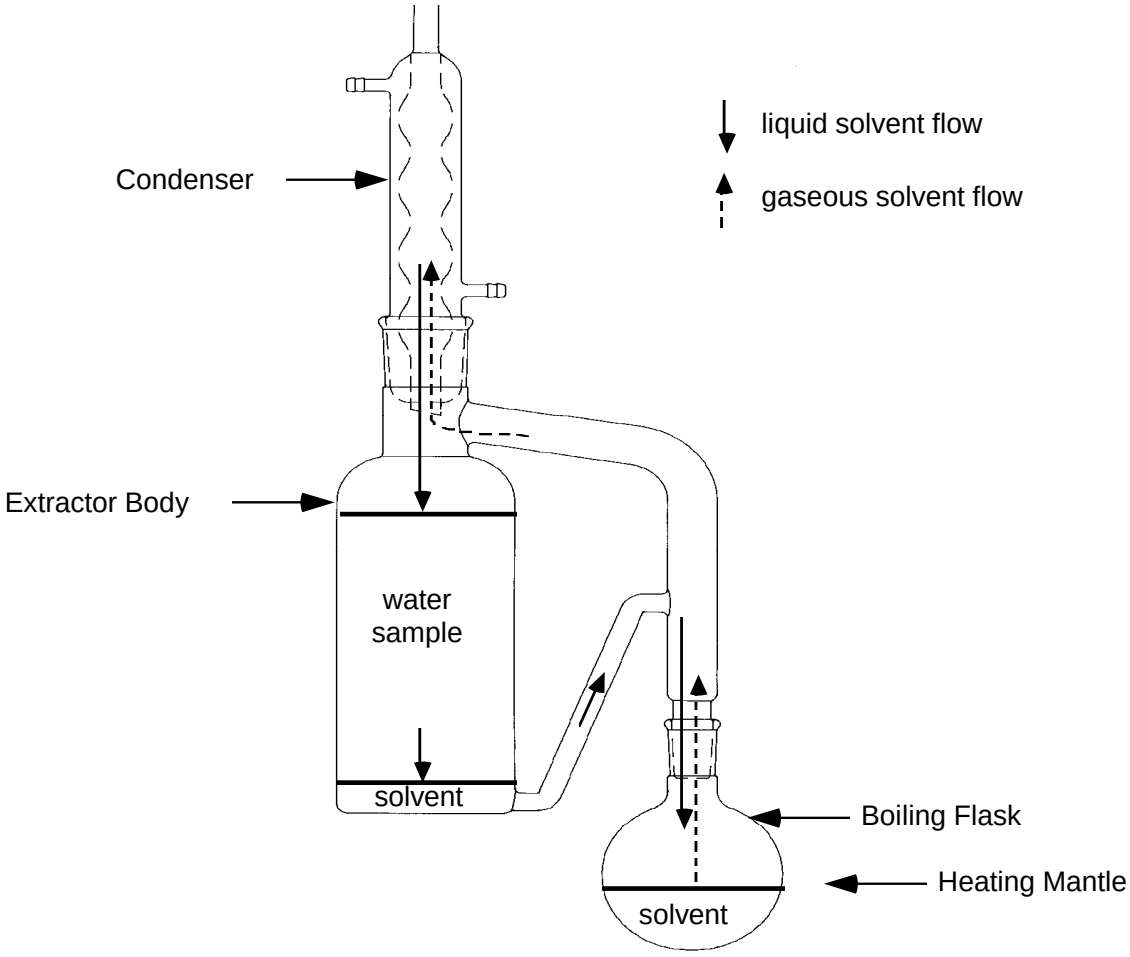
10.2.11 For a TCLP method blank, 200 mL (semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

10.2.12 Add reagent water to the extractor body until approximately 125 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation

and solvent cycling. Attach cold condenser (about 10°C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours for both the 3500 and 600 series methods.

10.2.13 If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. If desired, the acid and base fractions may be kept separate by replacing the boiling flask with a clean flask and fresh solvent. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours for both the 3500 and 600 series methods.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.



10.2.14 Turn off the heating mantle and allow the extractor to cool.

10.2.15 Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with

glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

10.2.16 Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

10.2.17 Collect the dried extract in a K-D or other glass container. Rinse the flask that contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

10.2.18 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.3 for concentration.

10.3 Concentration

According to the method, type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

Refer to Figure 3 – Concentration and Cleanup flowchart.

10.3.1 Kuderna-Danish (KD) Method:

10.3.1.1 Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. For procedures where the final volume is 10 mL, a 250 mL Erlenmyer flask may be used as an alternative to the KD flask.

10.3.1.2 Add one or two clean boiling chips and the dried extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).

10.3.1.3 Place the KD apparatus on a water bath maintained at 60-65 ^{o}C so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

10.3.1.4 Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (see Table 2) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent. An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add 10 mL of exchange solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost. If this happens, the extract must be discarded and the extraction started over with fresh sample.

10.3.1.5 Remove the KD apparatus from the water bath and allow it to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

10.3.1.6 If the final volume is 5 or 10 mL, the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 10.3.2.

10.3.2 Nitrogen Evaporation to Final Concentration

10.3.2.1 Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

10.3.2.2 Place the tube in a warm water bath that is at approximately 35^{o}C and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

Note: Extracts for method 608.3 may be concentrated at temperature 50-55^{o}C.

10.3.2.3 During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through the process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost. If this happens, the extract must be discarded and the extraction started over with fresh sample.

Vial Calibration Note: Using a Class A volumetric pipette dispense the appropriate volume of solvent into the vial being calibrated, mark the meniscus and use this vial when marking the final volume line on subsequent sample vials of that type and lot. See SOP PT-QA-026 and work instruction PT-QA-WI-008 for details.

10.3.2.4 An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

10.4 If sample extract cleanup is required please refer to SOP PT-OP-028 for the appropriate cleanup technique.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Not applicable – refer to analytical method SOPs.

12.0 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual and SOP PT-QA-007, must be performed initially, annually and any time a significant change is made to the analytical system.

13.0 POLLUTION CONTROL

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2 Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

14.0 WASTE MANAGEMENT

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1 Methylene Chloride extraction waste. This waste is collected in waste containers identified as "Methylene Chloride Waste", Waste #2.

14.1.2 Extracted water samples. This waste is collected in a waste container identified as "Extraction Water", Waste #35. The bottom organic layer is drained into a container identified as "Methylene Chloride Waste", Waste #2. The remaining aqueous layer is neutralized to a pH between 6 and 9 and discharged down lab sink/ drain.

14.1.3 Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride from the extract drying step. This waste is collected in a container identified as "Lab Trash Waste", Waste #12.

14.1.4 Assorted flammable solvent waste from various rinses. This waste is collected in waste containers identified as "Mixed Flammable Solvent Waste", Waste 3.

14.1.5 Methylene chloride waste from various rinses. This waste is collected in waste containers identified as “Methylene Chloride Waste”, Waste #2.

14.1.6 Miscellaneous disposable glassware contaminated with acids, caustics, solvents and sample residue. This waste is collected in a container identified as “Lab Trash Waste”, Waste #12.

15.0 REFERENCES – CROSS-REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3541 3550B, 3580A, 3600C, 3620B, 3640A, 3660B, and 3665A

15.2 Wisconsin Department of Natural Resources, NR 219.04, Analytical Test Methods and Procedures, April 2010

15.3 Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001)

15.4 40 CFR Part 136, Appendix A, United States Environmental Protection Agency. 2016, Methods 608.3 and 625.1

15.5 SOP PT-QA-001, Employee Training and Orientation

15.6 SOP PT-QA-003, Glassware Clean-up for Organic/Inorganic Procedures

15.7 SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.8 SOP PT-QA-007, Determination of Method Detection Limits (MDL)

15.9 SOP PT-QA-008, Thermometer Calibration and Temperature Monitoring

15.10 SOP PT-QA-012, Selection and Calibration of Balances and Weights

15.11 SOP PT-QA-016, Nonconformance and Corrective Action System

15.12 SOP PT-QA-021, Quality Control Program

15.13 SOP PT-QA-026, Container Accuracy Verification – Gravimetric

15.14 SOP PT-QA-031, Internal Chain of Custody

15.15 Pittsburgh Facility Addendum EH&S Manual, PT-HS-001

15.16 PT-OP-WI-001, TestAmerica Pittsburgh Organic Prep Work Instruction for Initial/Final Volumes, Exchange Solvents, LCS and Matrix Spiking Components and Concentrations

16.0 METHOD MODIFICATIONS

16.1 Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

16.2 Spiking levels for method 608.3 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

17.0 ATTACHMENTS

17.1 Table 1 – Liquid/Liquid Extraction Conditions

17.2 Table 2 – Initial Volumes, Exchange Solvents, and Final Volumes

17.3 Figure 1 – Separatory Funnel Extraction

17.4 Figure 2 – Continuous Liquid/Liquid Extraction

17.5 Figure 3 – Concentration and Cleanup

18.0 REVISION HISTORY

18.1 Revision 9, 02/01/07

18.2 Revision 9, 02/01/07

18.3 Revision 10, 09/24/07

18.4 Revision 11, 01/16/09

18.5 Revision 12, 7/1/2010

18.6 Revision 13, 3/11/2011

18.7 Revision 14, 4/22/2011

18.8 Revision 15, 12/2/2013

18.9 Revision 16, 9/10/2015

18.10 Changes to current revision

SOP section	Change from	Change to	Reason
7.2.2 & 7.2.3	Reference to Tables 5 & 6	Reference to Work Instruction PT-OP-WI-001	Correction
9.3	At least an MS required for methods 608 and 625	required for all methods	Correction
9.7.2, 9.8.1		Added spiked prior to start of extraction	Clarification
10.2.12 & 10.2.13	Removed “(24 hours required for Method 625)”	Added “for both the 3500 and 600 series methods.”	Update to 608.3 and 625.1 Method requirements
10.1.2 & 10.2.3	Moved from first sentence of 10.1.5 & 10.2.5	Moved Mark the meniscus to correct place in flow of procedure	Correction
10.1.3.1 & 10.2.4.1	Moved from 10.1.6 & 10.2.6	pH adjustment instructions moved to correct place in flow of procedure	Correction
10.1.7 & 10.2.7	Rinse the sample bottle with 60mL of methylene chloride	Add 60mL of methylene chloride to the sample bottle. Cap and shake for approximately 30 seconds	Clarification
10.1.13	Repeat the extraction process two more times….	Using a second portion of 60mL methylene chloride, rinse the sample bottle and transfer it to the separatory funnel. Repeat the extraction process a third time with a fresh 60mL portion….	Clarification
10.2.7.1		Added Repeat bottle rinse with an additional 50-100mL methylene chloride	Correction
10.3.1.3	Water bath (70-75°C)	Water batch maintained at 60-65°C	Correction

10.3.2.2		Added note that 608.3 extracts may be concentrated at 50-55°C	Clarification
12.3		Added reference to SOP PT-QA-007	Clarification
15.4	Reference to 40 CFR Part 136, 1984, methods 608 and 625	2016, methods 608.3 and 625.1	Correction for reference update
Table 2	Removed the soil and waste initial volumes, exchange solvent and final volumes since this is a water SOP		Correction

Table 1		
Liquid/Liquid Extraction Conditions		
Determinative Method	**Initial Ext. pH[1]**	**Secondary Ext. pH[1]**
BNA (8270)	1-2	11-12
BNA (625)	11-12	1-2
Pesticides (8081 & 608)	5-9	None
PCB Aroclors (8082 & 608)	5.9	None
PCB Congeners	5-9	None
OP Pesticides (8141)	As received	None

[1] If the laboratory has validated acid only 8270C and 8270D extraction for the target compound list required, then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See Section 12).

Table 2

Initial Volumes, Exchange Solvents, and Final Volumes

Group	Method	Initial Water Vol. (mL)	Initial TCLP Vol. (mL)	Exchange Solvent for Analysis	Final Volume for Analysis (mL)
GC/MS Semivolatiles	625	1000	NA	NA	10
	625 LL	1000	NA	NA	1.0
	625 LL LVI	250	NA	NA	0.25
	8270/3520C	1000	NA	NA	10
	8270 LL/3520C LL	1000	NA	NA	1.0
	8270 LVI/3520C	250	NA	NA	2.5
	8270 LL LVI/3520C	250	NA	NA	0.25
	8270 LL LVI/3510C	250	NA	NA	2.5
	8270 TCLP/3520C	NA	1000/ 200	NA	1.0/10
	8270 TCLP/3510C	NA	200	NA	10
	625/8270/3520C CRAEE	1000	NA	NA	1.0
	625/8270/3520C Dupont	100	NA	NA	1.0
Pesticides (8081A/B)	8081/3510C	1000	NA	Hexane	40
	8081 LL/3510C LL	1000	NA	Hexane	1.0
	8081/ 3510C LVI	250	NA	Hexane	10
	8081/3510C TCLP	NA	100	Hexane	40
	8081/3580A TCLP	NA	1.0	Hexane	40
PCB Aroclors (8082/A)	8082/3510C	1000	NA	Hexane	40
	8082 LL/3510C LL	1000	NA	Hexane	1.0
	8082/3510C LVI	250	NA	Hexane	10
	8082/3580A	NA	NA	Hexane	40
	8082/3510C TCLP	1000	NA	Hexane	40
	8082/3510C Safety Kleen	100	NA	Hexane	4.0
Pesticide and PCB Aroclors	608.3	1000	NA	Hexane	1.0ml
PCB Congeners (8082A)	8082A_Con/3510C	1000	NA	Hexane	2.0
OPP's (8141A/B)	8141/3510C	1000	NA	Hexane	5.0
	8141 LL/3510C LL	1000	NA	Hexane	1.0
Herbicides	8151A/8151A_AP	1000	NA	Hexane	10
	8151A/8151A_AP TCLP	NA	100	Hexane	10
	8151A/8151A_AP North Canton	1000	NA	Hexane	10

Figure 1 - Separatory Funnel Extraction

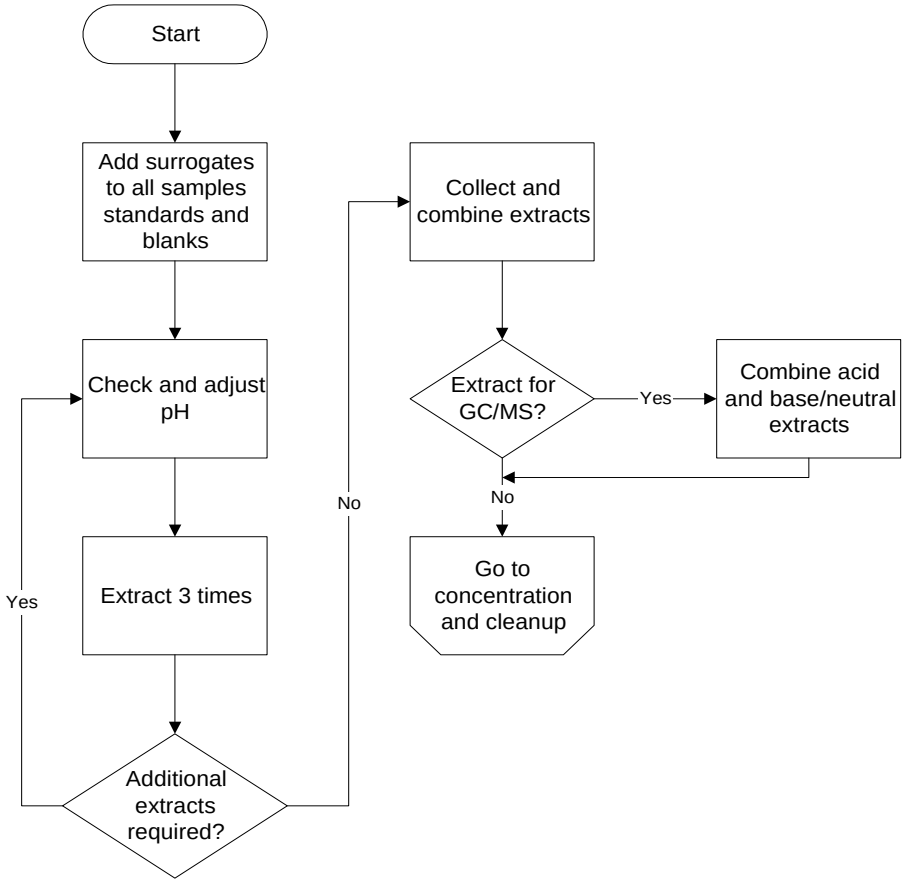


Figure 2 - Continuous Liquid/Liquid Extraction

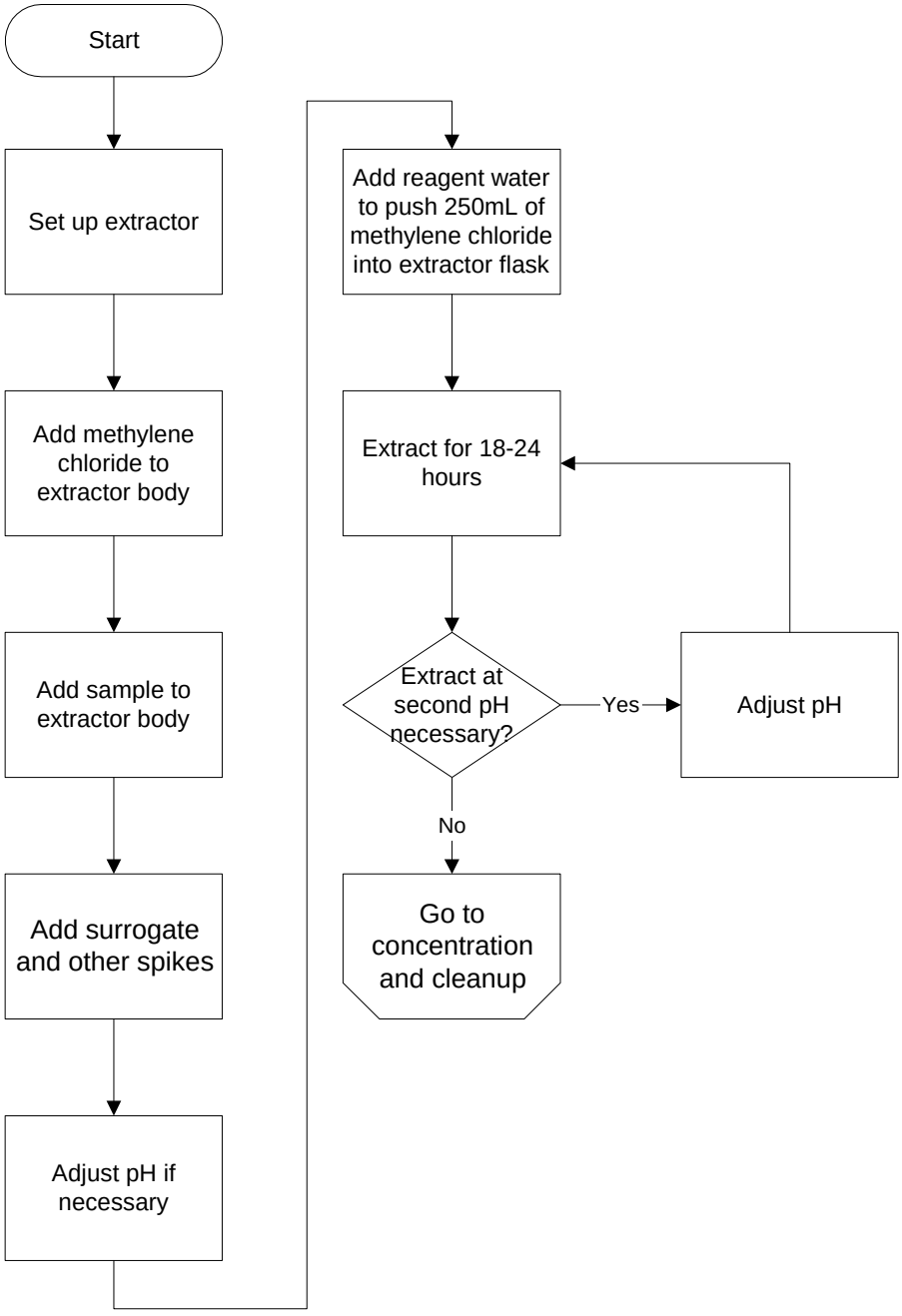
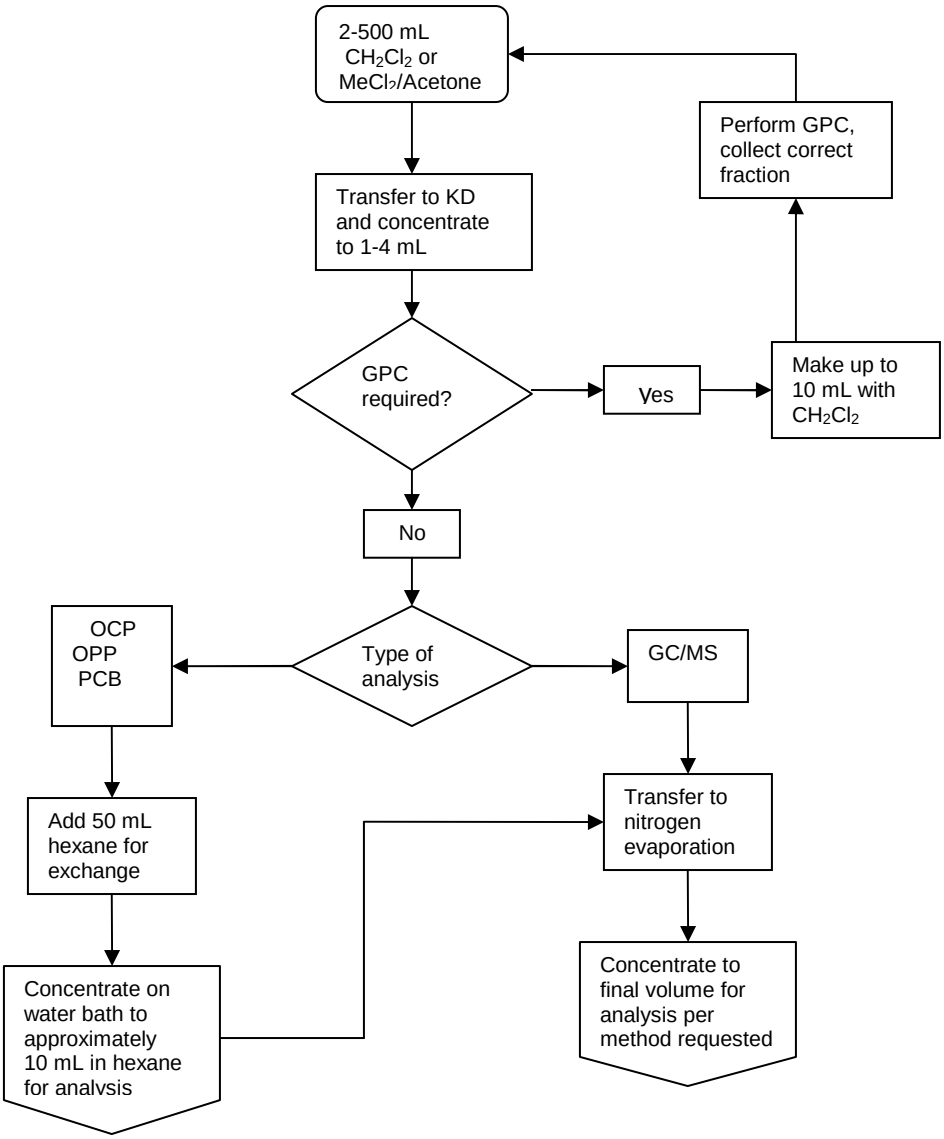


Figure 3 - Concentration and Cleanup



TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Extraction of Organic Compounds from Solids, Sediments, Tissue and Wipes

Method(s): SW846 3500 Series

Approvals (Signature/Date):

11/24/2017	11/27/2017
Sharon Bacha Date	Steve Jackson Date
Organics Department Manager	Regional Safety Coordinator
11/24/2017	11/27/2017
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes procedures for preparation (extraction) of semivolatile organic analytes in soil, sediment, tissue, waste and wipe matrices for analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.2 Extraction procedures for the following determinative methods are covered:

8081A, 8081B, 8082, 8082A 8141A, 8141B, 8270C and 8270D.

1.2.1 For sediment samples being analyzed in support of Dredged Material Management programs, method modifications are often necessary, to compensate for the high moisture content, to meet project goals. This may include increased sample weight or decreased final extract volumes. Typically these volume modifications are up to a factor of 2.

1.3 The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.4 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 High Level (Client Specific) Sonication Extraction

A measured weight of sample, typically 2 grams, is mixed with anhydrous sodium sulfate to for a free flowing powder. This is solvent extracted once using an microtip ultrasonic horn.

2.2 Accelerated Soxhlet (Soxtherm®) Extraction

A measured weight of sample, typically 15 g, or one whole wipe sample is mixed with anhydrous sodium sulfate and magnesium sulfate to form a free flowing powder. This is extracted with an accelerated soxtherm unit.

2.3 Concentration

Procedures are presented for drying and concentration of the extract to final volume for analysis.

3.0 DEFINITIONS

3.1 Definitions of terms used in this SOP may be found in the glossary of the Pittsburgh Quality Assurance Manual (PT-QA-M-001).

3.2 TALS – TestAmerica Laboratory Information Management System

3.3 NCM – Non-Conformance Memo, a communication system for the laboratory to document anomalies or non-conformances encountered with samples and their analysis.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 Samples containing or suspected to contain cyanide or sulfide concentrations at or greater than 250 ppm or 500 ppm, respectively, shall be processed in a fume hood.

5.3 Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP, and should not be used.

5.4 During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints, which can become stuck. Technicians must use Kevlar or other cut/puncture resistant gloves when separating stuck joints.

5.5 Ultrasonic disrupters can produce high intensity noise and must be used in an area with adequate noise protection.

5.6 The following is a list of the materials used in this method, which have a serious or significant hazard rating. This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit[i]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

[i] Exposure limit refers to the OSHA regulatory exposure limit.

5.7 Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.8 The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible.

5.9 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6.0 EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2 Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	High Level Sonication	Accelerated Soxtherm	Conc
20 or 40 mL VOA Vials	X		
Solvent Dispenser Pump or 100 mL Graduated Cylinder	X		
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		X	X
Cooling Condensers		X	
Heating Mantle: Rheostat controlled		X	
Auto-timer for heating mantle		X	
Beakers: 250 & 400 mL, graduated	X	X	
Balance: >100 g capacity, accurate ±0.1 g	X	X	
Soxtherm® Extractor Gerhardt Model S 306A		X	
Glass Thimbles		X	
Sonicator (at least 300 watts)	X		
Sonicator horn, microtip	X		
Kuderna-Danish (K-D) Apparatus: 500 mL			X
Concentrator Tube: 10 mL, attached to K-D with clips			X
Snyder Column: Three-ball macro			X
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5℃) up to 95℃. The bath m ust be used in a hood or with a solvent recovery system.			X
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap			X
Nitrogen Blowdown Apparatus			X
Nitrogen: reagent grade.			X
Culture tubes: 10 mL, 16 mmx100 mm			X
Syringe: 1 mL	X	X	
Phase Separation Paper	X	X	
Glass Wool	X	X	
Glass Funnel: 75 X 75 mm	X	X	X
Disposable Pipettes	X	X	X
Aluminum foil	X	X	X
Paper Towels	X	X	X

EQUIPMENT AND SUPPLIES	High Level Sonication	Accelerated Soxtherm	Conc
Ottawa Sand		X	

7.0 REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the SDS prior to the use of any reagent or standard.

7.1 Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	High Level Sonication	Accelerated Soxtherm	Conc.
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400℃ a minimum of two hours.	X	X	
Magnesium Sulfate, Anhydrous powder		X	
Extraction/Exchange Solvents: Methylene chloride, hexane, acetone, pesticide quality or equivalent	X	X	X
Acetone: Used for cleaning	X	X	X
50:50 Sodium Sulfate/Magnesium Sulfate	X	X	

7.2 Standards

7.2.1 Stock Standards

Stock standards are purchased as certified solutions or prepared from neat. Semivolatile stock standards are stored at $\leq 6.0^{o}$C. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.2.2 Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 2 of PT-OP-WI-001. Surrogate spiking standards are prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.2.3 Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 3 of PT-OP-WI-001. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time
Soils[1]	4oz Jar	15 grams	Cool, >0.0˚C but ≤ 6.0ºC	14 Days	40 Days from extraction
Sediment	4oz Jar	30 grams	Cool, >0.0˚C but ≤ 6.0ºC	14 Days	40 Days from extraction
Tissues	4oz Jar	15 grams	Frozen	1 year	40 Days from extraction
Wipes	4 oz jar	1 wipe	Cool, >0.0˚C but ≤ 6.0ºC	14 Days	40 Days from extraction

[1] Soils include solids, sludges, and organic liquids (wastes).

8.1 For method 8141B, solid sample extraction must be started within 7 days of collection.

8.2 Some, but not all, states accept a 1 year holding time for PCB solid samples. The holding time in TALS is set to 14 days to reflect those states/projects that will not accept this extended holding time. Confirm with QA or the Project Manager that a longer holding time may be applied per project.

9.0 QUALITY CONTROL

9.1 Insufficient Sample Volume Provided

9.1.1 If insufficient sample is available to process a MS/MSD, then an LCS Duplicate may be processed. The LCS pair is then evaluated according to the MS/MSD criteria. Use of a LCS pair in place of a MS/MSD must be documented using the "MS/MSD – Insufficient Volume" NCM.

Because subsamples cannot be taken from a wipe sample for MS/MSD analyses, wipe samples will always be processed with a LCS/LCSD.

9.1.2 It is acceptable to prepare an MS without an MSD, if there is sufficient sample available for only one QC.

9.2 Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count for 20 samples in a preparation batch. Field QC samples are included.

9.3 The following quality control samples are prepared with each batch of samples. For QC control limits, refer to the individual analytical methods SOPs and TALS.

Quality Controls	Frequency
Method Blank (MB)	1 per preparation batch[1]
Laboratory Control Sample (LCS)	1 per preparation batch[1]
Matrix Spike (MS)[2]	1 per preparation batch[1]
Matrix Spike Duplicate (MSD)[2]	1 per preparation batch[1]
Surrogates	All samples and QC

[1]A preparation batch is limited to 20 samples.

[2]The sample used for MS/MSD is randomly selected, unless specifically requested by a client.

9.4 Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.4.1 Solid method blanks use the same target weight of 50:50 sodium sulfate/magnesium sulfate as the extracted weights of the associated samples, spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

NOTE: For batches containing samples from South Carolina, certified clean Ottawa sand is used as a blank matrix, in addition to the 50:50 sodium sulfate/magnesium sulfate.

9.4.2 Method blanks for wipes consist of clean, unused gauze pads (that are the same as those used for the associated wipe samples) that are spiked with the surrogates and carried through the entire analytical procedure, including any cleanup steps.

9.5 Laboratory Control Sample (LCS)

Laboratory Control Samples are well characterized, laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.5.1 The LCS is made up in the same way as the method blank but spiked with the LCS standard as well as surrogates. (See section 9.4.1 and 9.4.2.)

9.6 Surrogates

9.6.1 Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.6.2 Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and matrix spike.

10.0 PROCEDURE

Procedures for high level sonication extraction (10.1), accelerated soxtherm extraction (10.2), waste dilution (10.3) and extract concentration (10.4) are presented in this section.

10.1 High Level Sonication Procedure

10.1.1 Refer to Figure 1 – High Level Sonication Extraction flowchart.

10.1.1.1 Weigh 2 g of sample into a 20 mL vial. Record the weight to the nearest 0.1 g in the appropriate column on the TALS LIMS worksheet. Use 2 g of sodium sulfate for the method blank and the LCS.

10.1.1.2 Add 2 grams of sodium sulfate to each sample and mix well.

10.1.1.3 Add 1 mL of surrogate to all samples including QC samples. Add 1 mL of the matrix spike solution to the LCS, MS and MSD. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database in TALS LIMS.

Add the surrogates and matrix spiking compounds to the sample aliquot after mixing the sample with the sodium sulfate drying agent. This will be done in accordance with the memorandum from the USEPA dated August 5, 2010, which supersedes previous Method instructions (see Attachment 1). The EPA points out in the memorandum that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix.

10.1.1.4 Add 9.0 mL of extraction solvent (8.0 mL to the LCS, MS, MSD) so that the final volume is 10.0 mL. The extraction solvent is as follows:

- For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the solvent is hexane.
- For GC/MS semivolatiles, the solvent is methylene chloride.

10.1.1.5 Place the bottom surface of a 1/8” tapered microtip attached to a 1/2” horn approximately ½ inch below the surface of the solvent, but above the solid layer.

10.1.1.6 Sonicate each sample for 2 minutes. A Fisher Scientific 550 sonicator is used, the output should be set at 10 with mode switch on pulse, and the percent-duty cycle knob set at 100% full power.

10.1.1.7 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the extract through the glass wool into a suitable container.

10.1.1.8 If the samples do not require cleanups or additional concentration, than the extract is ready for analysis

10.1.1.9 If cleanups (SOP PT-OP-028) or additional concentration (10.4) are required, collect a standard volume (i.e., 5.0 mL, which represents ½ of the extract). Either account for the "loss" of half of the extract in the final sample calculations, or concentrate the extract to ½ of the standard final volume to compensate for the loss.

10.1.2 High Level Procedure - Calgon Samples

10.1.2.1 Weigh 2 g of sample into a 40 mL vial. Record the weight to the nearest 0.1 g in the appropriate column on the TALS LIMS worksheet. Use 2 g of sodium sulfate for the method blank and the LCS.

10.1.2.2 Add 2 grams of sodium sulfate to each sample and mix well.

10.1.2.3 Add 1 mL of surrogate to all samples including QC samples. Add 1 mL of the matrix spike solution to the LCS, MS and MSD. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database.

NOTE: Add the surrogates and matrix spiking compounds to the sample aliquot after mixing the sample with the sodium sulfate drying agent. This will be done in accordance with the memorandum from the USEPA dated August 5, 2010, which supersedes previous Method instructions (see Attachment 1). The EPA points out in the memorandum that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix.

10.1.2.4 Add 19.0 mL of extraction solvent (18.0 mL to the LCS, MS, MSD) so that the final volume is 20.0 mL. The extraction solvent is as follows:

10.1.2.5 For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the solvent is hexane.

10.1.2.6 For GC/MS semivolatiles, the solvent is methylene chloride.

10.1.2.7 Shake each sample for 2 minutes.

10.1.2.8 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the extract through the glass wool into a suitable container.

10.1.2.9 If the samples do not require cleanups or additional concentration, than the 20 mL extract is ready for analysis

10.1.2.10 If cleanups (PT-OP-028) or additional concentration (10.4) are required, collected a standard volume (i.e., 10.0 mL, which represents ½ of the extract). Either account for the "loss" of half of the extract in the final sample calculations, or concentrate the extract to ½ of the standard final volume to compensate for the loss.

10.1.3 Sonicator Tuning:

10.1.3.1 Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

10.2 Accelerated Soxhlet (Soxtherm®):

Refer to Figure 2 – Accelerated Soxtherm Extraction (Soxtherm) flowchart.

10.2.1 Decant and discard any water layer on a sediment/soil sample. **Note:** For sediment samples associated with most Dredged Material Management projects, the water layer is considered part of the whole sediment and should not be decanted, but re-mixed into the sample. Check project requirements before decanting any water layer. Homogenize the sample by mixing thoroughly.

10.2.2 Tissue samples should be homogenized prior to extraction. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client. Document in the TALS LIMS worksheet if a water layer was discarded.

10.2.3 For wipe samples, the entire contents of the original sample container will be extracted (i.e., no subsample will be taken) following the procedure for solid samples.

10.2.4 Remove surrogate and matrix spiking solutions from the refrigerator and allow these solutions to warm to room temperature.

10.2.5 Weigh 15 g of sample ± 0.5 g (30 g for sediments due to the assumption of 50% moisture) into a beaker, recording the weight to the nearest 0.1 g on the TALS LIMS worksheet. Use 15 g of 50:50 sodium sulfate/magnesium sulfate for the method blank and LCS. Add 15 g of anhydrous 50:50 sodium sulfate/magnesium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/50:50 sodium sulfate/magnesium sulfate mixture to a soxtherm thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the thimble is required.

10.2.5.1 Sample weights less than 15 g but over 5 g may be used if the appropriate reporting limits can be met.

10.2.6 Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using 50:50 sodium sulfate/magnesium sulfate as the matrix for the MB and LCS. Use a new, clean gauze pad as the blank matrix for wipe samples and follow the procedure for extraction of solid samples. The weight of 50:50 sodium sulfate/magnesium sulfate used should be approximately the weight of soil used in each sample.

10.2.7 Add the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to PT-OP-WI-001 for details of the spiking solutions. Record spiking volumes and standard numbers on the TALS LIMS worksheet. Return spiking solutions promptly to refrigerator.

NOTE: Add the surrogates and matrix spiking compounds to the sample aliquot after mixing the sample with the sodium sulfate drying agent. This will be done in accordance with the memorandum from the USEPA dated August 5, 2010, which supersedes previous Method instructions (see Attachment 1). The EPA points out in the memorandum that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix.

Note: The same volume of surrogates and matrix spiking compounds is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

10.2.8 Place thimble in beaker containing clean boiling chips and add approximately 140 mL of solvent (see below). Place beakers into positions on the accelerated soxtherm unit. Run the appropriate program for the extraction solvent. Periodically, check the system for leaks at the joints.

10.2.8.1 For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the extraction solvent is 1:1 hexane/acetone except if GPC cleanup is being done. If GPC cleanup is being done, the extraction solvent is 1:1 methylene chloride/acetone.

10.2.8.2 For all other parameters, the extraction solvent is 1:1 methylene chloride/acetone.

10.2.9 Upon completion of the program, remove the beaker from the accelerated soxtherm unit and dispose of the extracted sample.

10.2.10 Collect the extract in a K-D or other glass container. Rinse the flask that contained the solvent extract with 5-10 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

10.2.11 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.4 for concentration and PT-OP-028 for cleanup.

10.3 Waste Dilution:

10.3.1 This method is used for materials that are soluble in an organic solvent.

10.3.2 Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

10.3.3 Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, and then discard the solvent.

10.3.4 Tare the vial, and then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.1 g.

10.3.5 Add 1 mL of surrogate solution to each sample. Add 1 mL of matrix spike solution to the MS, MSD and LCS. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database.

10.3.6 Dilute to 10 mL with the appropriate solvent (hexane for organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners); acetonitrile for PAHs by HPLC; methylene chloride for GC/MS semivolatiles).

10.3.7 Add 2 g $\pm$ 0.1 g sodium sulfate to the sample. Cap and shake for 2 minutes.

10.3.8 Add 4-5 g sodium sulfate to a small funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

10.3.9 Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 40 mL for method 8082 and 10 mL for method 8270.

10.3.10 Label the sample, which is now ready for cleanup or analysis.

10.4 Concentration:

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 1 for the appropriate final volumes and concentrations.

Refer to Figure 3 – Concentration and Cleanup flowchart.

10.4.1 Kuderna-Danish (KD) Method:

10.4.1.1 Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. For procedures where the final volume is 10 mL, a 250 mL Erlenmyer flask may be used as an alternative to the KD flask.

10.4.1.2 Add one or two clean boiling chips and the dried extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).

10.4.1.3 Place the KD apparatus on a water bath (80-90^{o}C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

10.4.1.4 Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (see Table 1) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 1 for details on final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent.

An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add 10 mL of exchange solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

10.4.1.5 Remove the KD apparatus from the water bath and allow it to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

10.4.1.6 If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 10.4.2.

10.4.2 Nitrogen Evaporation to Final Concentration

10.4.2.1 Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

10.4.2.2 Place the tube in a warm water bath that is at approximately 35^{o}C and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

10.4.2.3 During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through the process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

Vial Calibration Note: Using a Class A volumetric pipette dispense the appropriate volume of solvent into the vial being calibrated, mark the meniscus and use this vial when marking the final volume line on subsequent sample vials. See SOP PT-QA-026 and work instruction PT-QA-WI-008 for details.

10.4.2.4 An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

11.0 CALCULATIONS / DATA REDUCTION

Not applicable.

12.0 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

13.0 POLLUTION CONTROL

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2 Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

14.0 WASTE MANAGEMENT

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1 Methylene Chloride extraction waste. This waste is collected in waste containers identified as "Methylene Chloride Waste", Waste #2.

14.1.2 Extracted water samples. This waste is collected in a waste container identified as “Extraction Water”, Waste #35. The bottom organic layer is drained into a container identified as “Methylene Chloride Waste”, Waste #2. The remaining aqueous layer is neutralized to a pH between 6 and 9 and discharged down lab sink/ drain.

14.1.3 Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride from the extract drying step. This waste is collected in a container identified as “Lab Trash Waste”, Waste #12.

14.1.4 Assorted flammable solvent waste from various rinses. This waste is collected in waste containers identified as “Mixed Flammable Solvent Waste”, Waste 3.

14.1.5 Methylene chloride waste from various rinses. This waste is collected in waste containers identified as “Methylene Chloride Waste”, Waste #2.

14.1.6 Miscellaneous disposable glassware contaminated with acids, caustics, solvents and sample residue. This waste is collected in a container identified as “Lab Trash Waste”, Waste #12.

15.0 REFERENCES – CROSS-REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3541 and 3550B

15.2 Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Update IV, Methods 3500C, Method 3550C and Method 3620C, Rev. 3, February 2007

15.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update IV, Revision 2, February 2007, Method 8141B

15.4 “Spiking (Prior To vs. After Sample Drying) Issue in SW-846 Organic Extraction Methods” Memorandum, United States Environmental Protection Agency, Washington DC, 20460. Dated August 5, 2010

15.5 Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001)

15.6 SOP PT-QA-001, Employee Training and Orientation.

15.7 SOP PT-QA-003, Glassware Clean-up for Organic/Inorganic Procedures

15.8 SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.9 SOP PT-QA-007, Determination of Method Detection Limits (MDL)

15.10 SOP PT-QA-008, Thermometer Calibration and Temperature Monitoring

15.11 SOP PT-QA-012, Selection and Calibration of Balances and Weights

15.12 SOP PT-QA-016, Nonconformance and Corrective Action System

15.13 SOP # PT-QA-021, Quality Control Program

15.14 SOP PT-QA-026, Container Accuracy Verification – Gravimetric

15.15 SOP PT-QA-031, Internal Chain of Custody

15.16 Pittsburgh Facility Addendum EH&S Manual, PT-HS-001

15.17 PT-OP-WI-001, TestAmerica Pittsburgh Organic Prep Work Instruction for Initial/Final Volumes, Exchange Solvents, LCS and Matrix Spiking Components and Concentrations

16.0 METHOD MODIFICATIONS

16.1 Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

17.0 ATTACHMENTS

17.1 Table 1 – Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids), Method 8270C and 8270D.

17.2 Table 2 – Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids), Methods 8081A, 8081B, 8082, 8082A, 8141A and 8141B

17.3 Figure 1 – Sonication Extraction

17.4 Figure 2 – Accelerated Soxtherm Extraction (Soxtherm)

17.5 Figure 3 – Concentration and Cleanup

17.6 Attachment 1 - USEPA Memorandum on Spiking Prior to vs. After adding drying agent.

18.0 REVISION HISTORY

18.1 Revision 0, 10/2/2015

18.2 Revision 1, 7/20/2016

18.3 Changes to current revision

SOP section	Change from	Change to	Reason
9.1.1		Added “Insufficient Volume” NCM	Clarification
9.4.1 and 10.2.6	MB/LCS matrix sodium sulfate	MB/LCS matrix 50:50 sodium sulfate/magnesium sulfate	PADEP Audit Findings C78 and C88

Table 1
Initial Weights and Final Volumes per Matrix and Method

Method	Matrix	Initial Sample Weight (g)	Surrogate & Matrix Spike Volume (mL)	Final Extract Volume (mL)
Semivolatiles				
8270 / 3541	Soil	15		5.0
	Sediment	30		5.0
	Tissue	15		5.0
8270_LL / 3541_LL	Soil	15		0.5
	Sediment	30		0.5
8270 / 3550	Solid	2.0		20
8270 / 3580	Solid	1.0		10
Pesticides				
8081 / 3541	Soil	15		20
	Sediment	15		10
	Tissue	15		20
8081_LL / 3541_LL	Soil	15		1.0
	Sediment	30		0.5
8081 / 3580	Solid	1.0		40
PCBs				
8082 / 3541	Soil	15		20
	Sediment	15		10
	Tissue	15		20
8082_LL / 3541_LL	Soil	30		1.0
	Sediment	30		1.0
8082 Congeners				
8082 / 3541	Soil	10		20
	Sediment	10		10
O-P Pesticides				
8141 / 3541	Soil	15		2.5
	Sediment	24		2.0
	Tissue	15		2.5
8141_LL / 3541_LL	Soil	30		1.0

Figure 1 – High Level Sonication Extraction

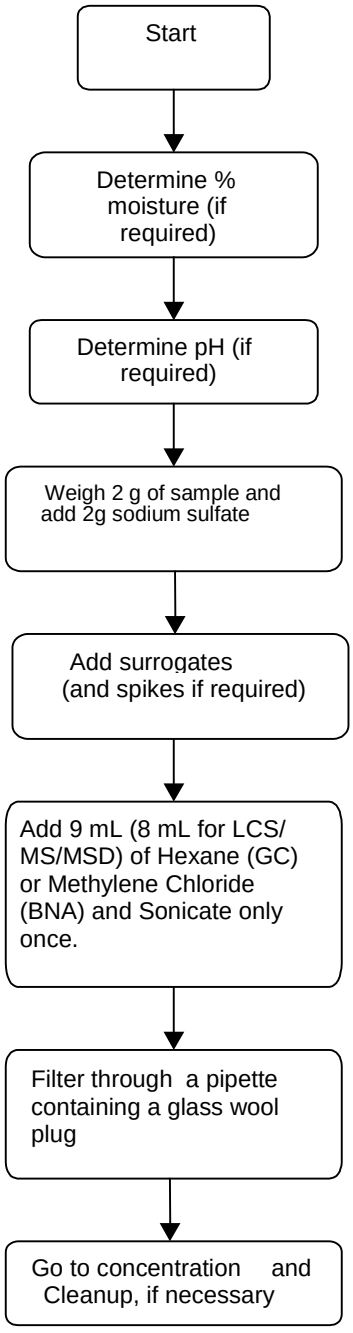


Figure 2 - Accelerated Soxtherm Extraction (Soxtherm®)

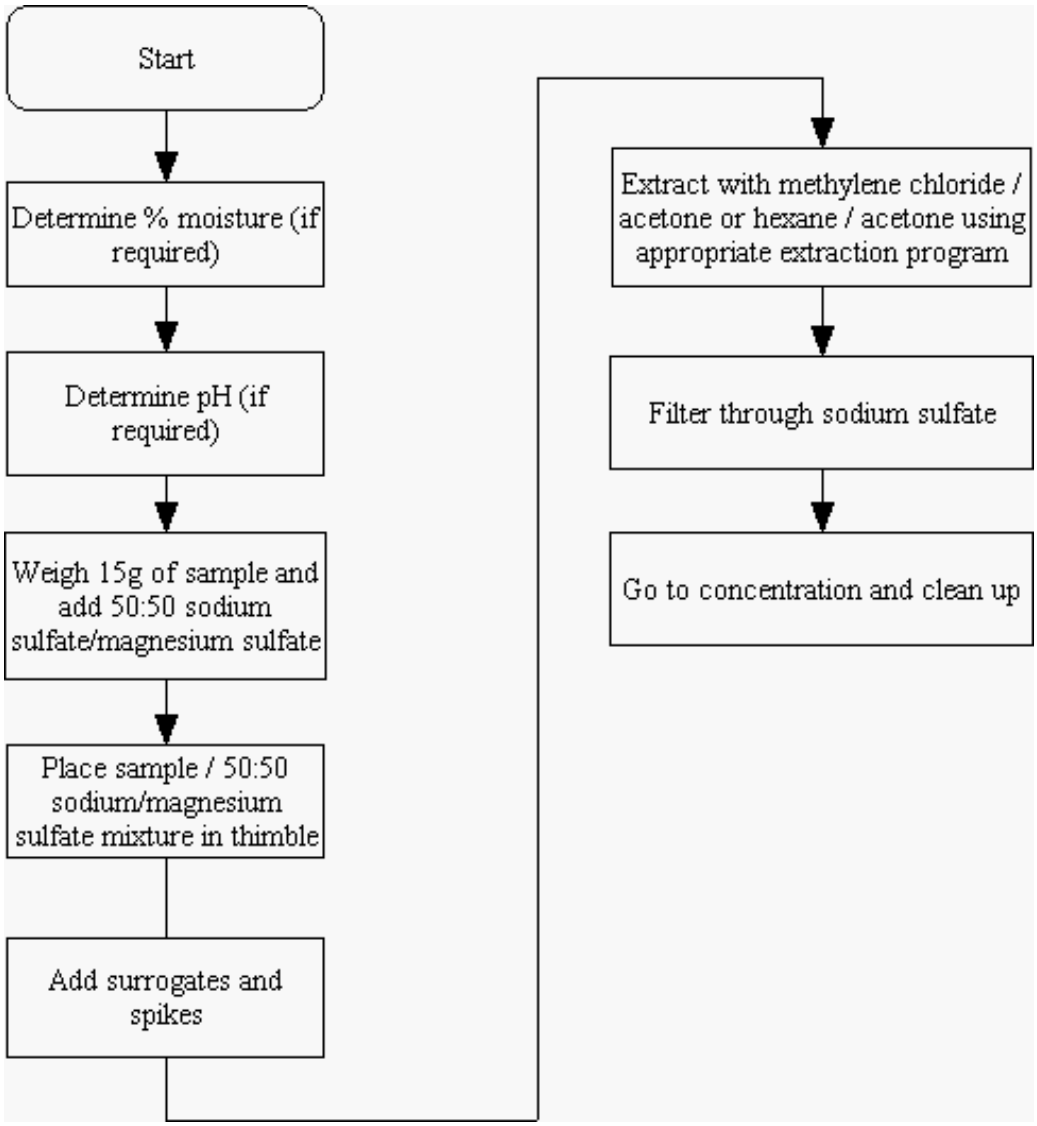
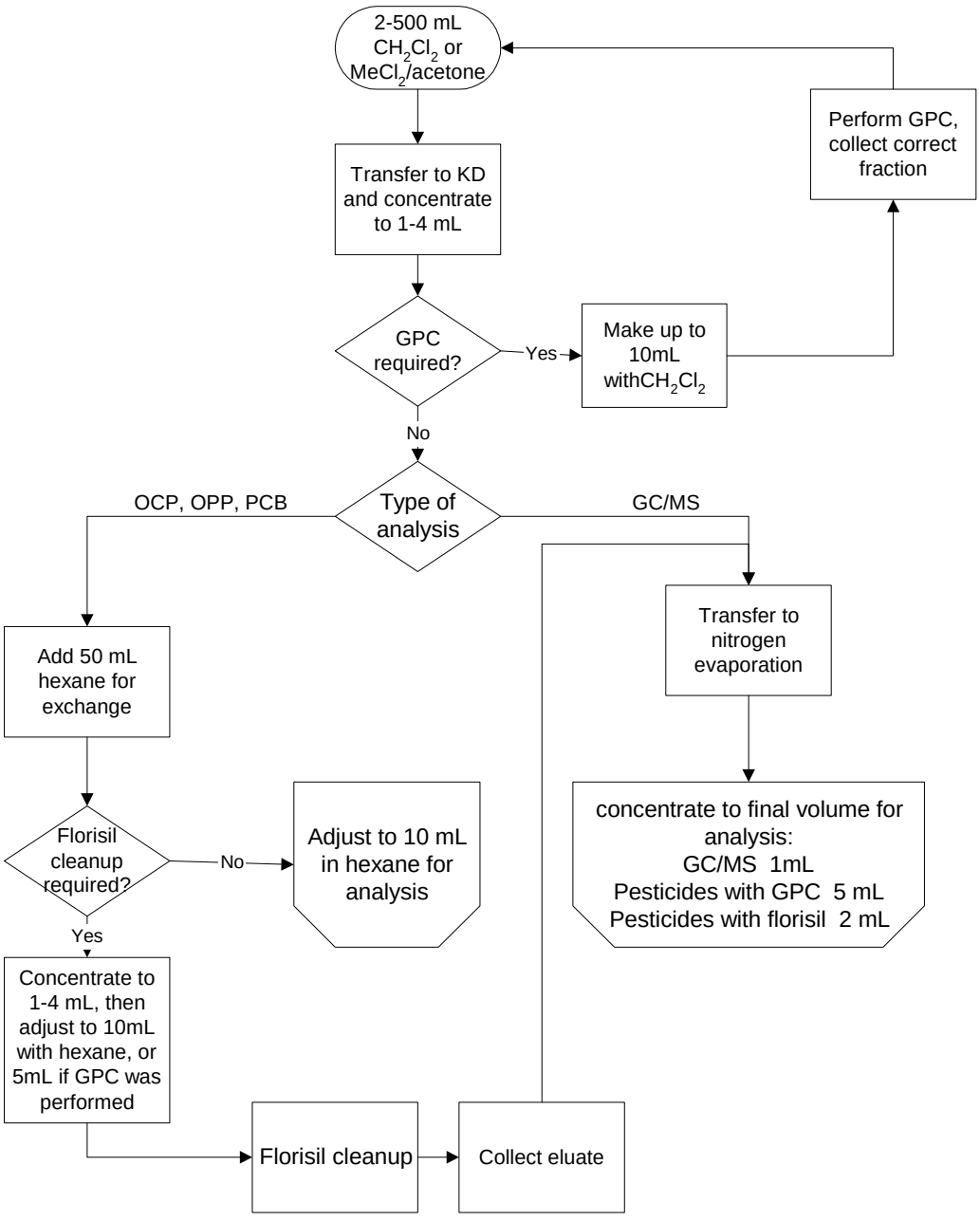


Figure 3 - Concentration and Cleanup



ATTACHMENT 1: MEMORANDUM from USEPA concerning Spiking Procedures in SW-846 Solid Extraction methods.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF SOLID WASTE
AND EMERGENCY RESPONSE

AUG 5 2010

MEMORANDUM

SUBJECT: Spiking (Prior To vs. After Sample Drying) Issue in SW-846 Organic Extraction Methods

FROM: James Michael, Chief, Waste Characterization Branch
Materials Recovery and Waste Management Division (MC-5304P)
Office of Resource Conservation and Recovery, USEPA

TO: EPA Regional Laboratory Directors I-X
EPA Regional QA Officers I-X
User Community for the SW-846 Methods Manual

This letter is to inform you that the Office of Resource Conservation and Recovery (ORCR, formally OSW) is currently evaluating a quality control (QC) spiking inconsistency that commercial and EPA regional laboratories raised for the extraction of semivolatile and nonvolatile organic compounds in solids. In the interim, we are recommending that you not follow the cautionary notes in three SW-846 methods, specifically the notes in Section 9.3.1 of Method 3500C (for organic extraction and sample preparation), and Section 11.5 of Method 3545A (pressurized fluid extraction) and Section 11.3 of Method 3550C (ultrasonic extraction).

These cautionary notes were inserted into three Update IV SW-846 methods that were published on January 3, 2008 (73 FR 486-489). These notes state that, "it is CRITICAL that any compounds added to a sample, including surrogates, are added to the sample aliquot PRIOR TO any additional processing steps. This means that the surrogates and matrix spike compounds should be added to the sample PRIOR TO adding drying agents such as sodium sulfate to solid samples." The note in Method 3500C further states that, "As each 3500 series extraction procedure is revised, the order of the procedural steps will be made consistent with this note. However, until such time as all those methods are revised, the instructions in this note SUPERSEDE those in each extraction method."

Commercial and EPA Regional laboratories have pointed out that adding surrogates and other spiked compounds to environmental and QC samples prior to mixing with drying agents may cause major recovery issues depending on the analyte and/or the matrix. Additional instructions requiring evaporation of the solvent from the surrogate and spiking solutions compound the problem. For example, when the spike solutions are added to a clay sample, they may roll off without absorption to the matrix. The spiking solvent could evaporate quickly, before the solutions can be effectively mixed with the sample. Spiking in this manner has been

shown to cause considerable losses of the more volatile and light-sensitive compounds, resulting in poor recovery. One study showed recovery for more than 1/3 of the semivolatile analyte list can easily drop 50-100%.

In addition, we found that there is no such cautionary note in two other organic extraction methods that were published at the same time as the three above mentioned methods. These two methods, specifically Methods 3546 (microwave extraction) and 3562 (super critical fluid extraction), recommend spiking surrogates and other compounds after the sample drying procedure.

At this time ORCR is evaluating the information and records that were used in support of said spiking procedural change; communicating with commercial labs; and reviewing Department of Defense and Contract Laboratory Program protocols to verify what spiking protocols the analytical community is following. We plan on working with commercial and EPA Regional laboratories to acquire data for ORCR's consideration to resolve this spiking inconsistency and revise those three methods as necessary. Until that time, ORCR recommends that you not follow the language in these notes.

Should you have question regarding this issue, please contact Shen-yi Yang, of my staff at (703) 308-0437.

cc: Shen-yi Yang, MRWMD
Kim Kirkland, MRWMD
Charles Sellers, MRWMD
Mark Baldwin, MRWMD

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Cleanup of Organic Compounds from Waters, Solids, Sediments, Tissue and Wipes

Method(s): SW846 3600 Series and CarboPrep 90

Approvals (Signature/Date):

11/4/2015	11/4/2015
Sharon Bacha Date	Steve Jackson Date
Organics Department Manager	Regional Safety Coordinator
11/4/2015	11/4/2015
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

This SOP was formerly part of PT-OP-001

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes cleanup procedures that are appropriate for the target analytes of interest. These cleanup procedures are applied to the extracts prepared by one of the extraction methods, to eliminate sample interference.

1.2 Cleanup procedures for the following determinative methods are covered: 8081A, 8081B, 8082, 8082A, 8082A Congeners, 8141A, 8141B, 8270C and 8270D.

1.3 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 Cleanup Procedures are presented for removing interferents from sample extracts.

3.0 DEFINITIONS

3.1 Definitions of terms used in this SOP may be found in the glossary of the Pittsburgh Quality Assurance Manual (PT-QA-M-001).

3.2 TALS – TestAmerica Laboratory Information Management System

3.3 NCM – Non-Conformance Memo – a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch or a QC failure.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Florisil and Silica Gel cartridges may contain phthalate esters which can interfere with many method analytes, not just the phthalate esters themselves; the copper technique for sulfur cleanup requires that the copper powder be very reactive, however care must be taken to remove all traces of the acid used to prepare the copper in order to avoid degradation of some analytes; the sulfuric acid/permanganate technique will not destroy chlorinated benzenes, chlorinated naphthalenes and a number of chlorinated pesticides; and the CarboPrep Cartridge method interferes with TCMX surrogate recovery, however the Carboprep Quick method does not show the same issue.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

5.3 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE:** This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit[i]	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Florisil	**Irritant**	**TLV 10mg/m^3 PEL 5mg/m^3**	**May cause irritation if inhaled or adsorbed through the skin.**
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sulfuric Acid[ii]	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Copper Powder	Flammable Irritant	1 mg/m^3 - TWA	If swallowed, wash out mouth with water, provided person is conscious, then call a physician; if inhaled, remove to fresh air, CPR if not breathing and oxygen if difficulty in breathing; In case of skin contact, flush the affected area for 15 minutes with water. Remove contaminated clothing and shoes and call a physician; In case of contact with the eyes, flush with water for at least 15minutes. Assure adequate flushing by separating the eyelids with the fingers. Call a physician.
Tetrabutyl-ammonium hydrogen sulfate	Irritant	None listed	Irritant to the skin, eyes, digestive tract (if swallowed) and respiratory tract (if inhaled). Flush skin and eyes with water for 15 minutes, then seek medical attention; If ingested, DO NOT induce vomiting, instead rinse mouth and drink 2-4 cupfuls of milk or water, then seek medical attention; If inhaled, get fresh air immediately. If difficulty in breathing persists give oxygen then seek medical attention.
Sodium sulfite	Irritant	5 mg/m^3 - TWA	Inhalation may cause irritation to the mucous membranes of the upper respiratory tract. Ingestion may cause gastric irritation by the liberation of sulfurous acid. Large doses may result in circulatory disturbances, diarrhea and CNS depression. Estimated fatal dose is 0.5 to > 5g/kg. May cause skin and eye irritation, redness and pain.
Potassium Permanganate	Oxidizer	5 mg/m^3 – for Mn compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.

[i] Exposure limit refers to the OSHA regulatory exposure limit.
[ii] Always add acid to water to prevent violent reactions.

5.4 Eye protection that protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

6.0 EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	Silica Gel	CarboPrep 90	Acid-Base Partition
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	X						
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	X						
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	X						
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.	X						
Strip chart recorder, recording integrator, or laboratory data system.	X						
Syringe: 10 mL with Luerlok fitting.	X						
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	X						
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	X						
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		X					
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		X					
Vacuum pressure gauge.		X					
Rack for holding 10 mL volumetric flasks in the manifold.		X					
Mechanical shaker or mixer: Vortex Genie or equivalent.			X	X			
Separatory Funnels with Ground-Glass Stoppers: 125 m L or 250 mL			X				X

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid	Silica Gel	CarboPrep 90	Acid-Base Partition
Erlenmeyer Flasks: 125 mL	X						X
Disposable Pipettes		X	X	X			
Culture tubes: 10 mL, 16 mmx100 mm	X	X	X	X	X	X	
0.45µm syringe filter						X	

7.0 REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

7.1 Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid	Silica Gel	CarboPrep 90	Acid-Base Partition
Methylene Chloride	X						X
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (catalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		X					
Tetrabutylammonium hydrogen sulfate			X				
Sodium sulfite			X				
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			X				
2-Propanol			X				
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.						X	
Sulfuric acid, Concentrated				X			
Sodium hydroxide, Pellets		X					
Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water		X					X
Silica Gel Cartridge – Restek Part No. 24038					X		
Hexane				X	X		
CarboPrep 90 SPE Cartridge						X	
CarboPrep 90 Bulk Reagent						X	
1 :1 Sulfuric Acid							X

7.2 Standards

7.2.1 GPC calibration solution: prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride; however, it is soluble in warm corn oil. Therefore, weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard expires 6 months after preparation.

8.0 SAMPLE COLLECTION PRESERVATION, SHIPMENT AND STORAGE

8.1 Holding Times are not applicable to Cleanup procedures.

9.0 QUALITY CONTROL

9.1 All QC extracted with the sample batch according to SOP PT-OP-001 or PT-OP-026 is put through the clean-up procedure along with the samples.

10.0 PROCEDURE

10.1 Cleanup Techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity.

10.2 Gel Permeation Chromatography (GPC)

GPC is a generally applicable technique which can be used for cleanup of extracts for Semivolatiles (8270), Organochlorine pesticides (8081A/8081B), PCBs (8082/8082A), and Organophosphorus Pesticides (8141A/8141B) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., or equivalent. For GPC instrument operation see Appendix A.

10.2.1 GPC Column Preparation

10.2.1.1 Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

10.2.1.2 Add approximately 300 mL of methylene chloride and stir gently.

10.2.1.3 Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

10.2.1.4 Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

10.2.1.5 Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

10.2.1.6 Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible, with one continuous pour, trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

10.2.1.7 Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

10.2.1.8 Push the plunger until it meets the gel, and then compress the column bed about 4 cm.

10.2.1.9 Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

10.2.1.10 After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000”ID x 2”) in the outlet tube from the UV detector will prevent bubble formation, which causes a noisy UV baseline. The restrictor will not affect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

10.2.1.11 When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

10.2.2 Initial Calibration of the GPC Column

10.2.2.1 Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.2.2.2 Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22^{o}C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

10.2.2.3 Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 10.1.1.7.1):

10.2.2.4 Peaks must be observed and should be symmetrical for all compounds in the calibration solution.

10.2.2.5 Corn oil and phthalate peaks must exhibit >85% resolution.

10.2.2.6 Phthalate and methoxychlor peaks must exhibit >85% resolution.

10.2.2.7 Methoxychlor and perylene peaks must exhibit >85% resolution.

10.2.2.8 Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

10.2.2.9 A UV trace that does not meet the above criteria indicates the need for system maintenance and/or the need for a new column.

10.2.3 Determine appropriate collect and dump cycles.

10.2.3.1 The calibrated GPC program for organochlorine pesticides/PCB Aroclors should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

10.2.3.2 For GC/MS semivolatile and PAHs by HPLC extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

10.2.3.3 For PCB Congeners and Organophosphorus pesticides, this collection window should be appropriate but needs to be verified with spike solutions containing all analytes of interest.

10.2.3.4 Reinject the calibration solution after appropriate dump and collect cycles have been set.

10.2.3.5 Measure and record the volume of collected GPC eluate in a graduated cylinder.

10.2.3.6 The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

10.2.4 GPC calibration check

10.2.4.1 Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use. Ensure that UV trace requirements, flow rate and column pressure criteria are acceptable. Also, the retention time shift must be <5% when compared to retention times in the last calibration (previous week) UV trace. This means checking the retention time shift against the previous week's calibration and the RT shift must be <5%.

10.2.4.2 Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than ± 5% use this run as the start of a new initial calibration. Otherwise, proceed with the

recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

10.2.5 GPC Recovery Check for Organochlorine Pesticides/ PCB Aroclors

10.2.5.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 mL of the organochlorine pesticide matrix spiking solution (See PT-OP-WI-001) to 10 mL in methylene chloride. The second mixture is prepared by diluting 1 mL of the PCB Aroclor matrix spiking solution (see PT-OP-WI-001) to 10 mL with methylene chloride.

10.2.5.2 Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCB Aroclors only, then the pesticide recovery check is not necessary.

10.2.5.3 After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 10.2.

10.2.5.4 The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-110% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

10.2.6 GPC Recovery Check for All other Semivolatiles

10.2.6.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Dilute 1.0 mL of the GC/MS semivolatiles matrix spiking solution (PT-OP-WI-001) to 10 mL in methylene chloride for GC/MS Semivolatiles and PAHs by HPLC. For PCB Congeners and Organophosphorus pesticides, a solution containing all analytes of interest should be prepared in 10 mL of methylene chloride.

10.2.6.2 Load the spike mixture and a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

10.2.6.3 After collecting the GPC recovery check fraction, concentrate to 0.5 mL, and analyze by GC/MS for the GC/MS Semivolatiles and PAHs by HPLC. Analyze by GC/ECD for the PCB Congeners and GC/FPD for the Organophosphorus pesticides. Refer to the concentration section 10.2.

10.2.6.4 Recovery of the spiked analytes should be at least 60%. The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

10.2.7 Sample Extract Cleanup

10.2.7.1 Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 10.2.

10.2.7.2 Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 22^{o}C. The normal backpressure is 6-10 psi.

10.2.7.3 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

10.2.7.4 Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

10.2.7.5 Load the filtered samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B.

10.2.7.6 Set the collect, dump, and wash times determined by the calibration procedure.

10.2.7.7 Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

10.2.7.8 Collect each sample in a suitable glass container. Monitor sample volumes collected.

10.2.7.9 Any samples that were loaded into 2 or more positions must be recombined.

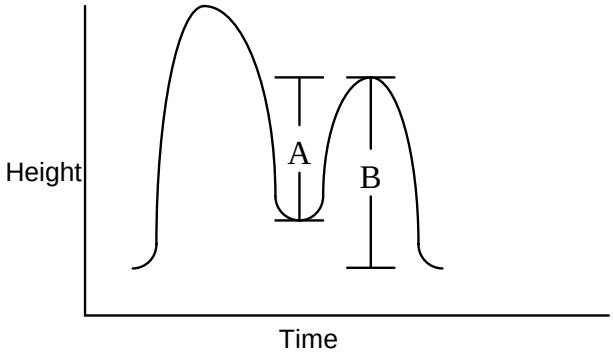
10.2.7.10 Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 10.2.

10.2.7.11 Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 10.2.

10.2.8 Calculations

10.2.8.1 Resolution: To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution } = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak

B = peak height of smaller peak

10.2.8.2 Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

10.2.8.3 Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

10.3 Florisil Cartridge Cleanup

Florisil cleanup is generally used for organochlorine pesticides (8081A/8081B/608) and PCB (8082/8082A/608), although it may be applied to other analytes. It separates compounds of different polarity from the target analytes. Sections 10.2.1 through 10.2.8 outline the procedure for organochlorine pesticides, while section 10.2.9 outlines modifications required for PCBs.

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assembly, or equivalent.

10.3.1 Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to SOP PT-OP-001 or PT-OP-026 for details of extract concentration.

10.3.2 Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

10.3.3 Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

10.3.4 Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

10.3.5 Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

10.3.6 After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

10.3.7 The organochlorine pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

10.3.8 Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the N-evap concentration Section 10.3.

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of Organochlorine Pesticide Calibration Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

10.3.9 Modifications for PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

10.4 Sulfur Removal

Sulfur cleanup is generally applied to sample extracts for analysis by methods 8081A/8081B, 8082/8082A, and 608 because the Electron Capture Detector (ECD) responds strongly to sulfur. It is performed after GPC and/or Florisil cleanup, if necessary.

10.4.1 Sulfur can be removed by one of two methods: copper or tetrabutylammonium sulfite (TBA) according to laboratory preference. The TBA procedure is the laboratory default procedure. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

10.4.2 Sulfur Removal with Copper

10.4.2.1 Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

10.4.2.2 Add approximately 2 g of cleaned copper powder to the sample extract tube.

10.4.2.3 Mix for one minute on a mechanical shaker.

10.4.2.4 If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

10.4.2.5 Transfer the supernate to a clean vial.

10.4.3 Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

10.4.3.1 Transfer 1.0 mL of sample extract into a culture tube.

10.4.3.2 Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

10.4.3.3 If a precipitate does not form, add sodium sulfite in approximately 0.1g portions until a solid residue remains after repeated shaking.

10.4.3.4 Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 10.1.3.3.1.

10.5 Sulfuric Acid Cleanup

This cleanup is only performed on extracts requiring PCB analysis (Aroclors and Congeners) because most organic matter is destroyed by sulfuric acid.

10.5.1 Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

10.5.2 Shake or vortex for about thirty seconds and allow extract to settle. (Centrifuge if necessary)

10.5.3 Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial.

10.5.4 **Caution:** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

10.5.5 If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

10.5.6 Properly dispose of the acid waste.

10.6 Silica Gel Cleanup

This cleanup is only performed on extracts requiring PCB analysis (Aroclors and Congeners).

10.6.1 A 1g silica gel cartridge, Restek part number 24038 or equivalent, is utilized.

10.6.2 Condition the cartridge with 4 mL of Hexane. Slowly open the cartridge valves to allow the hexane to pass through the sorbent beds to the lower frit. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes.

10.6.3 Slowly open cartridge valves to allow the hexane to pass through the cartridge. Close the cartridge valve when there is still approximately 1 mm of solvent above the sorbent bed.

10.6.4 Transfer 2 ml of sample to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2mL per minute.

10.6.5 When the entire extract has passed through the cartridge, but before the cartridge becomes dry, rinse the sample vial with 0.5mL of solvent, and add to the cartridge to complete the quantitative transfer.

10.6.6 Close the cartridge valve ensuring that the cartridge never goes dry.

10.6.7 Place a test tube into the sample rack corresponding to the cartridge position.

10.6.8 Add 5mL of hexane to the cartridge. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the test tube. Close the cartridge valve. Remove sample and concentrate down to the final volume using an N-Evap, see section 10.3. This eluate will contain the PCBs as well as Heptachlor, Aldrin, 4,4'-DDE, and 4,4'-DDT.

10.7 CarboPrep 90 Cleanup

This cleanup is only performed on extracts requiring analysis for Organichlorine Pesticides and/or PCBs.

10.7.1 Cartridge Method

10.7.1.1 Put approximately 2 ml of sample extract into a test tube and mark the sample volume on the tube.

10.7.1.2 Condition the cartridge by adding 2 ml of methylene chloride and allowing it to drip through the cartridge. Do not allow the cartridge packing to go dry in this or any subsequent step, until the final rinse has been completed.

10.7.1.3 Add 2 ml of hexane/methylene chloride (80%/20%) mixture and allow it to drip through the cartridge until almost empty.

10.7.1.4 Add the sample extract to the cartridge and place the test tube under the cartridge to collect the liquid as it drips through.

10.7.1.5 Rinse 3 times with 2 ml aliquots of hexane/methylene chloride (80%/20%) mixture, while not allowing the cartridge to go dry. After the final rinse, use a pipette bulb to force out all of the remaining liquid in the cartridge.

10.7.1.6 Concentrate the sample extract back down to the original volume according to the mark on the test tube using the N-Evap process in section 10.3. The extract is now ready for analysis.

10.7.1.7 **NOTE:** When using the Carboprep Cartridge Method the recovery of the TCMX surrogate is poor.

10.7.2 Quick Method

10.7.2.1 Add a half scoop of Carboprep 90 to approximately 2 ml of sample extract. Swirl for about one minute and allow the extract to settle. Add a half scoop of Copper Granules to 1 mL of sample or a whole scoop to 2 mL of sample, cap the vial and shake vigorously for 2 miuntes. Pipette out an aliquot of extract and filter through a 0.45 µm syringe filter. The extract is now ready for analysis.

10.7.2.2 Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Any affected samples are re-analyzed.

10.7.2.3 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

10.7.2.4 Compounds extracted from the sample matrix to which the detector will respond, such as single-component chlorinated pesticides, including the DDT analogs (DDT, DDE, and DDD).

Note: A standard of the DDT analogs should be injected to determine which of the PCB or Aroclor peaks may be subject to interferences on the analytical columns used. There may be substantial DDT interference with the last major Aroclor 1254 peak in some soil and sediment samples.

10.8 Acid-Base Partition

10.8.1 Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL or 250 mL separatory funnel.

10.8.2 Add 20 mL of methylene chloride to the separatory funnel.

10.8.3 Slowly add 20 mL of prechilled DI water which has been previously adjusted to a pH of 12-13 with 10N sodium hydroxide.

10.8.4 Seal and shake the separatory funnel for at least 2 minutes with periodic venting to release excess pressure.

10.8.5 Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If the emulsion interface between layers is more the one-third the size of the solvent layer, use mechanical techniques such as stirring, filtration of the emulsion through glass wool, centrifugation or other physical methods to complete the phase separation.

10.8.6 Drain off the aqueous phase into a 125 Erlenmeyer flask. Repeat the extraction 2 more times using 20 mL aliquots of dilute sodium hydroxide (pH 12-13) collecting the aqueous into the same 125 mL Erlenmeyer flask as the initial phase.

10.8.7 Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase, discard the methylene chloride and proceed to section 10.8.8. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to section 10.8.10.

10.8.8 Externally cool the 125 mL Erlenmeyer flask with ice while adjusting the aqueous phase to a pH of 1-2 with 1:1 Sulfuric Acid. Quantitatively transfer the cool aqueous phase to a clean 125 mL separatory funnel. Add 20 mL of methylene chloride to the separatory funnel and shake it for at least 2 minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

10.8.9 Add 20 mL of methylene chloride to the separatory funnel and extract a pH 1-2 a second and third time combining the extracts in the Erlenmeyer flask.

10.8.10 Dry the necessary fraction, acid or base/neutral, by passing it througha funnel containing anhydrous sodium sulfate. Collect the dried fraction in another Erlenmeyer flask. Rinse the Erlenmeyer flask which contained the solvent and pour through the anhydrous sodium sulfate to complete the quantitative transfer.

10.8.11 The fractions are now ready to be concentrated to the required final volume, proceed to section 10.9.

10.9 Concentration:

10.9.1 According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to PT-OP-WI-001 for the appropriate final volumes and concentrations.

10.9.2 Refer to Figure 1 – Concentration and Cleanup flowchart.

11.0 CALCULATIONS / DATA REDUCTION

Not applicable

12.0 METHOD PERFORMANCE

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

13.0 POLLUTION CONTROL

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2 Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

14.0 WASTE MANAGEMENT

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1 Methylene Chloride extraction waste. This waste is collected in waste containers identified as "Methylene Chloride Waste", Waste #2.

14.1.2 Extracted water samples. This waste is collected in a waste container identified as "Extraction Water", Waste #35. The bottom organic layer is drained into a container identified as "Methylene Chloride Waste", Waste #2. The remaining aqueous layer is neutralized to a pH between 6 and 9 and discharged down lab sink/ drain.

14.1.3 Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride from the extract drying step. This waste is collected in a container identified as "Lab Trash Waste", Waste #12.

14.1.4 Assorted flammable solvent waste from various rinses. This waste is collected in waste containers identified as "Mixed Flammable Solvent Waste", Waste 3.

14.1.5 Methylene chloride waste from various rinses. This waste is collected in waste containers identified as "Methylene Chloride Waste", Waste #2.

14.1.6 Spent sulfuric acid waste is collected in a container identified as "Acid Waste", Waste #5.

14.1.7 Miscellaneous disposable glassware contaminated with acids, caustics, solvents and sample residue. This waste is collected in a container identified as "Lab Trash Waste", Waste #12.

15.0 REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3600C, 3620B, 3640A, 3650B, 3660B, and 3665A

15.2 Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Update IV, Method 3620C, Rev. 3, February 2007

15.3 Restek CarboPrep 90 SPE Cartridge procedure

15.4 Pittsburgh Laboratory Quality Assurance Manual (PT-QA-M-001)

15.5 SOP PT-QA-001, Employee Training and Orientation

15.6 SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.7 SOP PT-QA-012, Selection and Calibration of Balances and Weights

15.8 SOP PT-QA-016, Nonconformance and Corrective Action System

15.9 SOP PT-QA-021, Quality Control Program

15.10 SOP PT-QA-026, Container Accuracy Verification – Gravimetric

15.11 SOP PT-QA-031, Internal Chain of Custody

15.12 Pittsburgh Facility Addendum EH&S Manual, PT-HS-001

15.13 PT-OP-WI-001, TestAmerica Pittsburgh Organic Prep Work Instruction for Initial/Final Volumes, Exchange Solvents, LCS and Matrix Spiking Components and Concentrations

16.0 METHOD MODIFICATIONS

16.1 None

17.0 ATTACHMENTS

17.1 Figure 1 – Concentration and Cleanup

17.2 Appendix A – GPC Operation

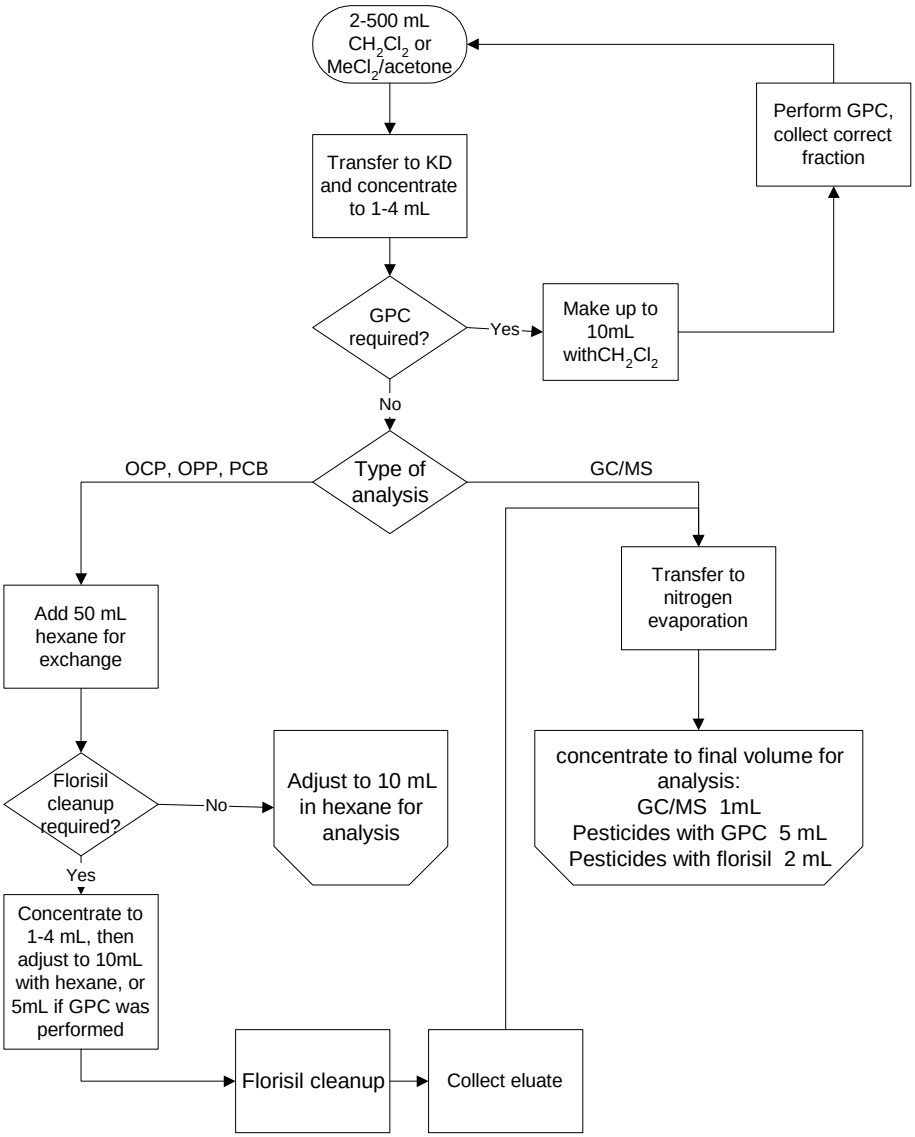
18.0 REVISION HISTORY

18.1 Original issue, 9/15/2015

18.2 Revision 1, 11/xx/2015

SOP section	Change from	Change to	Reason
Table under 5.3		Added NaOH to the Table	Correction
Table under section 6.1 and 7.1		Added the Acid-Base Partition equipment, supplies and reagents	Correction
10.8		Added Acid-Base Partition Procedure.	Correction
15.1		Added 3650B the Acid-Base Partition Method reference	Correction

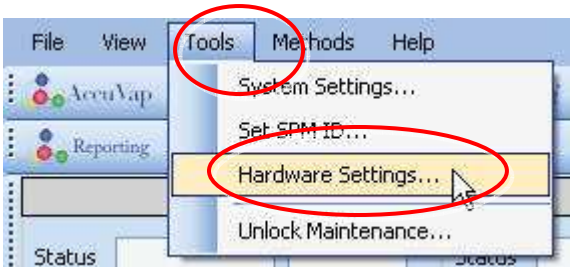
Figure 1 - Concentration and Cleanup



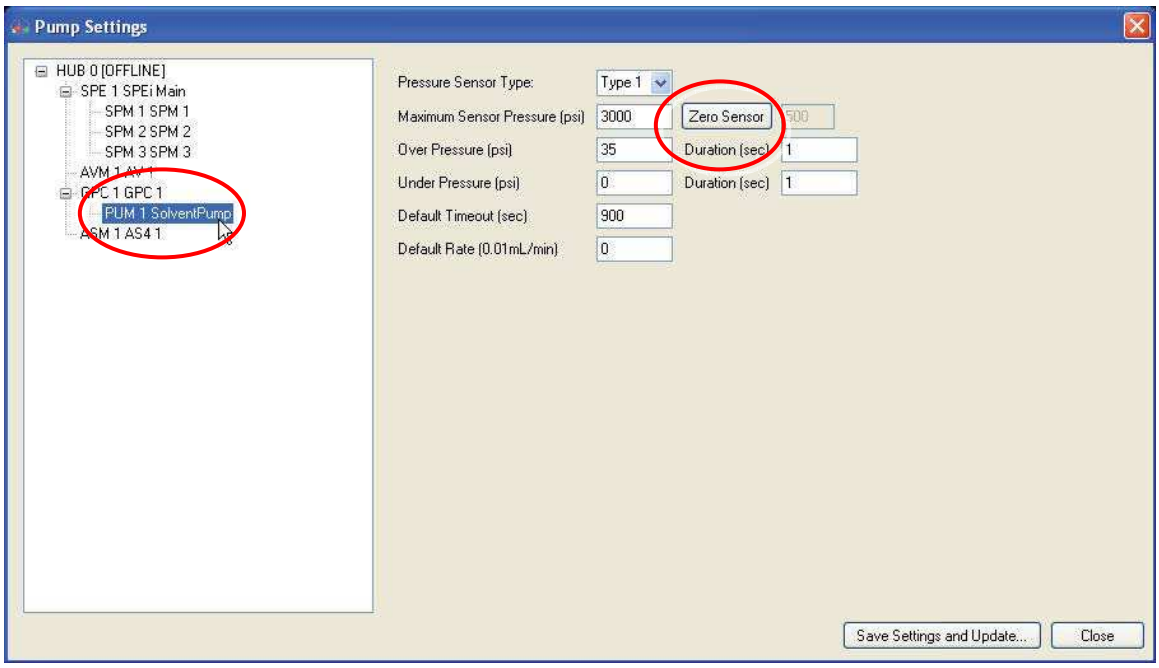
Appendix A
PrepLinc Software, J2 Brand, GPC Instrument Operation:

1. Fill the solvent reservoir with methylene chloride and allow the solvent to acclimate to room temperature.

2. Zero the solvent pump by clicking on Tools then Hardware Settings,



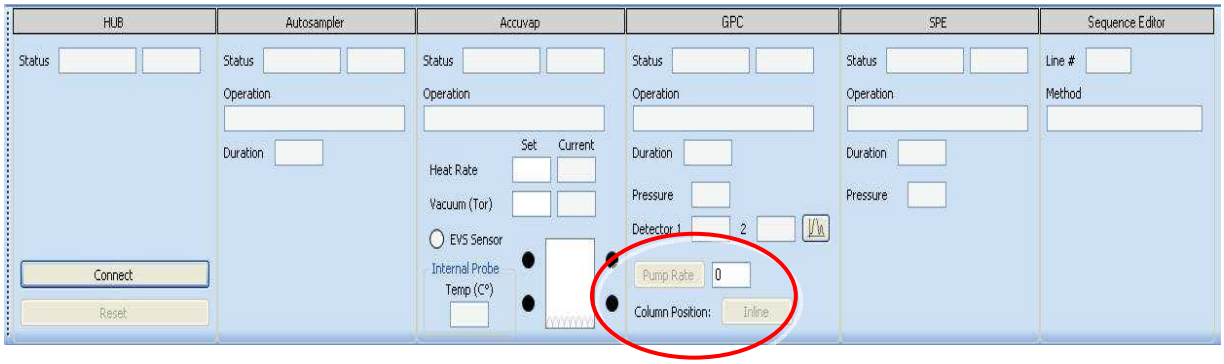
which will pop-up the Pump Settings Screen, where you will click on PUM 1 SolventPump and finally 'Zero Sensor' to zero the pressure when there is no back pressure on the system.



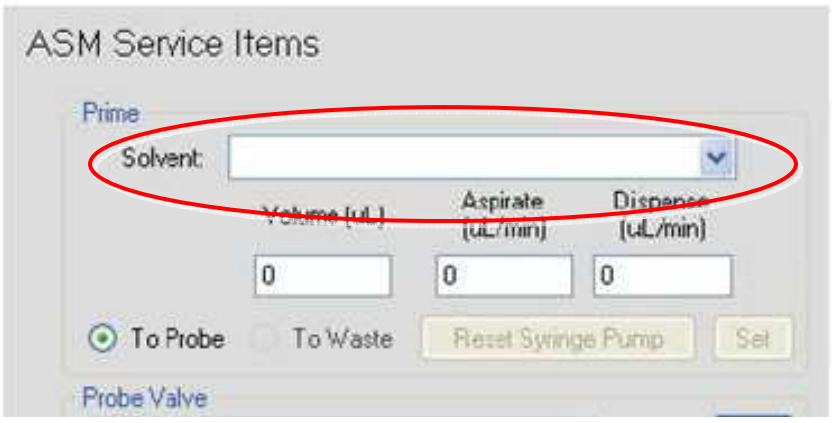
The pump should run for approximately one hour before starting the sequence to allow the pump to equilibrate. Equilibration allows the column pressure and the solvent flow rate to stabilize before the run begins.

3. Upon initialize the solvent pump the GPC column is also brought on line by clicking the GPC box, followed by the Sequence Editor box, then the Column Position box to place the column 'In-line'. Once the column is in position enter the flow rate, i.e. 5 mL/min, in the box next to the

Pump Rate button then click the Pump Rate button to prime the column. (see snapshot below).



4. Prime the syringe by first clicking the 'AS4' button, 'Service Items' then select the solvent to be used to prime the syringe and finally click 'Set' (see snapshot below). After the syringe finishes priming, the column pressure should read between 8 and 12 psi.



5. Load each sample in a disposable test tube after nitrogen blowdown. Pour 10 mls of sample in an empty test tube and mark all others using a calibrated tube.

6. Place the samples in the sample tray starting with the first sample in the front most left slot and place each successive sample behind the first working toward the back of the tray.

7. Follow the same procedure as in 10.2.5.7 for the placement of the corresponding collection tubes.

8. Enter a Sequence by clicking on the

Sequence Editor icon on the Menu Toolbar.

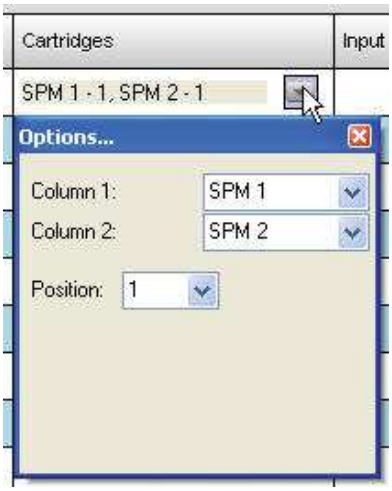
9. The Sequence Editor is where the sample processing is defined and the samples are cued. The Sequence Editor is in a spreadsheet-like format. The columns are defined as follows:

Sequence Editor

	Sample	Priority	Status	Device	Method	Inject Volume (uL)	Cartridges	Input Tray	Output Tray	Type	ID	Batch
1		☐	UNPROCESSED									
2		☐	UNPROCESSED									
3		☐	UNPROCESSED									
4		☐	UNPROCESSED									
5		☐	UNPROCESSED									
6		☐	UNPROCESSED									
7		☐	UNPROCESSED									
8		☐	UNPROCESSED									
9		☐	UNPROCESSED									
10		☐	UNPROCESSED									
11		☐	UNPROCESSED									
12		☐	UNPROCESSED									
13		☐	UNPROCESSED									

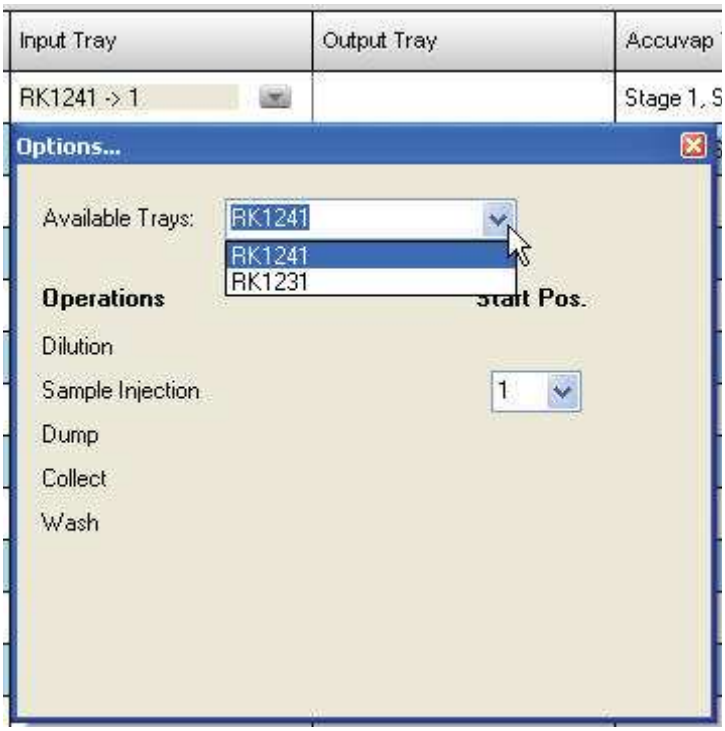
- Line ID #: The first column indicates the line number of the sequence. The line number does not always correspond to the sample number.
- Sample: Indicates the sample number. There can be multiple lines for a sample, like in the case of a Linc method that process samples through multiple methods on multiple devices.
- Priority: Check this box if the sample should be processed before other samples that are ahead of it in the que. The samples that are marked "Priority" will be processed in their numerical order.
- Status: Shows the status of the current sample. "Unprocessed", "Processing" or "Processed".
- Device: Select the device for the process. If a Linc method will be used, choose "Linc" from the list.
- Method: Choose the method for the sample to be processed with by clicking the folder icon and browsing for the method.
- Inject Volume: This field will automatically fill with the volume of sample defined in the chosen method.

- Click the down arrow to view options. It is possible to choose a different column number. The system will default to sample 1 being processed through column 1, etc.



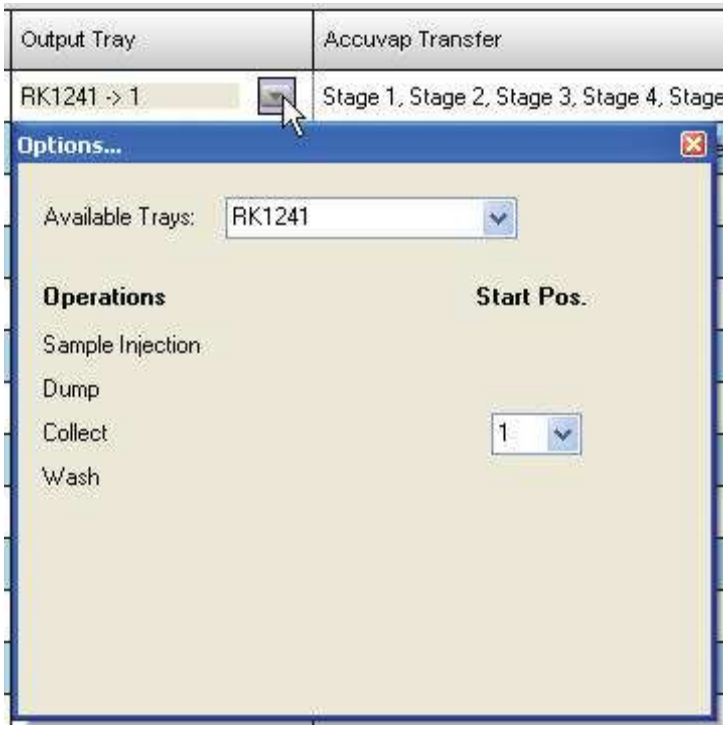
- Input: Click the down arrow to define the tray holding the sample and the position of the sample vial. Choose a tray from the drop-down list in the "Available Trays" field. A summary of the method will be displayed. To the right of the Sample Injection step there is a list of the vial positions to choose from. Choose the vial number for the specified tray where the sample will be located.

View for example GPC Method



- Output: Click the down arrow to define the tray where the sample will be collected after processing. This field will only be active when the AccuVap is **NOT** used for concentration prior to final collection.
- Choose a tray for the drop-down list in the "Available Tray" field. A summary of the method will be displayed. For every possible collection there will be a number choice to the right. Choose the vial where the sample will be collected. Multiple samples can be collected into the same vial, but care must be given to ensure the vial is large enough to hold all collections.

View for example GPC Method



- Type, ID and Batch: These fields are available for the user to define the sample in the sequence. Enter sample ID number, Batch identification number and Type of sample (QC,Blank, sample, etc). Or use these fields in any way desired for reporting purposes.

- Example Sequence Views -

GPC Only Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
GPC 1	Simple GPC	5000		RK1241 (90) - 1	RK1255 - 1	

Nothing is displayed in the "Cartridges" or "AccuVap" fields because the method does not involve these devices.

SPE Single Column Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
SPE 1	SPErevElu	004000	SPM_1 - 1	RK1241 (90) - 1	RK1255 - 1	

The "Cartridges" field shows that only one column is being used for each sample. The "AccuVap" field is blank.

GPC with SPE Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
GPC 1	GPCwSPE	000000	SPM_1 - 1	RK1241 (90) - 1	RK1255 - 1	

The "Cartridges" field shows which SPE column will be inline with the GPC for that GPC sample. The "AccuVap" field is blank.

GPC Column Calibration Method

Device	Method	Volume	Cartridges	Input	Output	Accuvap
GPC 1	CO770_CAL	5000		RK1241 (90) - 1		

Nothing is displayed in the "Cartridges" or "AccuVap" fields because the method does not involve these devices. There is nothing displayed in the "Output" field because there is no collect fraction for the method. When you click the down arrow there is no vial position number to choose from:

10. After all samples have been added to the sequence click 'Start' and you will then be prompted to name and save the sequence. Once the sequence has been saved, the GPC will automatically start the run.
11. As each sample is processed, the color on the sample tray will be light green and will change to dark green in the 'Status Column' after the sample processing is completed (see snapshot below).

Sequence Editor

	Sample	Priority	Status	Device	Method	Inject Volume (uL)	Cartridges	Input Tray	Output Tray	Type	ID	Batch
1			UNPROCESSED									
2			UNPROCESSED									
3			UNPROCESSED									
4			UNPROCESSED									
5			UNPROCESSED									
6			UNPROCESSED									
7			UNPROCESSED									
8			UNPROCESSED									
9			UNPROCESSED									
10			UNPROCESSED									
11			UNPROCESSED									
12			UNPROCESSED									
13			UNPROCESSED									

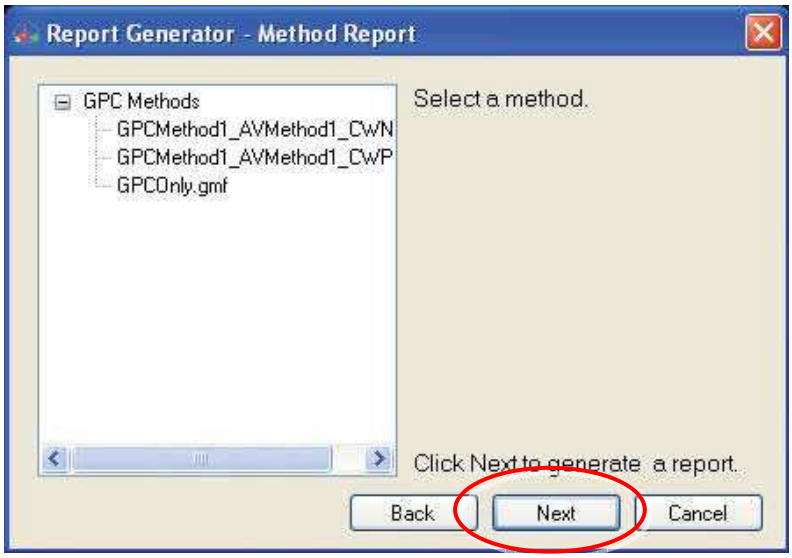
12. Reporting - The PrepLinc software contains a set of pre-defined reports that the user can print for a sequence, a particular sample or to see the parameters of a particular method.

- A Reporting Wizard guides the user through report creation. Click on the "Reporting" button on the toolbar.

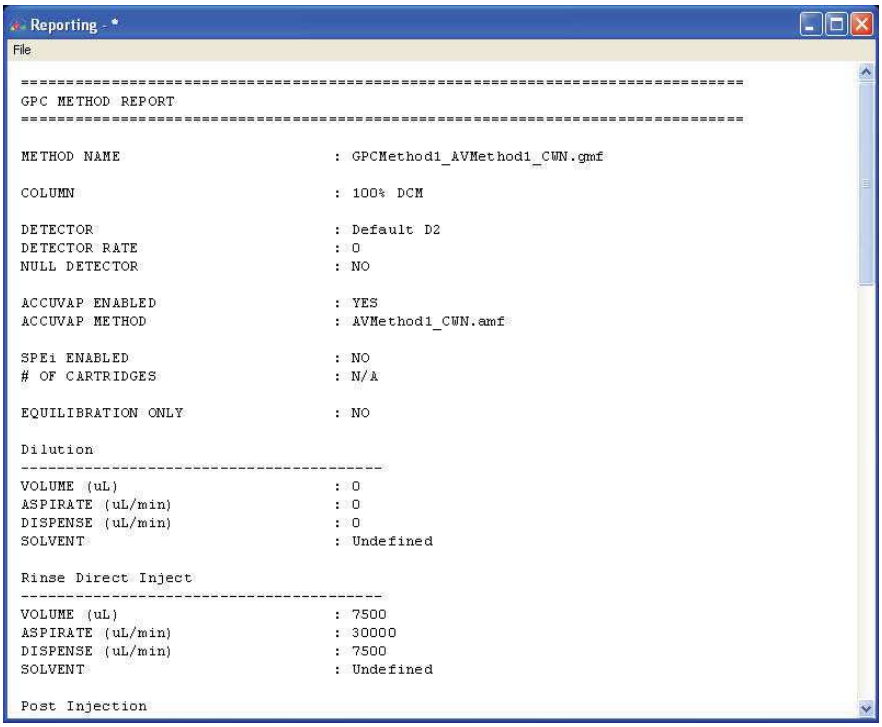
- From the first screen of the Wizard, select the report type you would like to generate.

- Method Report
  The method report lists all the parameters for the selected saved method. After choosing "Method Report" from the list, click the Next button.

  A list of the saved method for that module will be displayed. Click on the method desired for the report and click the Next button.



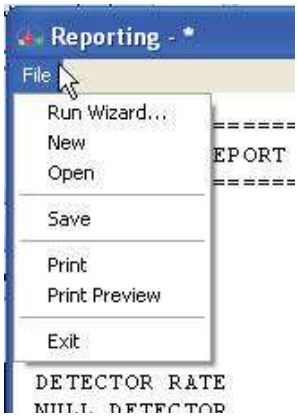
The report will appear in the "Report Generator" window.



The example report shown above is for a GPC Cleanup method. Every parameter available for a GPC method and it's the corresponding value is listed.

- Printing & Saving Reports

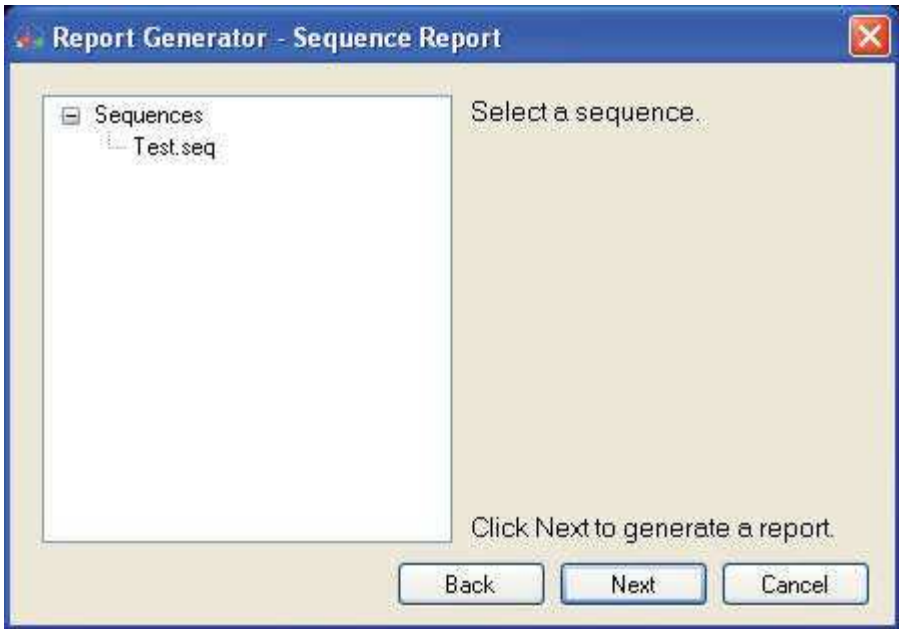
To Print or Save the displayed report, click on the "File" drop-down menu button at the top of the Report Generator window. Select the action desired from the list.



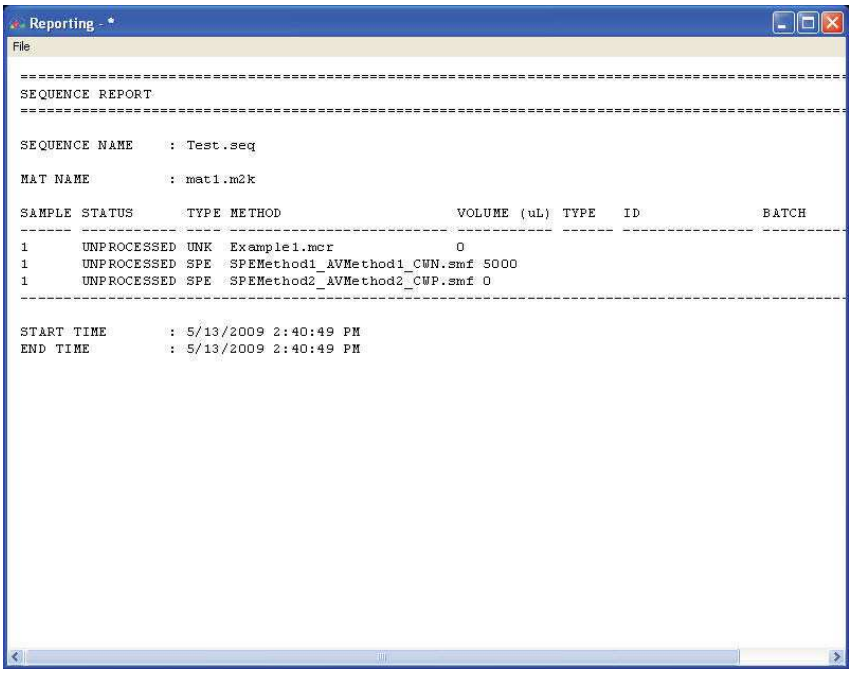
- Generate Another Report
  From the File drop-down menu, choose “Run Wizard” to start the Reporting Wizard over again.

- Sequence Report
  The Sequence Report is a list of all the samples processed, the method used to processes them and any errors that occurred during a given sequence. The Sequence Report also shows the time and date the sequence was processed. The Sequence Report can only be generated once the sequence is completed processing.

  After choosing Sequence Report from the first screen of the Wizard, a list of completed sequences will be displayed. Choose the desired sequence and click the Next button.



The report will appear in the “Report Generator” window.

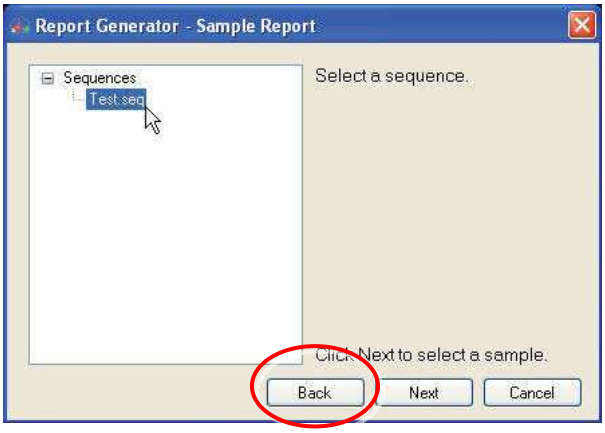


The example report above shows what will be reported for each sequence: Sequence Name, Mat Name, list of samples processed, Sequence Start and End times.

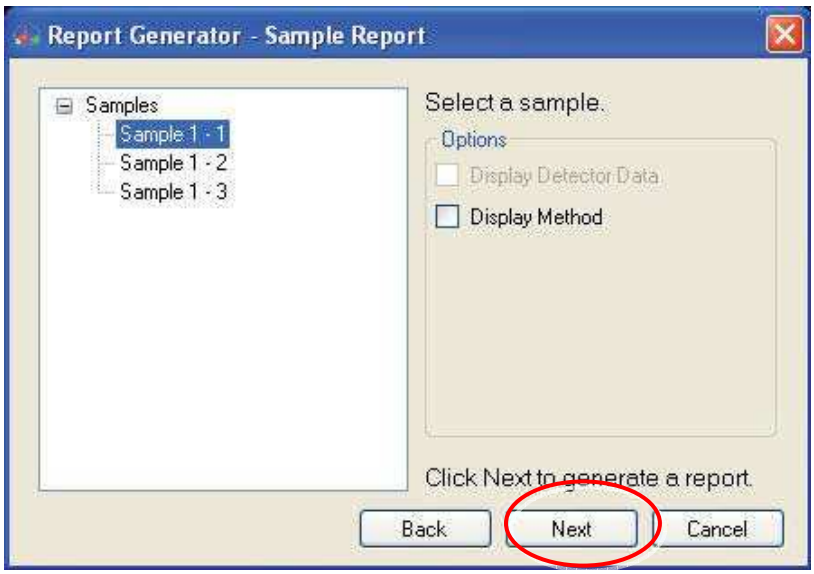
- Sample Report

The Sample Report lists details of a particular sample within a sequence.

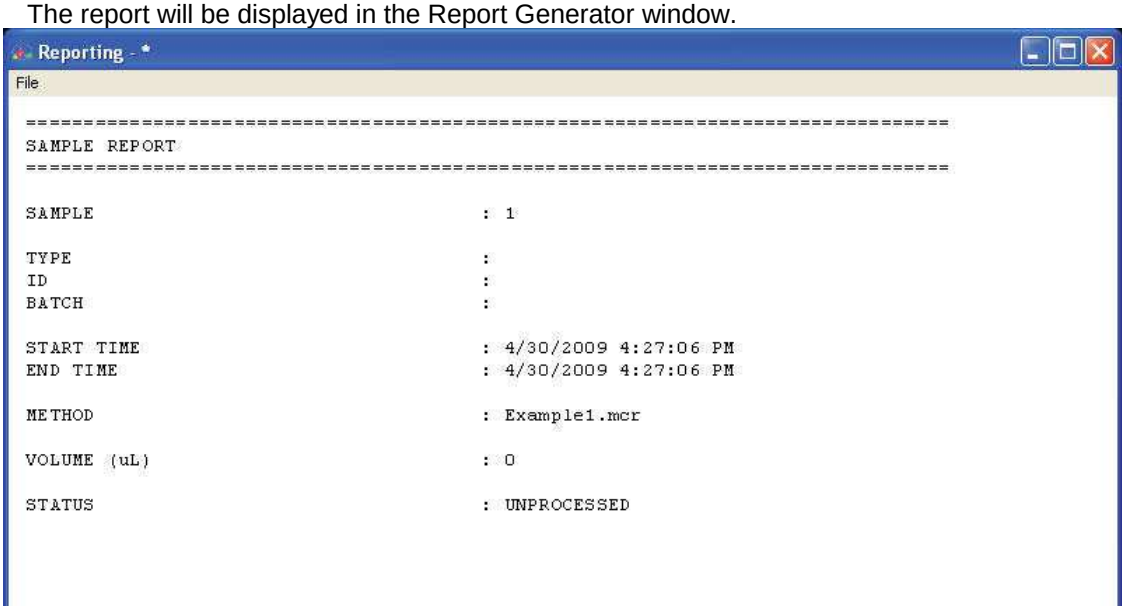
After choosing “Sample Report” from the first wizard screen, a list of processed sequences. Choose the sequence name in which the sample was processed and click the Next button.



A list of the samples processed in the chosen sequence will be displayed on the next screen. Choose the name of the sample desired for the report from the list. If there is detector data saved for the sample, the "Display Detector Data" check box will be active to the right. The option is also given to include detailed method information on the Sample Report. If either of these options are desired, click the appropriate check box and click the Next button.



The report will be displayed in the Report Generator window.

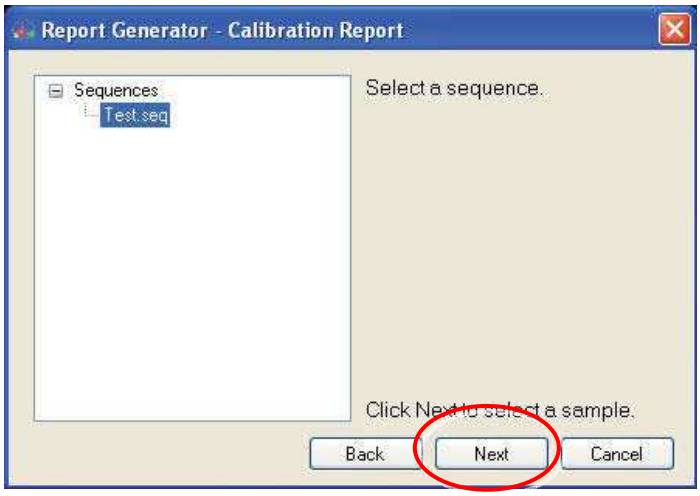


The Sample Report contains information about the sample that is not displayed on the Sconce Report.

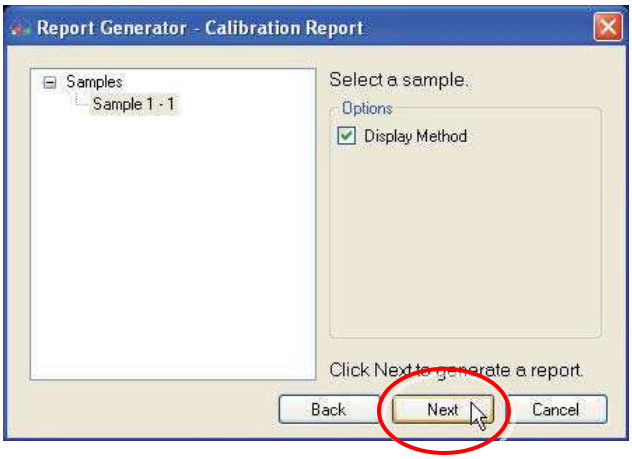
- Column Calibration Report

The Column Calibration Report shows the annotated chromatogram,sample information and resolution pass/fail results. The report can also show the full method summary for the sample, if desired.

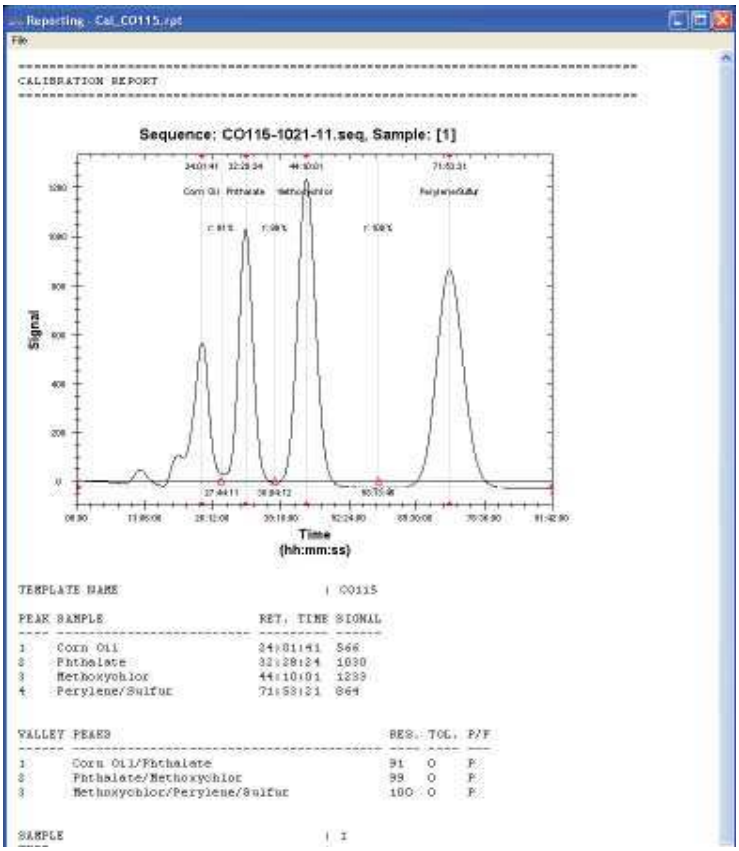
After choosing “Column Calibration Report” from the first wizard screen, a list of processed sequences will be displayed. Choose the appropriate sequence and click the Next button.



A list of the samples processed in the sequence will be displayed on the next screen. Choose the name of the calibration sample from the list. The Option “Display Method” will become active. Click the check box if you would like the method details to be included in the Column Calibration Report. Click the Next button.



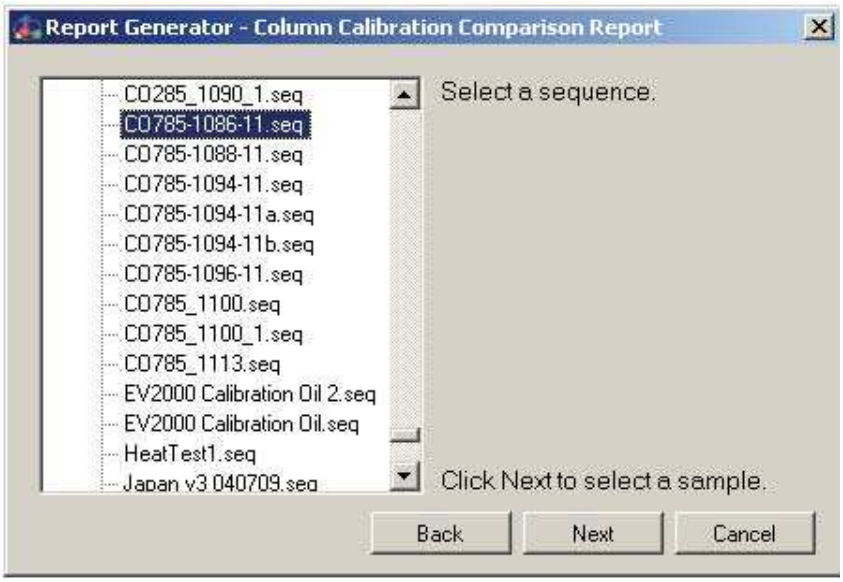
The report will be displayed in the Report Generator window.

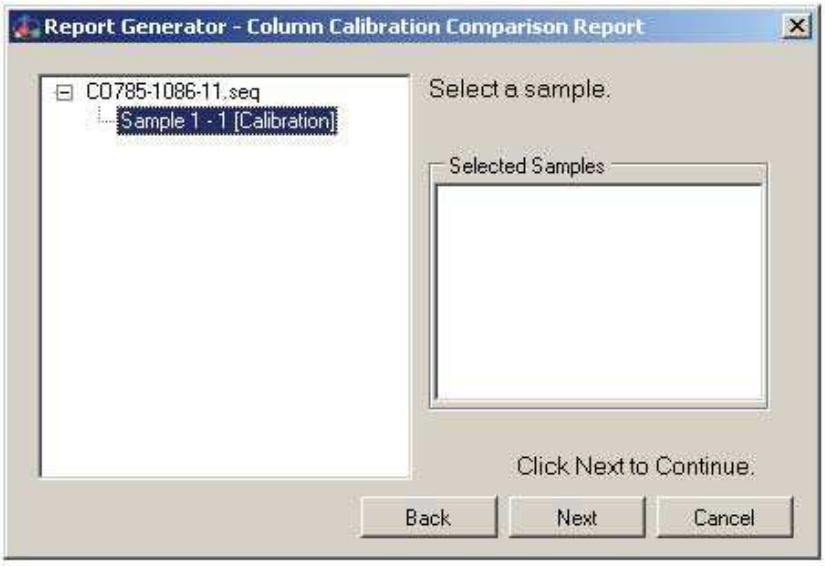


- Column Calibration Comparison Report

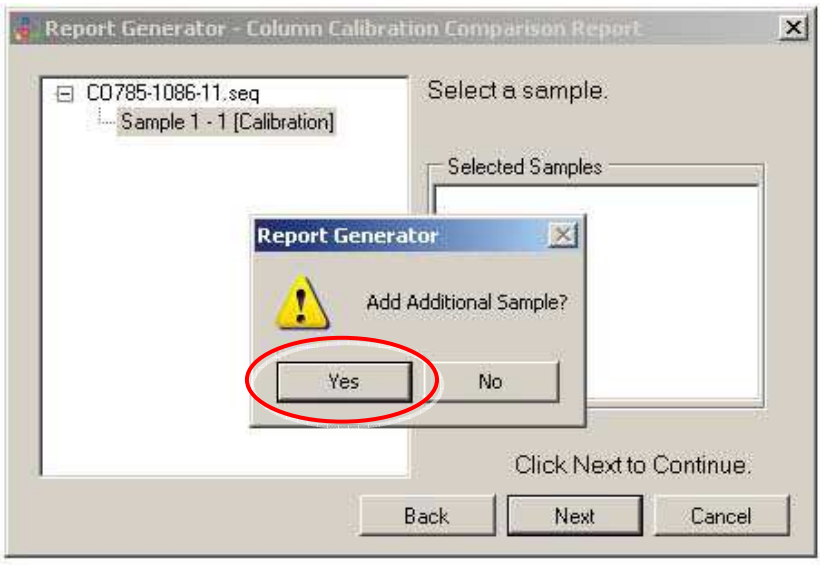
  The Column Calibration Comparison Report takes information from two annotated chromatograms and compares certain data from them to determine a pass/fail for the calibration based on EPA methods.

  After choosing “Column Calibration Comparison Report” from the first wizard screen, a list of processed sequences will be displayed. Choose the appropriate sequence and click the Next button. Choose the sample number in the Sequence that corresponds to the calibration.

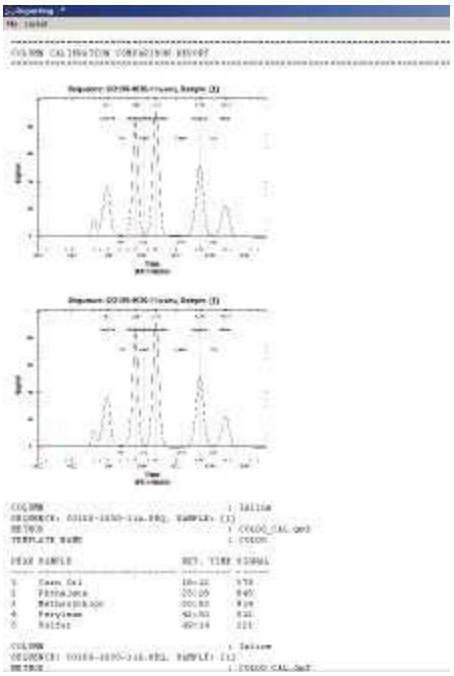


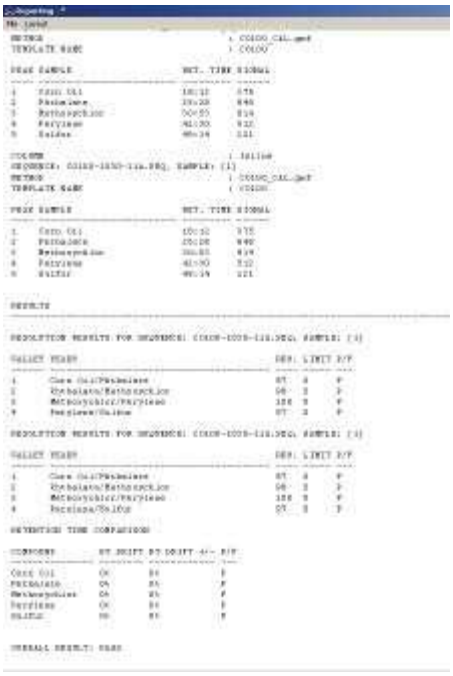


To add an additional sample for comparison, click Yes.



You will then repeat the steps above to choose the Sequence and Sample for comparison. The report that is generated will look similar to the images below. It will show summary information for each sample and then the comparison pass/fail indications.





Title: Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated Hexane Extractable Material (SGT-HEM; TPH) Method 1664A/1664B and SW-846 Method 9070A

Methods: Method 1664A/1664B and 9070A

Approvals (Signature/Date):

11/14/2017	11/14/2017
Roseann Ruyechan Date	Steve Jackson Date
Inorganics Department Manager	Regional Safety Coordinator
11/24/2017	11/14/2017
Virginia Zusman Date	Deborah Lowe Date
Quality Assurance Manager	Laboratory Director

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1.0 Scope and Application

1.1 This method quantifies the n-hexane extractable material (HEM; Oil and Grease) and n-hexane extractable material that is not adsorbed by silica gel (SGT-HEM or TPH (non-polar material)) in surface and saline waters and aqueous wastes. Generally, the extractables consist of non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and similar materials.

1.2 This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation, and Liability Act; and other EPA regulatory programs. "Oil and grease" is a conventional pollutant under the Clean Water Act and codified at 40 CFR 401.16. The term "n-hexane extractable material" reflects that this method can be used to determine materials other than oils and greases. Similarly, the term "silica gel treated n-hexane extractable material" reflects that this method can be used to determine material that is not adsorbed by silica gel (non-polar material).

1.3 If only SGT-HEM is required, the HEM determination can be skipped only if the HEM concentration is known. If the HEM concentration is not known, then the HEM determination must be performed prior to the SGT-HEM determination.

1.4 This method is applicable to surface waters, sewages, and aqueous wastes containing approximately 5 mg/L to approximately 1000 mg/L using a 1L sample. The reporting limit for both HEM and SGT-HEM is 5 mg/L. These limits may be extended to higher levels by analysis of a smaller sample volume collected separately. Dilutions are not appropriate for this procedure, except as specifically described for silica gel treatment in section 10.23.2.

1.5 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated in PT-QA-M-001, Quality Assurance Manual.

2.0 Summary of Method

2.1 Using a solid phase extraction manifold, a 1.0 L aqueous sample (acidified to pH <2) is filtered through an extraction disk. The extractable materials are rinsed from this disk with n-hexane, collected into a 40 ml VOA vial. The extract is filtered through phase separation filter paper into a pre-weighed pan, for evaporation on the Speedvap 9000 II. This step concentrates the HEM portion of the sample. The pans are allowed to cool in a desiccator, and then re-weighed to determine the HEM concentration.

2.2 In order to determine the SGT-HEM (TPH), the residue from the sample is then reconstituted with hexane and treated with silica gel. The silica gel treated extract is filtered into a pre-weighed pan, for evaporation on the Speedvap 9001. This step concentrates the SGT-HEM portion of the sample. The pans are allowed to cool in a desiccator, and then re-weighed to determine the SGT-HEM concentration.

3.0 Definitions

3.1 N-hexane extractable material (HEM): Material that is extracted from a sample with hexane and determined by this method (oil and grease). Examples of this material include relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and other materials with similar characteristics.

3.2 Silica gel treated n-hexane extractable material (SGT-HEM): Material that is extracted from a sample with hexane and determined by this method that is not adsorbed by silica gel (TPH).

3.3 TALS: TestAmerica Laboratory Information Management System

3.4 NCM: Non-Conformance Memo, a communication system for the laboratory to document anomalies or non-conformances encountered with samples and their analysis.

3.5 See TestAmerica Pittsburgh Laboratory's Quality Assurance Manual (PT-QA-M-001) for glossary of common terms.

4.0 Interferences

4.1 This method is not designed to quantify substances which volatilize at temperatures below approximately 85°C. Petroleum products, ranging from gasoline to #2 fuel oils, may be partially lost during the extraction and concentration process. Certain crude or heavy oils contain portions of material not soluble in n-hexane, often resulting in low recoveries.

4.2 All glassware and other apparatus in contact with the sample must be thoroughly washed and solvent rinsed to eliminate contamination from artifacts. In addition, reagent grade or better solvents must be used to ensure that the glassware, etc. is free of artifacts. The hexane, silica gel, phase separation paper, and any drying agents used, must be shown to be free from residue down to the MDL level.

4.3 For samples consisting of complex matrices (such as particulates or detergents) that may interfere with the extraction process, a smaller sample size may be used.

4.4 Care must be taken to avoid contamination of the final extract with sodium sulfate, silica gel and/or water. This can be avoided by filtering the HEM or SGT-HEM very slowly. Should contamination occur, apparent by visible amounts of

crystalline material in the residue, the residue must be re-suspended in n-hexane. The re-suspended material can be filtered with additional solvent washings of the flask through phase separator filter paper. The method then resumes with the evaporation process.

4.5 Samples must be brought to room temperature prior to analysis in order to reduce the amount of solid material adhering to the walls of the collection containers. Erroneous low results may be obtained from samples analyzed at refrigeration temperatures.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 The following is a list of the materials used in this method, which have a serious or significant hazard rating. This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3 Eye protection that protects against splash, Laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. . Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit, or under other adequate ventilation.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of an TestAmerica Pittsburgh Associate. The situation must be reported immediately to a supervisor or the EH&S coordinator.

6.0 Equipment and Supplies

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Analytical balance capable of weighing to 0.1 mg

6.2 Vacuum source and tubing to connect apparatus

6.3 Waste receptacle and tubing to connect manifold

6.4 Horizon SpeedVap 9000II

6.5 UCT ENVIRO-CLEAN® Oil and Grease extraction apparatus equipped for each unit with the following:

- 6.5.1 1.0 L reservoir funnel
- 6.5.2 Rinsing flask (one per manifold set-up)
- 6.5.3 UCT ENVIRO-CLEAN® Oil and Grease cartridges – 37mm diameter polypropylene cartridge design
- 6.5.4 Oil-less vacuum pump for the UCT cartridge system (Rocker Model 400)

6.6 Desiccator

6.7 70 & 150 ml Disposable Evaporation Pans

6.8 Glass, class A, graduated cylinders, 1 L and 100 mL

6.9 pH indicator strips

6.10 40 mL VOA vials or other suitable glass container used as Collection flasks

6.11 Phase separation filter paper

6.12 Glass filter funnels

6.13 Glass Stir Rods, 4 x 125 mm or similar

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the SDS prior to the use of any reagent or standard. Quantities different from what is specified can be prepared, provided that the ratios remain the same.

All chemicals must be ACS reagent grade or better. Solvents must be of a grade shown to produce residue <1.0mg/L when evaporated.

7.1 Reagent water- Super Q or DI water

7.2 Hydrochloric acid or sulfuric acid, 6N: Mix equal volumes of concentrated HCl and reagent water or 1 part H_2SO_4 and 5 parts reagent water to produce an approximately 6N solution.

7.3 Acetone

7.4 n-Hexane, 85% minimum purity, 99.0% minimum saturated C6 isomers

7.5 Methanol

7.6 Silica Gel: Anhydrous, 75-150µm, 30 Å pore size (Dry at 200-250^{o}C for a minimum 24 hours and store in a desiccator or tightly sealed containers)

7.6.1 Verify that the n-hexane soluble material content of the silica gel is <5mg per 30g. Extract 30g of silica gel with 40-50mL of n-hexane by shaking in a closed container, using a wrist action or shaker table, for 15 minutes. Filter the extract into a tared evaporating dish with phase separation filter paper and evaporate the solvent. The final residue must be <0.0050 g (<0.17mg residue / g silica gel).

7.7 Hexadecane/stearic acid Spiking Standard (Used for LCS and MS/MSD)

7.7.1 Purchased Speedisk Oil and Grease standards kit of 2 mg/mL stearic acid and 2 mg/mL hexadecane in acetone. Spike 10.0 mL of the solution into a 1 L aliquot of acidified reagent water (acidified with 5 mL of 1:1 HCl)for the LCS, or separate sample bottles for MS/MSD. The resulting concentrations in the LCS are 40 mg/L HEM and 20 mg/L SGT-HEM (stearic acid is removed by the silica gel treatment.

7.8 Laboratory Prepared Spiking Solution (optional)

7.8.1 The spiking solution may be prepared by weighing 200 ± 2 mg hexadecane and 200 ± 2 mg stearic acid into a 100 mL volumetric flask. Dilute to volume with acetone. Store in the dark at room temperature. To minimize

evaporation of acetone, wrap the stopper and neck area of the flask with parafilm. Sonicate and warm to provide adequate dissolution of the solution. Prior to use, verify that the solution level is at the 100mL mark. In the event that some acetone has evaporated, bring the solution to volume again with acetone.

Note: Stearic acid tends to stick to everything. It is very important that all surfaces of the sample bottle, and anything else the sample comes in contact with, are rinsed well with hexane to ensure complete recovery.

8.0 Sample Collection, Preservation, Shipment and Storage

Listed below are the sampling requirements and holding time for this method.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	1 L amber *	1 L amber *	>0.0℃ but ≤6.0℃, pH to <2 with HCl or H_2S0_4	28 days	40 CFR Part 136

* Smaller sample containers may be used, but RLs will be affected.

8.1 Sample bottles are pre-preserved using 5 mL of 1:1 HCl or 5 mL of 1:1 H_2SO_4 for a 1 L sample. This should be sufficient to adjust the sample pH to <2. The sample pH must be confirmed prior to extraction.

8.2 Collect approximately one liter of representative sample in a glass bottle following conventional sampling practices, except that the bottle must not be pre-rinsed with sample before collection. To allow for potential QC failures, it is recommended that additional sample aliquots be collected. To allow for MS and/or MSD analysis, collect a 2nd and/or 3rd aliquot for at least one sample. When collecting additional aliquots, either collect simultaneously in parallel, if possible, or collect as grab samples in rapid succession.

8.3 The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of oil and grease. Therefore, samples must be collected as grab samples. If a composite measurement is required, individual grab samples collected at prescribed time intervals must be analyzed separately and the concentrations averaged. Alternatively, samples can be collected in the field and composited in the laboratory. For example, collect four individual 250-mL samples over the course of a day. In the laboratory, pour each 250-mL sample into a 1 Liter pre-preserved Glass Bottle, rinse each of the four bottles (and caps) sequentially with 30 mL of n-hexane, and use the 30 mL of n-hexane for the extraction.

8.4 If a sample is known or suspected to contain greater than 500mg/L of extractable material, collect a smaller volume of sample (the volume required will depend upon the estimated amount of extractable material) in another glass bottle. Add a proportionately smaller amount of HCl or H_2S0_4 solution to the smaller sample for preservation.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit[1]	
		HEM	SGT-HEM
Laboratory Control Sample (LCS)	1 per batch of 20 samples or less	78-114% recovery	64-132% recovery
Method Blank (MB)	1 per batch of 20 samples or less	< RL	< RL
Matrix Spike (MS)	1 per batch of 20 samples or less	78-114% recovery	64-132% recovery
Matrix Spike Duplicate (MSD)	1 per batch of 20 samples or less	78-114% recovery, RPD <18%	64-132% recovery, RPD <34%

[1]Control Limits are method specified and are maintained in LIMS

[2]The MS/MSD parent sample is randomly selected, unless specifically requested by a client.

9.2 Balance check: criteria for 2mg weight check is ±10%. Criteria for 1g weight check is ±0.5%.

9.2.1 If the balance check is outside of acceptance criteria, do not begin weighing pans. Clean the balance pan, recalibrate the balance and check the required weights again.

9.3 The Method Blank is 1 L of laboratory reagent water added to a pre-preserved bottle and taken through the same extraction and analysis process as the samples in the batch. MB must have a residue < 5 mg/L, and should have residue below the current MDL. Sample results will be qualified on the final report for MB's with results above the MDL.

9.3.1 It is not permissible to use blank correction on sample results.

9.3.2 Samples associated with method blanks, which fail the acceptance criteria, must be re-prepared and reanalyzed with an acceptable blank, unless:

- Sample results are non-detect – in which case results may be reported using the "Method Blank – Report, ND" NCM.
- Sample results are greater than 10 times the concentration seen in the blank – in which case results may be reported using the "Method Blank – Report, 10X" NCM.

9.3.3 If there is insufficient sample to reanalyze, inform the project manager of the blank contamination and report results using the "Method Blank – Insufficient Sample" NCM to document the failure.

9.4 The LCS is prepared in the same manner as the Method Blank, with 10mL of spike solution added as in section 7.7. Results must the control limits given in the QC table above.

9.4.1 Samples associated with a LCS, which fails the acceptance criteria, must be prepared and analyzed again with an acceptable LCS unless the LCS recovery is above the control limit, and the associated sample is non-detect. Non-detect results may be reported along with the "LCS/LCSD - %R High" NCM.

9.4.2 If there is insufficient sample volume to repeat the analysis, inform the project manager of the blank contamination and report results using the "LCS/LCSD – Insufficient Sample" NCM to document the failure.

9.5 A minimum of a Matrix Spike (MS) analysis must be performed with each analytical batch of 20 or fewer samples. If there is sufficient volume provided, a Matrix Spike Duplicate (MSD) shall also be included. If insufficient sample is available to prepare a MS, this must be documented with the "MS/MSD – Insufficient Volume" NCM.

9.5.1 If the MS (or MSD) does not meet the acceptance criteria given in the QC table above, evaluate the batch QC and parent sample result.

- If the batch LCS has acceptable recovery, results are reported using the "MS/MSD - %R, LCS Pass" NCM.
- If the parent sample concentration is greater than 4x the spiked amount, the MS recovery cannot be accurately calculated, and the "MS/MSD – High Targets" NCM should be used to document this.

9.6 If sample reanalysis due to QC failure will be past the holding time, inform the project manager of the QC failure and obtain client instructions on how to proceed. The decision on whether to report the original result or perform reanalysis past the holding time must be documented in the case narrative.

9.7 The cleanliness of the silica gel (see section 7.6) must be documented for each lot prior to use.

9.8 Each time a modification is made to this written procedure, including types of equipment used, the laboratory must repeat the initial demonstration of capability and MDL study. (See requirements in section 12.)

10.0 Procedure

10.1 Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights before and after weighing each batch of samples. (See section 9.2.)

10.2 Allow the samples to warm to room temperature before beginning. (However, do not leave samples on the bench for more than 4 hours.)

10.3 Verify that the pH of the sample is less than 2 using the following procedure:

10.3.1 Dip a glass stir rod into the well-mixed sample.

10.3.2 Withdraw the glass stir rod and allow a drop of sample to fall on a pH strip. Record the sample pH on the TALS worksheet.

10.3.3 As some oil and grease may adhere to the stir rod, rinse the stir rod with hexane and collect into the funnel for filtering the extract into the final collection vessel. Phase separation filter paper must be used so that any water rinsed off by the hexane does not end up in the evaporating dish.

10.3.4 Use a new stir rod for each sample to avoid cross-contamination.

10.3.5 If the sample is at neutral or greater pH, add 5-6 mL of 6N HCl or H_2SO_4 solution or other appropriate amount to adjust the pH of the 1 L sample to < 2. Document the final pH on the TALS worksheet if the sample pH requires adjustment.

10.4 Weigh Disposable Evaporation Pans using an analytical balance and record the weights on the TALS worksheet. Always handle pans with tongs or gloves. Do not touch the pans with bare fingers, or oils from you skin may add weight to the pan.

10.5 Assemble a UCT ENVIRO-CLEAN® Oil and Grease Cartridge Extraction Station and mount a collection chamber on each active port.

10.6 Mount the cartridge and wash the sides with approximately 10 mL of hexane. Allow the cartridge to soak in the hexane for 1 minute. Draw the hexane through the cartridge using the vacuum pump and discard the hexane as waste. Draw full vacuum through the cartridge for 2 minutes to remove all the hexane.

10.7 Add 10 mL of methanol to the cartridge and slowly draw the methanol through the cartridge leaving a layer on the surface of the cartridge. **Do not let the sorbent dry out.** Soak for one minute then add 30 mL of DI water to the cartridge. Draw the water through the cartridge to waste.

10.7.1 **Do not allow the sorbent to completely dry before adding the sample**, otherwise repeat steps 10.6 and 10.7.

10.8 Mark the meniscus of the water on the sample bottle. For the LCS and MS/MSD aliquots, spike each in the bottle with the Spiking Standard (Refer to Section 7.7). Mix well.

10.9 Add the 1 liter water sample directly to the cartridge and draw through under full vacuum. This may take several minutes for complete flow through the cartridge depending upon the level of solids in the sample. Use a bottle holder on top of the cartridge if necessary to hold the upside-down bottle securely.

10.9.1 If very high solids are present, add glass wool to the cartridge prior to adding the sample to prevent clogging and achieve good flow. The glass wool must be thoroughly rinsed with hexane before use.

10.10 After the entire sample has filtered, allow the cartridge to dry under full vacuum for 10 minutes to remove excess water. Remove any water remaining in the bottom support of the cartridge with a paper towel. Do not touch the inside of the cartridge.

10.11 Rinse the sample bottle with 10 mL of hexane. Add the hexane to the cartridge, rinsing the sides of the cartridge and the bottle holder, if used. Soak for 3 minutes. Slowly draw the hexane through the cartridge and into the collection vial. Do not allow the vacuum to continually blow on the extract.

10.12 Immediately repeat step 10.11 two more times using 10 mL of hexane.

10.13 Fill the rinsed sample bottle to the meniscus marking, and measure the volume contained using a 1 Liter, class A, graduated cylinder. Record the sample volume on the batch worksheet.

10.14 Add another 10 mL of hexane to the cartridge, rinsing the bottle holder. Allow the cartridge to soak for 3 minutes. Draw the hexane through the cartridge. The total volume of the extract will be about 35 mL.

10.15 Remove the collection vial from the manifold and cover with a screw cap.

10.16 Place a piece of phase separation filter paper into a filter funnel. Rinse three times with hexane and dispose of the rinsate.

10.17 Filter the extract through phase separator filter paper into a pre-weighed 70 mL evaporation pan. Rinse the collection vial and filter paper twice with approximately 5 mL portions of hexane.

10.18 Set the Speedvap to 50^{o}C. Place the evaporating pans into the Speedvap and evaporate to near dryness, visibly. (Evaporating to total dryness may also remove some of the lighter hydrocarbons from the residue.)

10.19 Remove the pans from the Speedvap, and place them in a desiccator for at least one hour.

10.20 Weigh the pans on an analytical balance and record the weights to the nearest 0.1 mg on the TALS worksheet.

10.21 Repeat the cycle of desiccating and weighing until the sample weight loss is < 4% for the previous weight or less than 0.5 mg, whichever is less. If pan weight is not within 0.5 mg, put the sample back in the desiccator for ½ hour and perform a third weighing.

10.22 If only HEM (Oil & Grease) is required to be reported, proceed to result calculation in section 11.2. If SGT-HEM (TPH) is also required, continue with section 10.23.

10.23 SGT-HEM Determination:

If the HEM result is less than the SGT-HEM reporting limit (or MDL), the analyst may report SGT-HEM as less than the reporting limit and stop at this point. SGT-HEM should always be less than or equal to HEM.

10.23.1 Rinse the residue from the HEM determination into a suitable glass container with approximately 40 mL of hexane. This re-dissolved HEM is referred to as “the extract”.

10.23.2 Add 3.0 g of silica gel for every 100 mg of HEM in the extract up to a maximum of 30 grams of silica gel (maximum of 1000 mg of HEM).

- If the amount of silica gel needed exceeds 30 grams, then only process a portion of the extract. For example- if the amount of silica gel needed is calculated to be 60 grams, then use ½ of the extract. Account for this “dilution” in the final calculation for SGT-HEM.

For example: 6.4294 g Residue x 1000 = 6429.4 mg Residue

Based on the maximum concentration of 30 g of silica gel per 1000 mg of HEM a 10X dilution is done on this sample to bring the sample within range, resulting in 642.94 mg of Residue.

Then use 3 g of silica gel per 100 mg of HEM as follows:

642.94 mg/100 mg = 6.4294 mg HEM

6.4294 mg x 3 g silica gel = 19.2882 or 19.3 g of silica gel

So a 10X dilution would need approximately 19 g of silica gel

- The HEM in the extract should be rounded up to the next 100 mg. For example, if the HEM is 735 mg, the amount of silica gel added should be based on 800 mg or 24 grams of silica gel (3 g. x 8).

10.23.3 Shake or stir the sample flask for 15 minutes.

10.23.4 Filter with phase separator paper into a previously weighed 70 mL evaporation pan. Rinse the flask, silica gel and filter paper with several small amounts of hexane to complete the transfer.

10.23.5 Repeat steps 10.18 through 10.21.

10.23.6 Determine the SGT-HEM concentration using the equation in section 11.2.

11.0 Calculations / Data Reduction

11.1 **LCS % Recovery** = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

Note: the spike concentration for SGT-HEM is half of the HEM concentration due to the removal of stearic acid during the silica gel treatment.

11.2 **HEM or SGT-HEM (mg/L)** = $\frac{[\ A - B\ ] \times 1{,}000{,}000 \times DF}{\text{mL of sample}}$

Where:
A = final pan weight in grams.
B = initial pan weight in grams.
DF = Dilution factor (= 1 if no dilution performed)

11.3 MS/MSD $\%\ Spike\ Recovery\ (\%R) = \frac{SSR - SR}{SA} \times 100$

where:
SSR=Spiked Sample Result
SR=Sample Result
SA=Spike Added

11.4 Relative Percent Difference (RPD) between the MS and MSD (or LCS/LCSD):

$$RPD = \frac{|Conc.1 - Conc.2|}{(Conc.1 + Conc.2)/2} \times 100$$

Where: Conc. 1 and Conc. 2 are the concentrations (mg/L HEM or SGT-HEM) in the MS and MSD samples, respectively.

Note: the spike concentration for SGT-HEM is half of the HEM concentration due to the removal of stearic acid during the silica gel treatment.

12.0 Method Performance

12.1 The supervisor has the responsibility to ensure that an analyst who has been properly trained in its use and has the required experience performs this procedure. The training documentation will be forwarded to QA for inclusion in the training files. DOCs will be documented for each analyst in the training file.

12.2 **Demonstration of Capabilities(DOC)**

12.2.1 This requires the analysis of four LCS samples. The LCS sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin. Four aliquots of the LCS are prepared and analyzed using the procedures detailed in this SOP.

12.2.2 Recovery of each LCS standard analyzed as part of the IDOC must meet recovery limits of 83-101% for HEM and 83-116% for SGT-HEM. Precision between the four standards must be ≤ 11%RSD for HEM and ≤ 28%RSD for SGT-HEM.

12.2.3 Annually, a Continuing Demonstration of Capability must be documented for each analyst performing this method, using 4 consecutive batch LCS's. The LCS data may come from a single batch or multiple batches. LCS recovery limits listed in Table 9.1 must be met for all points. The %RSD of the set must meet precision criteria of the IDOC given in section 12.2.2.

12.3 **Method Detection Limit Study (MDL)**

12.3.1 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP PT-QA-007.

12.3.2 The calculated MDL for HEM and SGT-HEM from the MDL study must be ≤ 1.4 mg/L, or ≤ ⅓ the regulatory compliance limit, whichever is greater. Because compliance limits can vary, the laboratory will use 1.4 mg/L as the upper limit for MDL.

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the "Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.2 The following waste streams are produced when this method is carried out.

14.3 Solvent or oily waste. This waste is collected in a waste container identified as "Mixed Flammable Solvent Waste", Waste #3.

14.4 Contaminated filter Paper with Sodium Sulfate, Speed Disc, and aluminum pan. This waste is collected in containers identified as "Lab Trash", Waste #12.

15.0 References

15.1 Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, EPA-821-R-98-002, February 1999

15.2 Method 1664, Revision B: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, EPA-821-R-10-001, February 2010

15.3 EPA 2000. Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136), EPA/821-R-00-003, January 2000

15.4 Bakerbond application note. Extraction of Oil & Grease from water, EPA Method 1664

15.5 SW-846 Method 9070A: n-Hexane Extractable Material for Aqueous Samples

15.6 PT-QA-M-001, Pittsburgh Laboratory Quality Assurance Manual

15.7 PT-QA-003, Glassware Clean-up for Organic/Inorganic Procedures

15.8 PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.9 PT-QA-007, Detection Limits

15.10 PT-QA-009, Rounding and Significant Figures

15.11 PT-QA-016, Nonconformance & Corrective Action System

15.12 PT-QA-018, Technical Data Review Requirements

15.13 PT-QA-021, Pittsburgh Quality Control Program

15.14 PT-QA-031, Internal Chain of Custody

15.15 PT-HS-001, Pittsburgh Facility Addendum EH&S Manual

16.0 Method Modifications

16.1 Because a solid-phase extraction is performed; an allowable modification per Method 1664, Revision B, Section 1.7.1.1; the final extract will not have the water content potential from the separatory funnel method. For this reason, sodium sulfate is not added to the funnel for filtration of the extract prior to evaporation. Sodium sulfate was found to produce residues around or above the MDL in sample extracts filtered through it. The extracts are filtered through phase separation paper only.

17.0 Attachments

17.1 Figure 1 - Example HEM and SGT-HEM TALS worksheet

18.0 Revision History

18.1 Revision 6, 11/12/2008

18.2 Revision 7, 6/11/2009

18.3 Revision 8, 9/21/200

18.4 Revision 9, 7/1/2010

18.5 Revision 10, 11/4/2010

18.6 Revision 11, 6/8/2012

18.7 Revision 12, 6/3/2013

18.8 Revision 13, 6/16/2015

18.9 Revision 14, 7/20/2016

18.10 Changes to current revision

SOP section	Change from	Change to	Reason
1.4	10.22.2	10.23.2	Correction
7.6	Removed sodium sulfate		Not used for SPE
7.7 & 7.8 (were 7.8 & 7.9)	Combined and LCS purchased standard information	Made 7.9 laboratory prepared standard information	Clarification
7.8.1 NOTE		Clarified language for rinsing	Clarification
8.0	Removed that containers, preservation and holding times may vary		Correction
9.4	Reference to 7.8	7.7	Correction for section 7 change
9.6	Blank contamination	QC failure	Clarification
9.7	Reference to 7.7	7.6	Correction for section 7 change
10.8	Spike the MS and MSD aliquots with Matrix Spike solution (7.9)	For the LCS and MS/MSD aliquots, spike each in the bottle with the Spiking Standard (7.7)	Correction for section 7 change / Clarification
10.9.1	“prior to extraction to the cartridge prior to extraction…”	“prior to adding the sample…”	Correction
10.13		Added Fill the rinsed sample bottle to the meniscus marking, and measure the volume contained using a 1 Liter, class A, graduated cylinder. Record the sample volume on the batch worksheet.	Clarification for PADEP Audit Finding
10.23.1	The residue from the HEM determination is re-dissolved in a suitable…	Rinse the residue from the HEM determination into a suitable…	Clarification
10.22 10.23.5	10.22 10.17-10.20	10.23 10.18-10.21	Correction for addition of step 10.13
12.2.2	DOC	IDOC	Correction
12.2.3		Added instructions for continuing DOC.	Clarification

FIGURE 1 – Example TALS Worksheet for HEM

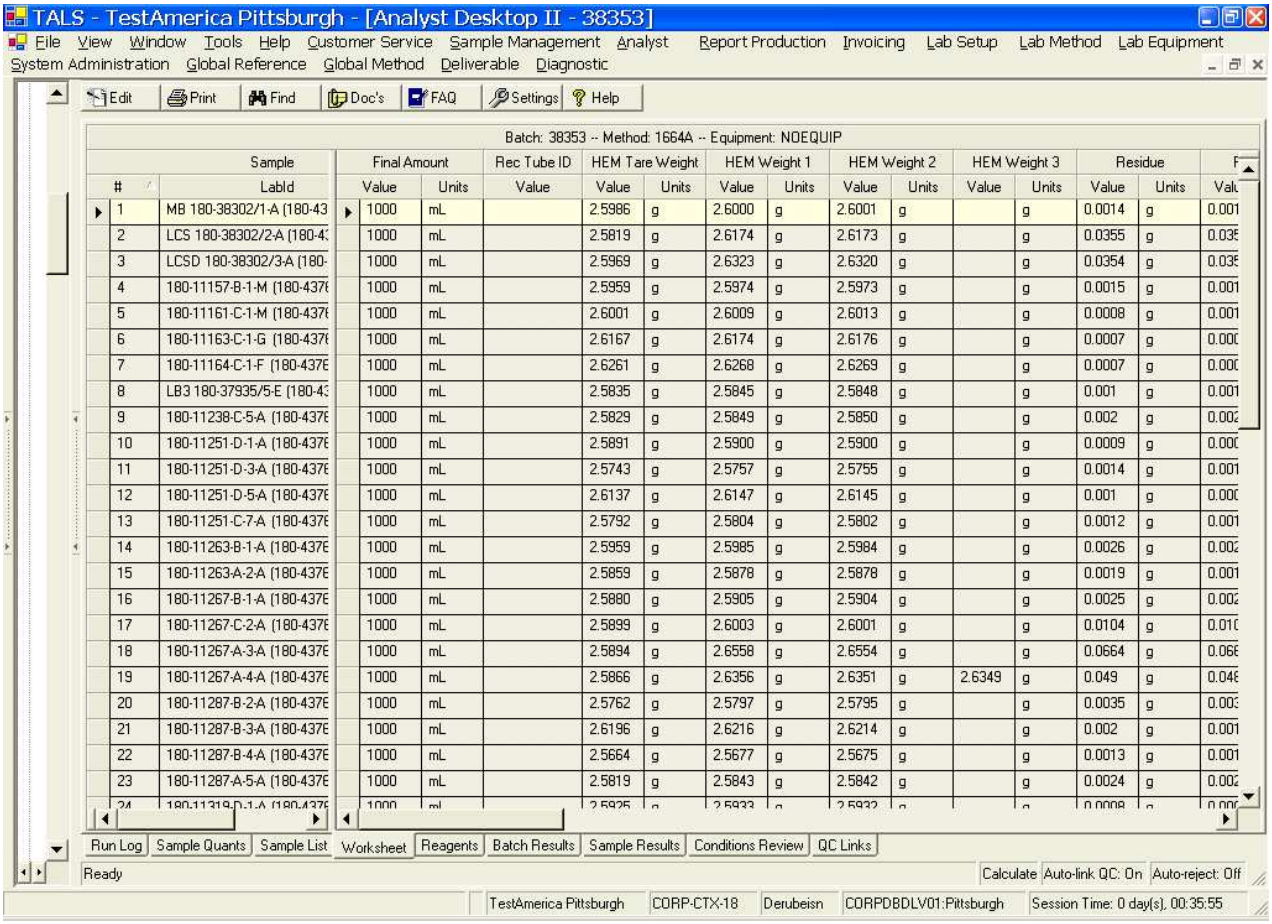
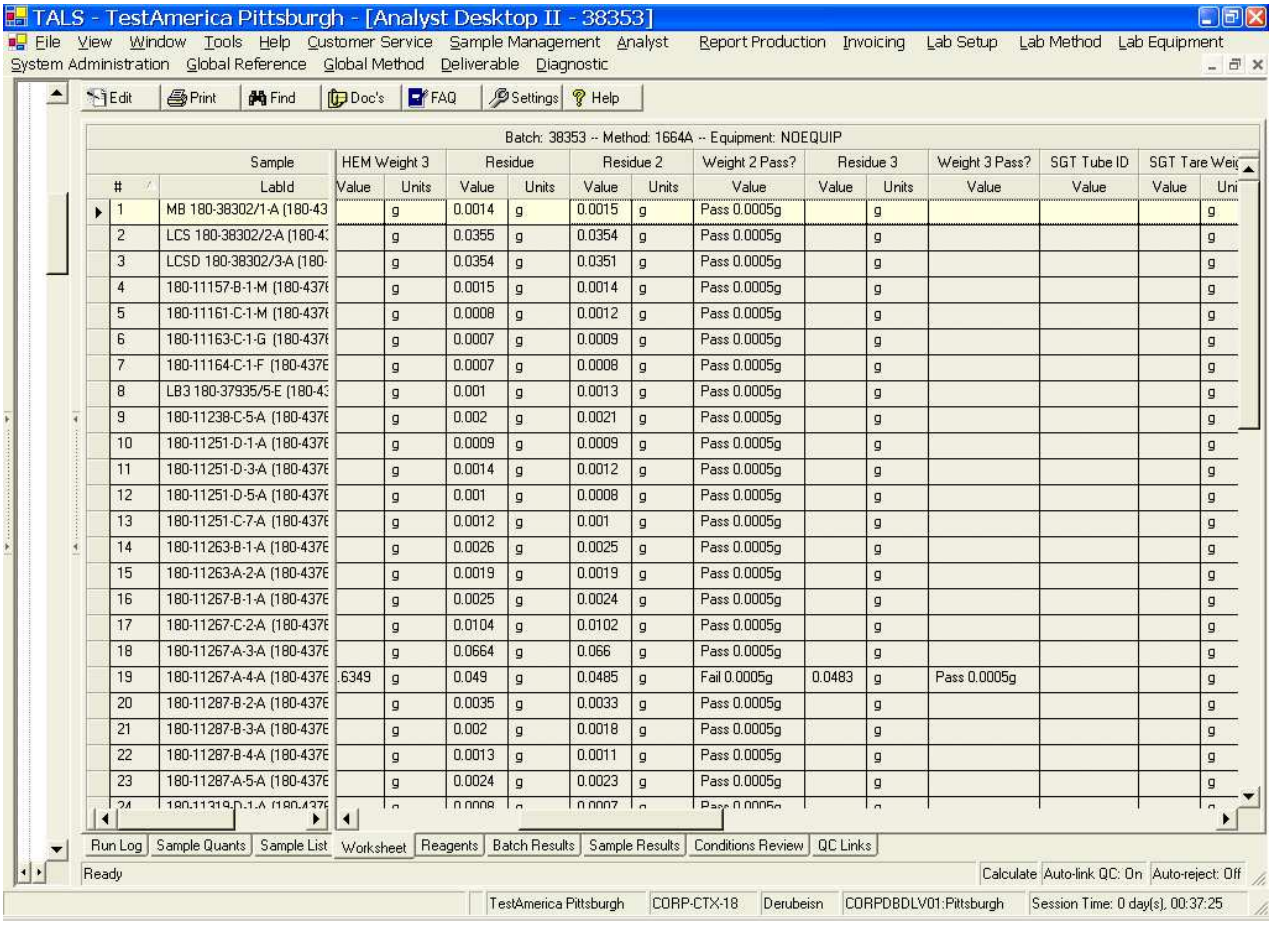


FIGURE 1 – Example TALS Worksheet for HEM cont.



#	Sample LabId	HEM Weight 3 Value	Units	Residue Value	Units	Residue 2 Value	Units	Weight 2 Pass? Value	Residue 3 Value	Units	Weight 3 Pass? Value	SGT Tube ID Value	SGT Tare Wei Value	Uni
1	MB 180-38302/1-A (180-43		g	0.0014	g	0.0015	g	Pass 0.0005g		g				g
2	LCS 180-38302/2-A (180-4		g	0.0355	g	0.0354	g	Pass 0.0005g		g				g
3	LCSD 180-38302/3-A (180-		g	0.0354	g	0.0351	g	Pass 0.0005g		g				g
4	180-11157-B-1-M (180-437		g	0.0015	g	0.0014	g	Pass 0.0005g		g				g
5	180-11161-C-1-M (180-437		g	0.0008	g	0.0012	g	Pass 0.0005g		g				g
6	180-11163-C-1-G (180-437		g	0.0007	g	0.0009	g	Pass 0.0005g		g				g
7	180-11164-C-1-F (180-437		g	0.0007	g	0.0008	g	Pass 0.0005g		g				g
8	LB3 180-37935/5-E (180-4		g	0.001	g	0.0013	g	Pass 0.0005g		g				g
9	180-11238-C-5-A (180-437		g	0.002	g	0.0021	g	Pass 0.0005g		g				g
10	180-11251-D-1-A (180-437		g	0.0009	g	0.0009	g	Pass 0.0005g		g				g
11	180-11251-D-3-A (180-437		g	0.0014	g	0.0012	g	Pass 0.0005g		g				g
12	180-11251-D-5-A (180-437		g	0.001	g	0.0008	g	Pass 0.0005g		g				g
13	180-11251-C-7-A (180-437		g	0.0012	g	0.001	g	Pass 0.0005g		g				g
14	180-11263-B-1-A (180-437		g	0.0026	g	0.0025	g	Pass 0.0005g		g				g
15	180-11263-A-2-A (180-437		g	0.0019	g	0.0019	g	Pass 0.0005g		g				g
16	180-11267-B-1-A (180-437		g	0.0025	g	0.0024	g	Pass 0.0005g		g				g
17	180-11267-C-2-A (180-437		g	0.0104	g	0.0102	g	Pass 0.0005g		g				g
18	180-11267-A-3-A (180-437		g	0.0664	g	0.066	g	Pass 0.0005g		g				g
19	180-11267-A-4-A (180-437	.6349	g	0.049	g	0.0485	g	Fail 0.0005g	0.0483	g	Pass 0.0005g			g
20	180-11287-B-2-A (180-437		g	0.0035	g	0.0033	g	Pass 0.0005g		g				g
21	180-11287-B-3-A (180-437		g	0.002	g	0.0018	g	Pass 0.0005g		g				g
22	180-11287-B-4-A (180-437		g	0.0013	g	0.0011	g	Pass 0.0005g		g				g
23	180-11287-A-5-A (180-437		g	0.0024	g	0.0023	g	Pass 0.0005g		g				g

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Determination of Total and Volatile Suspended Solids in Waters and Wastes

Method(s): EPA 160.4 and Standard Methods 2540D & 2540E

Approvals (Signature/Date):

1/6/2017	12/15/2016
Roseann Ruyechan Date	Steve Jackson Date
Inorganics Department Manager	Regional Safety Coordinator
12/12/2016	12/14/2016
Virginia Zusman Date	Deborah L. Lowe Date
Quality Assurance Manager	Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This SOP is applicable to the determination of total suspended solids and volatile suspended solids using gravimetric techniques. This SOP is based on the residue methods contained in EPA MCAWW and Standard Methods for the Examination of Water and Wastes (SM), 2011.

1.2. This SOP is applicable to drinking, surface, and saline waters and domestic and industrial wastes.

1.3. The Total Suspended Solids (TSS), or Non Filterable Residue, analysis protocol is based on SM 2540D.

1.4. The Volatile Suspended Solids (VSS) analysis protocol is based on EPA Method 160.4 and SM 2540E.

1.5. The methods cover a practical range of 2 mg/L to 20,000 mg/L.

1.6. The reporting limit is 2 mg/L for TSS and VSS, for a 1000mL sample.

1.7. On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated PT-QA-M-001, Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. Total Suspended Solids (TSS): A well-mixed sample is filtered through a pre-weighed glass fiber filter with a pore size of 2.0µm (or smaller). The residue on the filter is dried to constant weight at 103 -105°C. The increase in weight over that of the pre-weighed filter represents the TSS content. The filtrate from this procedure may be used for TDS determination. The filter from this procedure may also be used for VSS analysis.

2.2. Volatile Suspended Solids (VSS): The residue obtained from the determination of total suspended solids is ignited at 550°C. VSS is determined from the weight loss after ignition.

2.3. Total Dissolved Solids may be performed at the same time, using the filtrate from the TSS filtration. Refer to SOP PT-WC-045 for details of this analysis.

3. DEFINITIONS

3.1. TALS – TestAmerica Laboratory Information Management System

3.2. NCM – Non-Conformance Memo - a system within TALS for the lab to communicate to project management and others when there is an anomaly seen with the samples or batch, or a QC failure.

3.3. Refer to the glossary in the Laboratory Quality Assurance Manual (PT-QA-M-001), current version.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of analysis by running method blanks.

4.2. Non-homogeneous samples may give erroneous results. Samples should be mixed as thoroughly as possible before removing an aliquot for analysis.

4.3. Non-representative particulates such as leaves, sticks, and other detritus should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted on the benchsheet.

4.4. Samples containing large amounts of solids may filter slowly. Prolonged filtration times resulting from filter clogging may produce high TSS results due to increased colloidal materials captured on the clogged filter. Analysis volumes should be reduced for such samples.

4.5. Oil and grease in the samples will cause unreliable results due to difficulty in drying to constant weight. Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

4.6. Filtration apparatus, filter material, pre-washing, post-washing, and drying temperatures are specified because these variables have been shown to affect the results.

4.7. The temperature at which the residue is dried has an important bearing on the results because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

4.8. Each sample requires close attention to desiccation after drying. Minimize opening the desiccator because moist air enters. Some samples may be more hygroscopic than those used as the desiccant and may take absorb additional water from the air as they cool.

4.9. Too much residue on the filter will crust over, entrapping water that will not be driven off during drying. Total residue must be limited to 200 mg.

4.10. For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material prior to TSS determination.

4.11. The volatile solids tests are subject to many errors due to the loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics and decomposition of mineral salts during combustion. The results should not be considered an accurate measure of organic carbon in the sample.

4.12. Oils from hands can be transferred to the filters, causing a positive interference with these analyses. Handle filters only with forceps.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Pittsburgh Facility Addendum EH&S manual (PT-HS-001), and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Oily samples or those that contain volatile chemicals may ignite during this procedure. In the case of a fire, the muffle should be turned off and allowed to cool before the sample can be removed and put under a hood.

5.3. Always use tongs, forceps or heat resistant gloves when placing filter pans in or removing them from ovens. Extra care should be used when using a muffle furnace, as temperatures are extremely high. Gloves designed for dealing with extreme temperatures must be used when handling any sample container that has been in a muffle furnace.

5.4. There are no materials used in this method that have a significant or serious hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1. Analytical balance capable of weighing to 0.0001 g

6.2. Vacuum filtration apparatus

6.3. Vacuum pump equipped with moisture trap

6.4. Glass fiber filter disks, 47 mm, pore size $\leq$ 2µm, without organic binder - Whatman 934-AH, pre-cleaned and pre-weighed.

6.4.1. If VSS analysis is to be performed, Environmental Express Proweight Filters (part # F93447VOL) are used. Glass fiber filter disks, 47 mm, pore size ≤ 2µm, without organic binder, pre-cleaned and dried at 550°C and pre-weighed

6.4.2. If pre-cleaned filters are not used, the preparation steps in section 10.3.1.2 must be used prior to filtering samples.

6.5. Desiccators providing sufficient space for storage of samples in process separate from filters and evaporating dishes

6.6. Desiccant containing a color indicator of moisture concentration or an instrumental indicator

6.7. Drying oven set at 103 -105°C

6.8. Muffle furnace set at 550°C ± 50°C

6.9. Thermometers, NIST traceable

6.10. Graduated cylinders, to deliver (TD), assorted sizes, Class A

6.11. Aluminum weighing dishes large enough to hold a 47 mm filter - (Pre-weighed filters are purchased already in Aluminum dishes.)

6.12. Forceps

6.13. Zetex gloves or other gloves capable of providing protection at 550°C

6.14. Wide-bore serological volumetric pipettes

7. REAGENTS AND STANDARDS

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the SDS prior to the use of any reagent or standard.

7.1. Reagent water - Deionized water, with conductance <1 umhos/cm – to be used for blanks and rinses

7.2. The LCS standard solution is commercially purchased. The true value varies from lot to lot when received from the manufacturer and the calculation is adjusted accordingly by the laboratory. The standard is received with a certificate of analysis with the true value listed on it and is retained by the laboratory.

7.2.1. If the solution needs to be made by the laboratory the procedure is as follows: LCS solution (500 mg/L TSS and TDS, 1000 mg/L TS): Place 500.0 mg of diatomaceous earth (infusorial earth or celite 545) and 500 mg sodium chloride into a 1000 mL volumetric flask and dilute to volume with deionized water. Mix well. Prepare fresh every three months.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples should be collected in either plastic or glass bottles. No chemical preservation is required.

8.2. Samples must be stored at >0.0℃ but ≤6.0℃ to minimize microbiological decomposition of solids. Bring samples to room temperature before analysis.

8.3. To meet method SM2540D requirements, sufficient sample volume, **up to 1 L**, must be filtered to produce at least 2.5mg of final residue on the filter.

8.3.1. Smaller samples sizes may be used for samples that are high in solids. Historical data or visual inspection may be used to choose a different sample size for initial analysis, as long as the minimum (2.5mg) and maximum (200mg) limits are met.

8.4. Holding time for TSS and VSS determination is 7 days from the date of sampling to begin the analysis.

9. QUALITY CONTROL

The TestAmerica QC Program document (PT-QA-021) provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

9.1. Method Blank (MB): One method blank must be processed with each batch of 20 or fewer samples. The method blank consists of 1L of reagent water that is carried through the entire analytical procedure, including filtration as applicable. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or

false positive data. Blank results must be less than the RL. If the MB result is above the control limits, all associated samples must be reanalyzed unless one of the following conditions exists.

- If a Blank result is above the RL, but solids are not detected above the RL in the associated samples, the data may be reported with qualifiers and using the "Method Blank – Report, ND" NCM.

- If the sample concentrations are greater than 10x the concentration seen in the MB, results may be reported with qualifiers and using the "Method Blank – Report, 10X" NCM

9.1.1. High blank results indicate contamination. Make sure the filtering apparatus is clean before repeating the analysis.

9.1.2. If MB results are negative (filter weighs less after analysis), this indicates that the balance was not operating correctly or the filter/weighing dish was not completely dry when the initial weights were measured. If MB results are below the negative RL (a change of -0.0025g for example), all samples with concentrations <10X the RL should be reanalyzed if possible. If reanalysis is not possible, the negative blanks and possible negative bias for the sample results must be narrated using the "Other – Deficiency" NCM.

9.2. Laboratory Control Sample (LCS): One LCS must be processed with each batch of 20 or fewer samples. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.2.1. No LCS is available for volatile residue procedures.

9.2.2. Refer to Section 7.2.1 for instructions on how to prepare the LCS solution, unless using a purchased standard. The LCS analysis volume must be calculated to produce a final residue between 25 and 200mg.

9.2.3. The LCS percent recovery must be within 80 -120% of the true or certified value.

9.2.4. If LCS recovery is outside the control limits, all associated samples must be reanalyzed with an acceptable LCS, unless the original LCS recovery is high and samples results are <RL.

9.2.4.1. If reanalysis is not possible due to limited sample quantity or holding time considerations, the project manager must be notified so that the client can be informed. Results reported associated with a failed LCS must be reported with the appropriate result qualifier and the failure narrated through the appropriate NCM:

- For high LCS recovery and associated samples <RL, use "LCS/LCSD - %R High".
- If samples are reanalyzed due to failed LCS, and the reanalysis occurs past the holding time, use "LCS/LCSD - %R, RX/RA Batch, Outside".
- If there is insufficient sample volume to perform a reanalysis, use "LCS/LCSD – Insufficient Sample".

9.2.5. Poor LCS results are usually the result of contamination or poor mixing. Make sure to shake the LCS and all samples very well before pouring out the portion to be filtered or analyzed. Do not allow the sample to settle in the graduated cylinder.

9.3. Duplicate (D): A duplicate sample analysis is required with every 10 samples or less for all methods.

9.3.1. Sample and Duplicate results must agree within 10%RPD if both the sample and sample duplicate results are > 5x RL. For sample and/or duplicate results that are < 5x RL, the sample and duplicate difference must be <RL concentration.

9.3.2. The failure of the sample duplicates to meet precision criteria must be addressed in the case narrative.

9.3.3. Make sure to shake all samples very well before pouring out the portion to be filtered or analyzed to improve homogenization and precision. Do not allow the sample to settle in the graduated cylinder before analyzing.

9.3.4. On-going method precision is documented using LCS control charting.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Proper balance operation will be verified daily or prior to sample analysis by following the balance calibration SOP, PT-QA-12. Analytical balance calibration must be verified at least every 24 hours, and prior to using the balance each day. Weights used for calibration verification, prior to initial and read-back weighings, are documented in the TALS batch information.

10.1.1.1. For TSS and VSS, balances are verified using 2mg, 1g and 5g weights.

10.1.1.2. Balance reading for the 2mg weight must be 0.0018g - 0.0022g; for the 1g weight must be 0.9990g – 1.0010g; for the 5g weight must be 4.9950g – 5.0050g. If any reading falls outside these limits, the balance must be recalibrated and the verification performed again with all weights in the group.

10.1.2. Oven temperature must be checked daily and recorded in the oven temperature logbook. Oven temperature must be kept between 103-105^{o}C. Volatile Suspended Solids are ignited in the muffle furnace at 550 ± 50^{o}C. The temperature of the muffle furnace used for volatile residues analyses is documented at the time of use.

10.2. Procedure

10.2.1. Any variation in procedure shall be completely documented using a Nonconformance Memo and must be approved by a Supervisor or Manager. If contractually required, the client shall be notified.

10.2.2. All samples are to be electronically checked out of sample control with the TALS internal chain of custody (ICOC) program.

10.2.3. Proper sample identification is extremely important in any analytical procedure. Labeling of filters holders must be done in a manner to ensure connection with the proper sample. Labeling must be done in a way that will not be compromised by the heat used. For VSS, the sample ID is pressed into the Aluminum pan.

10.2.4. Non-representative particulates such as leaves, sticks, and other detritus should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted on the TALS Worksheet Notes or Batch Information Comments.

10.2.5. If samples are visibly oily, this should be noted on the TALS Worksheet Notes or Batch Information Comments.

10.2.6. If there is limited sample volume or high solids content, smaller amounts of sample may need to be processed than detailed in the following sections. This occurrence must be noted on the TALS Worksheet. Reporting limits are adjusted according to the actual sample volume used.

10.2.7. All weights are recorded to the nearest 0.1mg directly from the balance into the TALS Worksheet using balance upload. If the balance upload is not working, the weights are recorded in the Wet Chemistry Raw Data Logsheet for transfer to the TALS Worksheet. If the manual Logsheet is used, it must be scanned to a pdf and attached to the TALS batch as raw data.

10.2.8. Prepare TALS analytical batches prior to beginning analysis, as the batch must be available to upload initial weights and record sample volumes used.

10.2.9. Scan the barcode on the filter's pan for pre-weighed filters. This will upload both the pan ID and the filter weight into the "Dish" column on the TALS Worksheet. Manually enter the filter weight into the "Tare Weight Value" column. (See Figure 4.)

10.3. Total Suspended Solids – SM 2540D

10.3.1. Preparation of Glass Fiber Filter Disc:

10.3.1.1. Prepared and pre-weighed filters are purchased for use under this method. The certificate of analysis is retained for the filters. The filter lot number is documented in the TALS Batch Information. Scan the barcode on the filter's pan to enter the tare weight of the filter into the TALS Batch Worksheet.

- When a new lot/box of pre-weighed filters is opened for use, 5% of the filters are chosen at random, and weighed to confirm that the weights provided are correct, within 0.0004g. If the filter weight

does not agree, that filter is not used. If more than 5 filters checked per box do not agree, the box is not used for analysis.

- For TSS only analysis, use Whatman 934-AH filters. If VSS analysis is to be performed, Environmental Express Proweight filters.

10.3.1.2. If prepared/pre-weighed filters are not used:

- Place the glass fiber filter discs, one at a time, on the membrane filter apparatus with wrinkled surface side up.
- While vacuum is applied, wash the disc with three successive 20 mL volumes of reagent water.
- Remove all traces of water by continuing to apply vacuum after water has passed through and discard washings.
- Remove filter from membrane filter apparatus and place in a labeled, aluminum weighing dish. Dry the prepared filters in an oven at 103 -105°C for at least one hour.
- If volatile suspended solids (VSS) are to be determined as well as total suspended solids, the filter must be heated at 550 ± 50°C for 15 minutes.
- Using forceps, remove the pans from the oven and place in a desiccator and cool to room temperature.
- Weigh the cooled filter using an analytical balance to the nearest 0.1 mg. Handle the filters or pan/filter only with forceps. This weight is automatically uploaded into the TALS Worksheet and associated with the TALS sample batch using the Balance Link program (see Figure 4).
- Repeat the drying, cooling, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg.

10.3.2. Selection of Sample Volume

10.3.2.1. For the Method Blank and clean samples, filter 1000mL.

10.3.2.2. If during filtration of this initial volume, the filtration rate drops rapidly or if filtration time exceeds 5 - 10 minutes, a smaller volume of sample should be processed. Sample cannot be poured out of the filtration apparatus once added. If a smaller sample size is needed, the analysis must be started over.

10.3.2.3. If the sample appears high in TSS, start with a sample volume < 100mL. If the sample filters rapidly and no significant residue remains on the filter, more volume can be added. If volumes less than 10 mL are required, measure the sample volume using a wide-bore serological pipette, so as not to exclude larger particles from the sample aliquot.

10.3.2.4. For TSS, a residue of at least 2.5mg must be obtained, or a liter of water must be filtered.

10.3.3. Sample Analysis:

10.3.3.1. Assemble the filtering apparatus, and rinse with DI water.

10.3.3.2. Weigh filter, or scan pre-weighed filter pan, and enter the filter weight into the TALS worksheet. Place the filter in the apparatus, wrinkled surface side up. Pre-wet the filter using a few mL of reagent water and begin suction.

10.3.3.3. Shake the sample vigorously and quantitatively transfer the appropriate volume of the sample to the filter using a graduated cylinder or wide-bore pipette. For samples which are visibly high in TSS or are otherwise slow to filter, filter 25mL at a time until filtration slows. Record the volume of sample filtered (to the nearest mL) on the TALS Worksheet.

Note: If Total Dissolved Solids (TDS) is also required, the filtrate from the TSS analysis may be used. Refer to SOP PT-WC-045 for details of TDS analysis.

10.3.3.4. Remove all traces of water by continuing to apply vacuum after the sample has passed through.

10.3.3.5. With suction on, rinse the graduated cylinder, filter, suspended solids residue, and filter funnel wall with three 10 mL portions of reagent water allowing complete drainage between washings.

10.3.3.6. Remove all traces of water by continuing to apply vacuum for about three minutes after the sample has passed through.

10.3.3.7. Carefully remove the filter from the filter support and transfer back to its aluminum weighing dish.

10.3.3.8. Dry the filter at least one hour at 103 -105°C.

10.3.3.9. Record the date, time, and oven temperature on the TALS Batch Information when the samples are initially placed in the oven and again when they are removed from the oven (see Figure 3).

10.3.3.10. Using forceps, remove the weighing dish from the oven and place in a desiccator.

10.3.3.11. Cool the samples to room temperature in the desiccator. Weigh the filter and upload the weight to the TALS Worksheet (see Figure 4).

10.3.3.12. If the residue is >0.2g (200mg), start the analysis over again with a smaller sample volume. If insufficient volume is available for reanalysis, proceed with the steps below, and narrate that the results were determined from a residue >0.2g. Longer drying times may be required to reach constant weight.

10.3.3.13. Return the samples to the oven for at least another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained. Constant weight is considered a weight change < 0.5 mg or < 4% of the previous weight, whichever is less. If constant weight has not been achieved after three cycles of heating, cooling and weighing; document the 3 weights and do not perform any further cycles. Document that only 3 heating cycles were performed using an NCM. The lowest weight of the 3 is used for calculating the final result.

NOTE: All dates, times, temperatures and weights are recorded in the TALS Batch.

10.3.3.14. If volatile suspended solids are to be determined, treat the residue according to Section 10.4.

10.3.3.15. TALS will automatically calculate the sample result from the data entered into the Worksheet. Check the calculations using the formula given in Section 11.1. Use the lowest final weight achieved for calculating TSS.

10.4. Volatile Suspended Solids – 160.4 and SM 2540E

10.4.1. Heat the muffle furnace up to temperature (550 ± 50 °C).

10.4.2. Place the filter from the TSS analysis (Section 10.3.3.) into an Aluminum pan that does not have a paper label. Press the sample ID into the pan. Place the pans into the muffle furnace to ignite the residue.

10.4.3. Record the date, time, and muffle furnace temperature in the TALS Batch Information when the samples are initially placed in the oven and again when they are removed from the oven (see Figure 5 or 7).

10.4.4. Heat the samples for at least 20 minutes. Typically, 15 - 20 minutes ignition is sufficient for 200 mg of residue. Because TSS residue is restricted to <200mg, only a single ignition is required for VSS.

10.4.5. Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace and place in a desiccator and cool to room temperature.

10.4.6. Weigh the cooled dish, and upload the weight into the TALS Batch Worksheet (see Figure 6 or 8).

10.4.8 TALS will calculate the final results. Check calculations using the formula given in Section 11.2. Use the lowest final weight achieved for calculating VSS.

11. CALCULATIONS / DATA REDUCTION

11.1. Calculate Total Suspended Solids as follows:

$$\text{Total Suspended Solids, mg / L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of filter + residue (mg)
B = weight of filter (mg)
C = volume of sample filtered (mL)

11.2. Calculate Volatile Suspended Solids as follows:

$$\text{Volatile Suspended Solids, mg / L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of residue + filter before ignition (mg)
B = weight of residue + filter after ignition (mg)
C = volume of sample (mL)

11.3. The relative percent difference (RPD) of duplicates are calculated according to the following equation:

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where: DU1 = Sample result
DU2 = Sample duplicate result

11.4. LCS Percent Recovery

$$\text{LCS Percent Recovery} = \left(\frac{\text{Observed Conc. in LCS}}{\text{True LCS Conc.}}\right) \text{x } 100 \text{ Percent}$$

11.5. If multiple weighing cycles are required, the lowest final sample weight is used for calculating solids content.

11.6. If smaller or larger sample volumes are processed than are specified in the method, the reporting limit must be adjusted accordingly.

11.7. Sample results should be reported according to the following significant figure rules:

Significant Figures	Sample Result
2	< 10
3	≥ 10

12. METHOD PERFORMANCE

12.1. The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2. Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3. MDLs are not performed for this procedure. Results are not reported below the RL.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention" and the Pittsburgh Facility Addendum EH&S Manual (PT-HS-001).

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001.

14.2. The following waste streams are produced when this method is carried out.

14.2.1. Unpreserved waste samples. This waste is disposed down a lab sink.

14.2.2. Aluminum weighing tins, contaminated filter and filter residue generated by the analysis. This waste is disposed of in trashcans with the building trash.

15. REFERENCES

15.1. Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979: Method 160.4.

15.2. Standard Methods for the Examination of Water and Waste Water, 2011; Methods 2540D and 2540E

15.3. SOP PT-QA-021, TestAmerica Pittsburgh QC Program

15.4. SOP PT-QA-012, Selection and Calibration of Balances and Weights

15.5. TestAmerica Pittsburgh Laboratory Quality Assurance Manual, PT-QA-M-001

15.6. SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability

15.7. SOP PT-QA-008, Thermometer Calibration and Temperature Monitoring

15.8. SOP PT-QA-016, Nonconformance & Corrective Action System

15.9. SOP PT-QA-031, Internal Chain of Custody

15.10. SOP PT-HS-001, Pittsburgh Facility Addendum EH&S Manual

16. METHOD MODIFICATIONS

16.1. Samples are not taken through the drying, cooling, and weighing cycle more than three times. If the sample fails to reach constant weight within three cycles, this is documented in a Nonconformance Memo and the lowest final weight is used for the calculation.

17. ATTACHMENTS

17.1. Figure 1: Total Suspended Solids (TSS) Flow Chart

17.2. Figure 2: Volatile Suspended Solids (VSS) Flow Chart

17.3. Figure 3: TALS Batch Information – Method 2540D

17.4. Figure 4: TALS Batch Worksheet – Method 2540D

17.5. Figure 5: TALS Batch Information – Method 2540E

17.6. Figure 6: TALS Batch Worksheet – Method 2540E

17.7. Figure 7: TALS Batch Information – Method 160.4

17.8. Figure 8: TALS Batch Worksheet – Method 160.4

18. REVISION HISTORY

18.1. Revision 0, 11/24/2014

18.2. Changes to current revision

SOP section	Change from	Change to	Reason
3.2		Added definition of NCM	Clarification
6.14		Added Wide-bore serological volumetric pipette	Addition
6.11, 10.2.3 and 10.4.2	Al	Aluminum	Correction
8.1		Added “No chemical preservation is required.” as the last sentence	Clarification

10.3.1.2	"one hour, instead of 103 - 105°C"	"15 minutes"	Correction
10.3.2.3		Added text to note for volumes < 10 mL a wide-bore serological pipette will be used to measure this volume so as not to exclude larger particles from the sample aliquot	Correction
13.1		Added reference to PT-HS-001	SOP Review Sheet format
15.9 15.10 15.11		Added: PT-QA-031 PT-HS-001 PT-SR-001	Additions

Figure 1 - Total Suspended Solids (TSS)

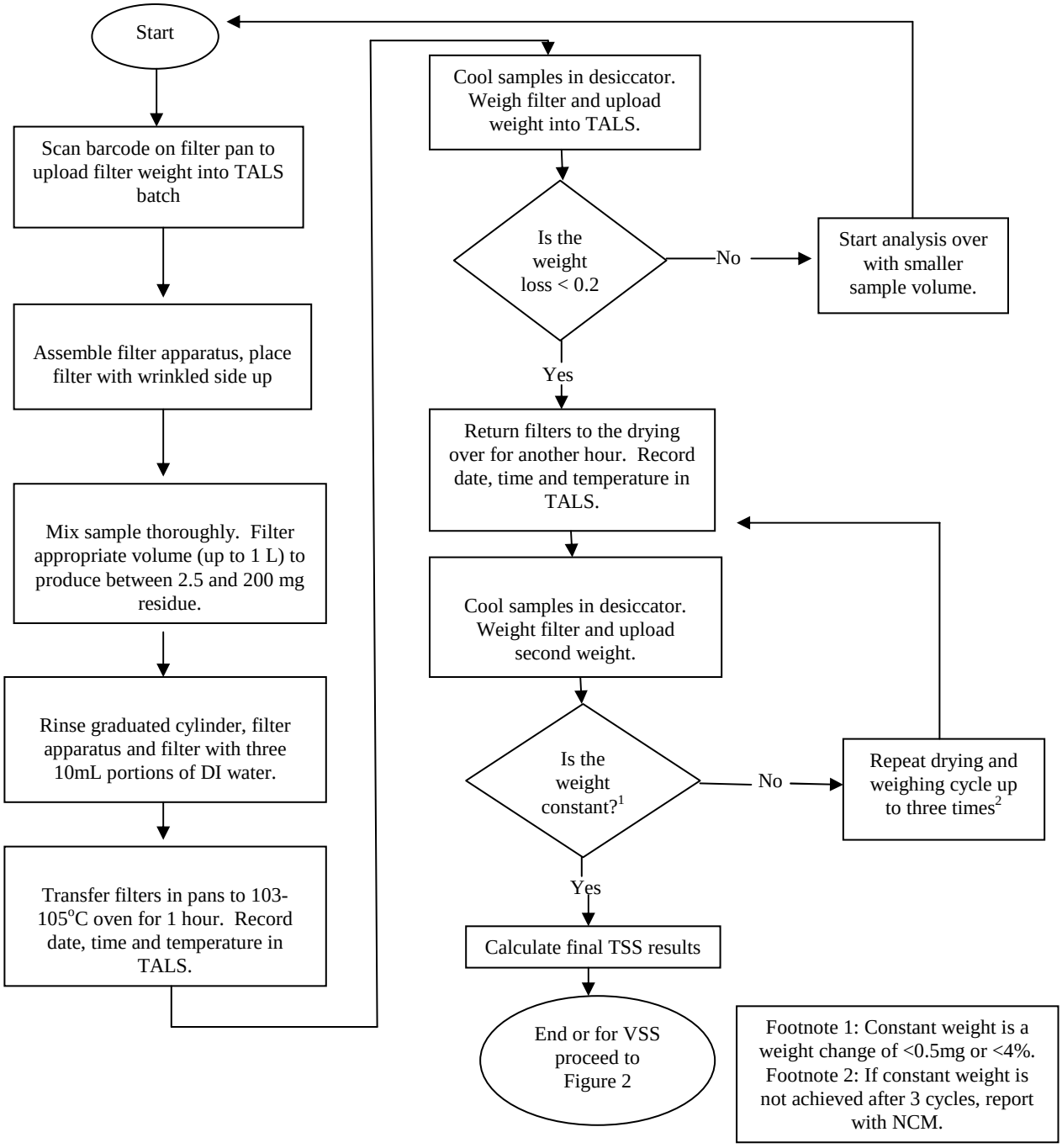
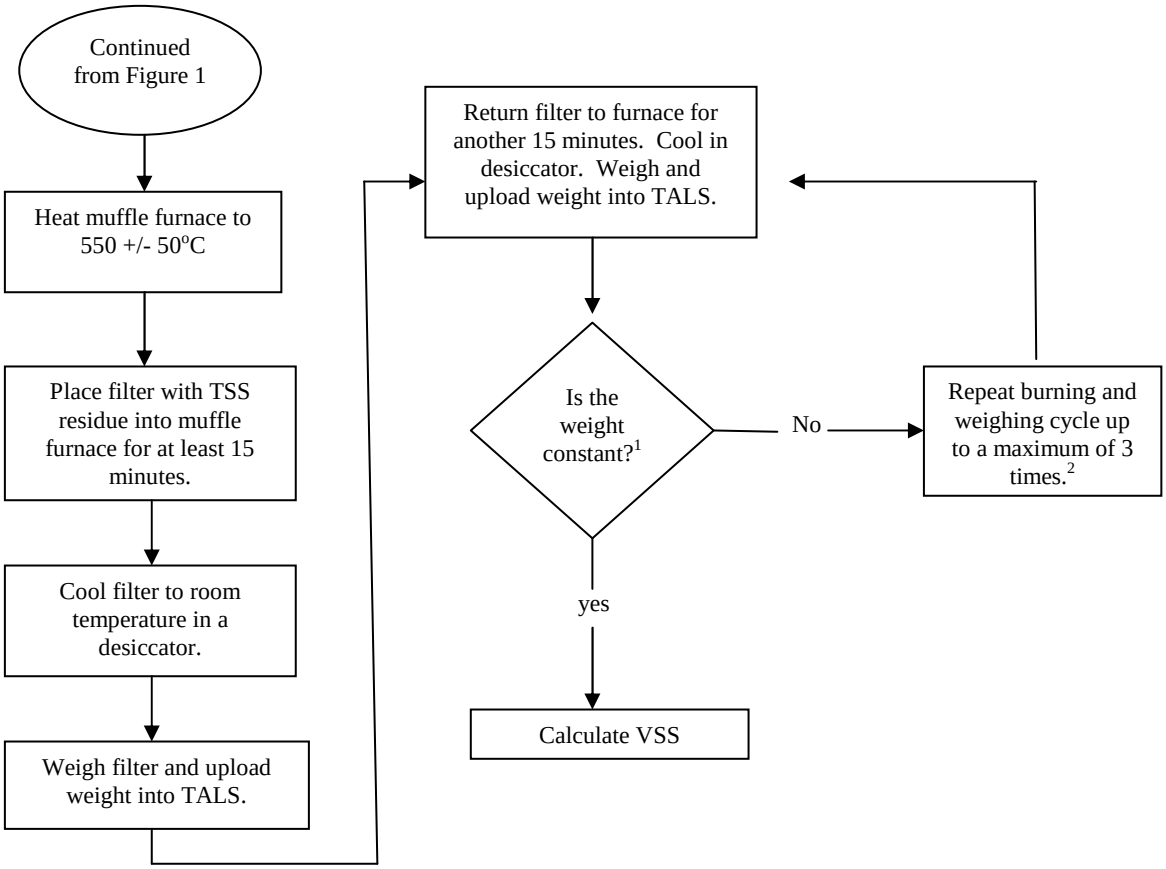
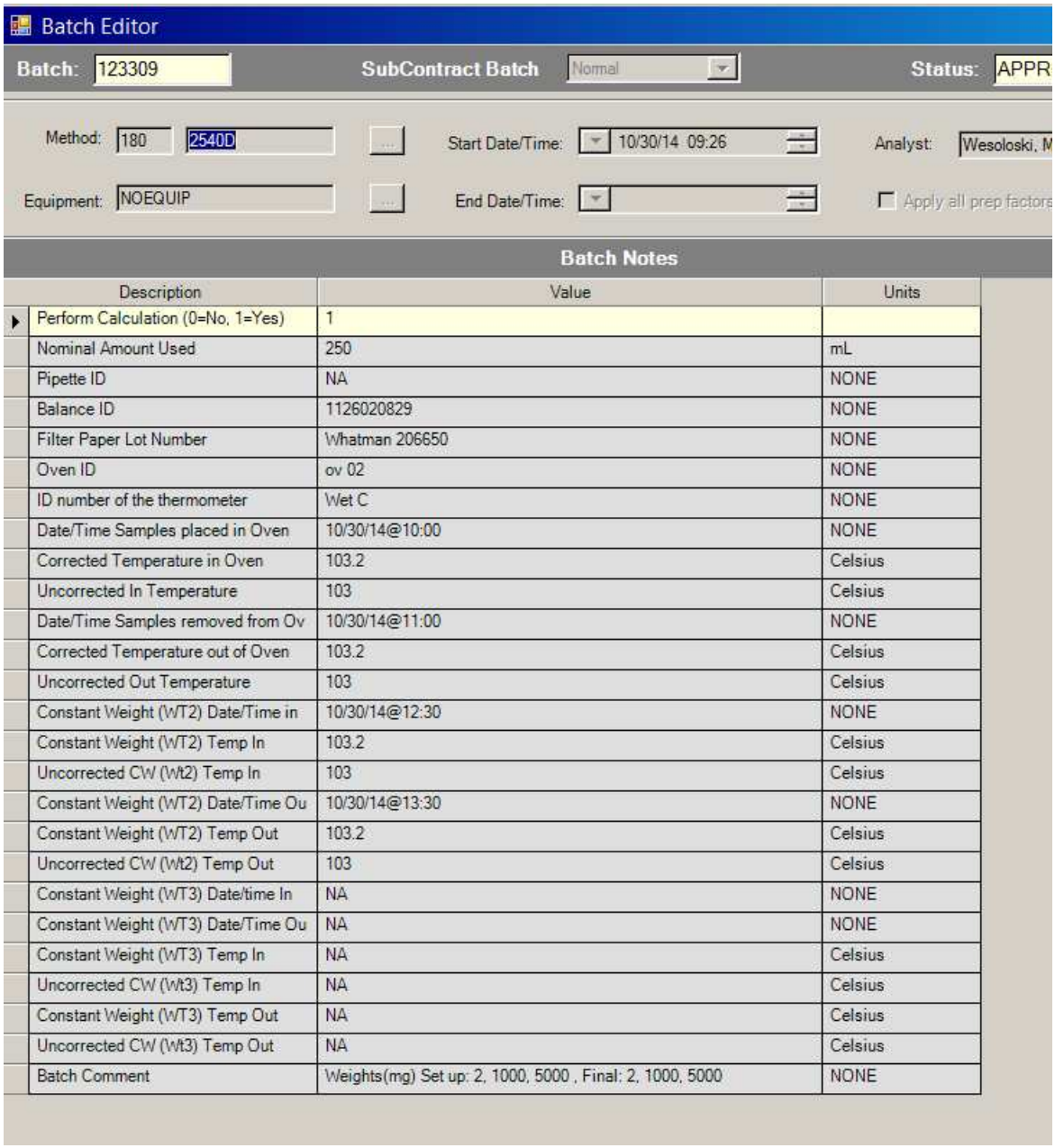


Figure 2 - Volatile Suspended Solids (VSS)



Footnote 1: Constant weight is a weight change of <0.5mg or <4%.
Footnote 2: If constant weight is not achieved after 3 cycles, report with NCM.

Figure 3 - TALS Batch Information – Method 2540D



Batch Editor

Batch: 123309 SubContract Batch Normal Status: APPR

Method: 180 2540D Start Date/Time: 10/30/14 09:26 Analyst: Wesoloski, M

Equipment: NOEQUIP End Date/Time: Apply all prep factors

Batch Notes

Description	Value	Units
Perform Calculation (0=No, 1=Yes)	1	
Nominal Amount Used	250	mL
Pipette ID	NA	NONE
Balance ID	1126020829	NONE
Filter Paper Lot Number	Whatman 206650	NONE
Oven ID	ov 02	NONE
ID number of the thermometer	Wet C	NONE
Date/Time Samples placed in Oven	10/30/14@10:00	NONE
Corrected Temperature in Oven	103.2	Celsius
Uncorrected In Temperature	103	Celsius
Date/Time Samples removed from Ov	10/30/14@11:00	NONE
Corrected Temperature out of Oven	103.2	Celsius
Uncorrected Out Temperature	103	Celsius
Constant Weight (WT2) Date/Time in	10/30/14@12:30	NONE
Constant Weight (WT2) Temp In	103.2	Celsius
Uncorrected CW (Wt2) Temp In	103	Celsius
Constant Weight (WT2) Date/Time Ou	10/30/14@13:30	NONE
Constant Weight (WT2) Temp Out	103.2	Celsius
Uncorrected CW (Wt2) Temp Out	103	Celsius
Constant Weight (WT3) Date/time In	NA	NONE
Constant Weight (WT3) Date/Time Ou	NA	NONE
Constant Weight (WT3) Temp In	NA	Celsius
Uncorrected CW (Wt3) Temp In	NA	Celsius
Constant Weight (WT3) Temp Out	NA	Celsius
Uncorrected CW (Wt3) Temp Out	NA	Celsius
Batch Comment	Weights(mg) Set up: 2, 1000, 5000 , Final: 2, 1000, 5000	NONE

Figure 4 - TALS Batch Worksheet – Method 2540D

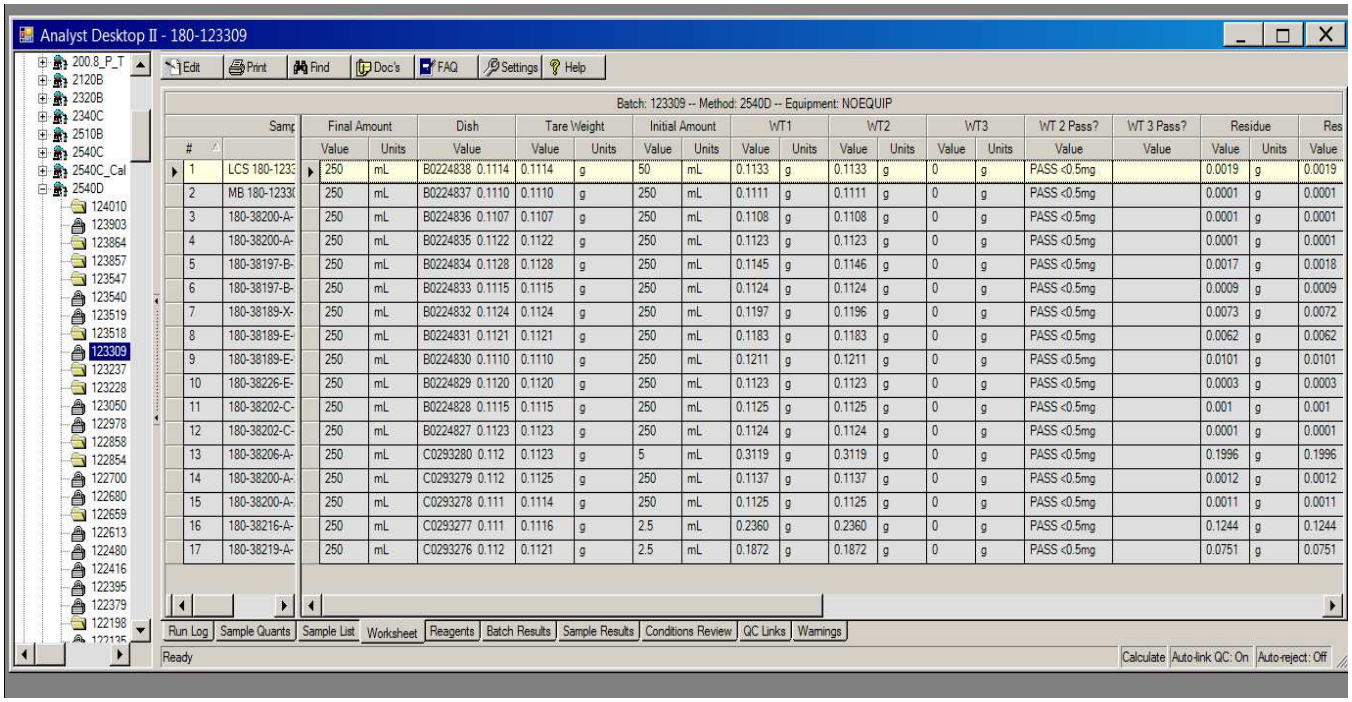
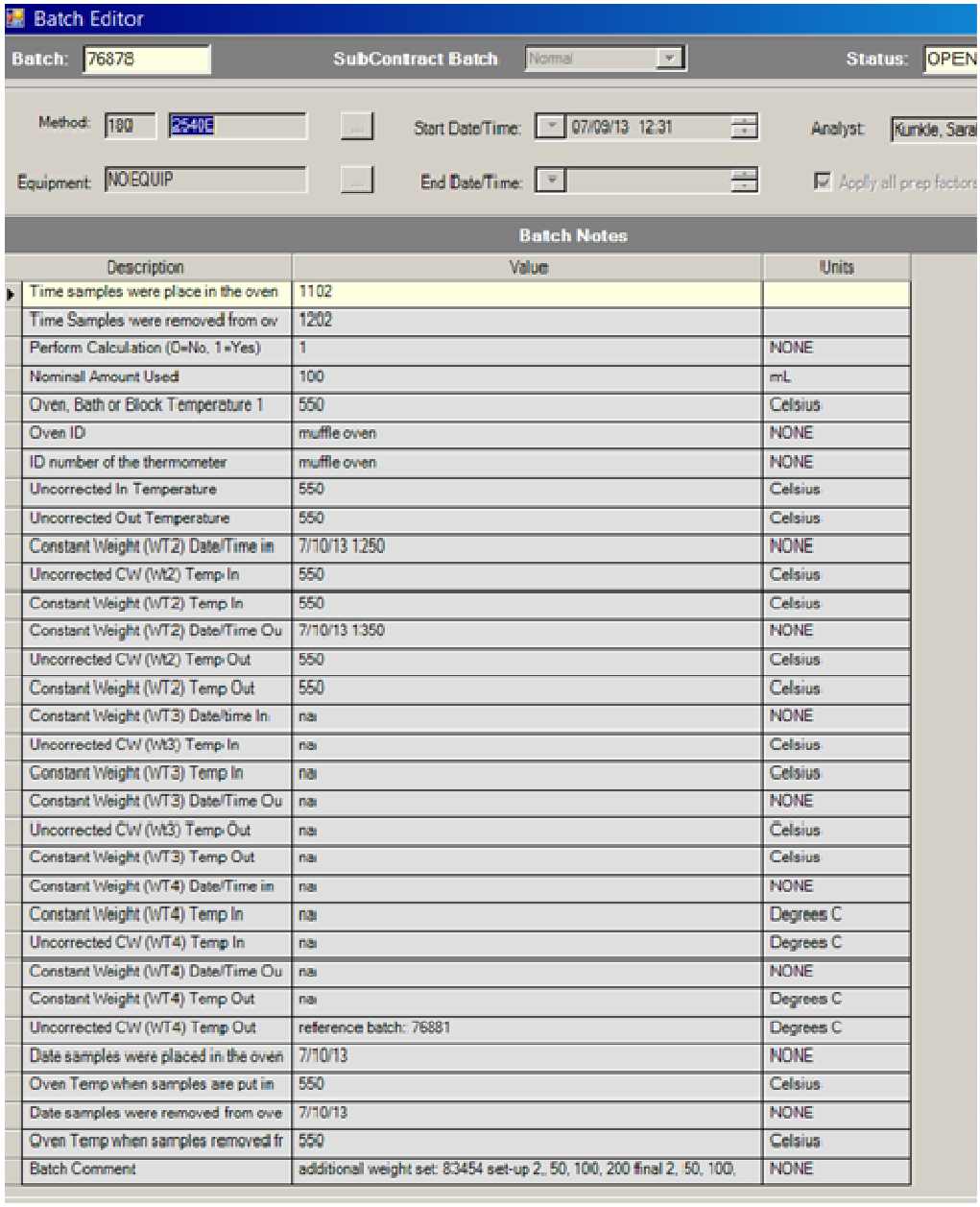


Figure 5 - TALS Batch Information – Method 2540E



Batch Editor

Batch: 76878 SubContract Batch: Normal Status: OPEN

Method: 180 2540E Start Date/Time: 07/09/13 12:31 Analyst: Kunkle, Sara

Equipment: NOEQUIP End Date/Time: Apply all prep factors

Batch Notes

Description	Value	Units
Time samples were place in the oven	1102	
Time Samples were removed from ov	1202	
Perform Calculation (0=No, 1=Yes)	1	NONE
Nominall Amount Used	100	mL
Oven, Bath or Block Temperature 1	550	Celsius
Oven ID	muffle oven	NONE
ID number of the thermometer	muffle oven	NONE
Uncorrected In Temperature	550	Celsius
Uncorrected Out Temperature	550	Celsius
Constant Weight (WT2) Date/Time in	7/10/13 1250	NONE
Uncorrected CW (Wt2) Temp In	550	Celsius
Constant Weight (WT2) Temp In	550	Celsius
Constant Weight (WT2) Date/Time Ou	7/10/13 1350	NONE
Uncorrected CW (Wt2) Temp Out	550	Celsius
Constant Weight (WT2) Temp Out	550	Celsius
Constant Weight (WT3) Date/time In	na	NONE
Uncorrected CW (Wt3) Temp In	na	Celsius
Constant Weight (WT3) Temp In	na	Celsius
Constant Weight (WT3) Date/Time Ou	na	NONE
Uncorrected CW (Wt3) Temp Out	na	Celsius
Constant Weight (WT3) Temp Out	na	Celsius
Constant Weight (WT4) Date/Time in	na	NONE
Constant Weight (WT4) Temp In	na	Degrees C
Uncorrected CW (WT4) Temp In	na	Degrees C
Constant Weight (WT4) Date/Time Ou	na	NONE
Constant Weight (WT4) Temp Out	na	Degrees C
Uncorrected CW (WT4) Temp Out	reference batch: 76881	Degrees C
Date samples were placed in the oven	7/10/13	NONE
Oven Temp when samples are put in	550	Celsius
Date samples were removed from ove	7/10/13	NONE
Oven Temp when samples removed fr	550	Celsius
Batch Comment	additional weight set: 83454 set-up 2, 50, 100, 200 final 2, 50, 100,	NONE

Figure 6 - TALS Batch Worksheet – Method 2540E

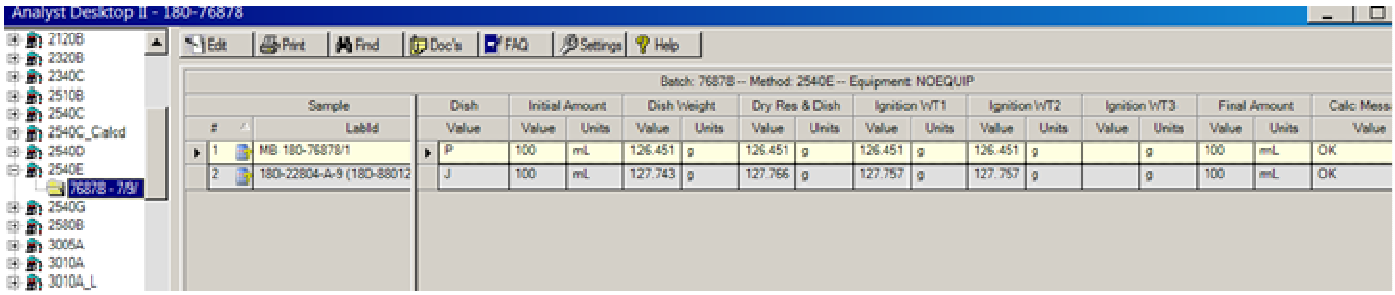
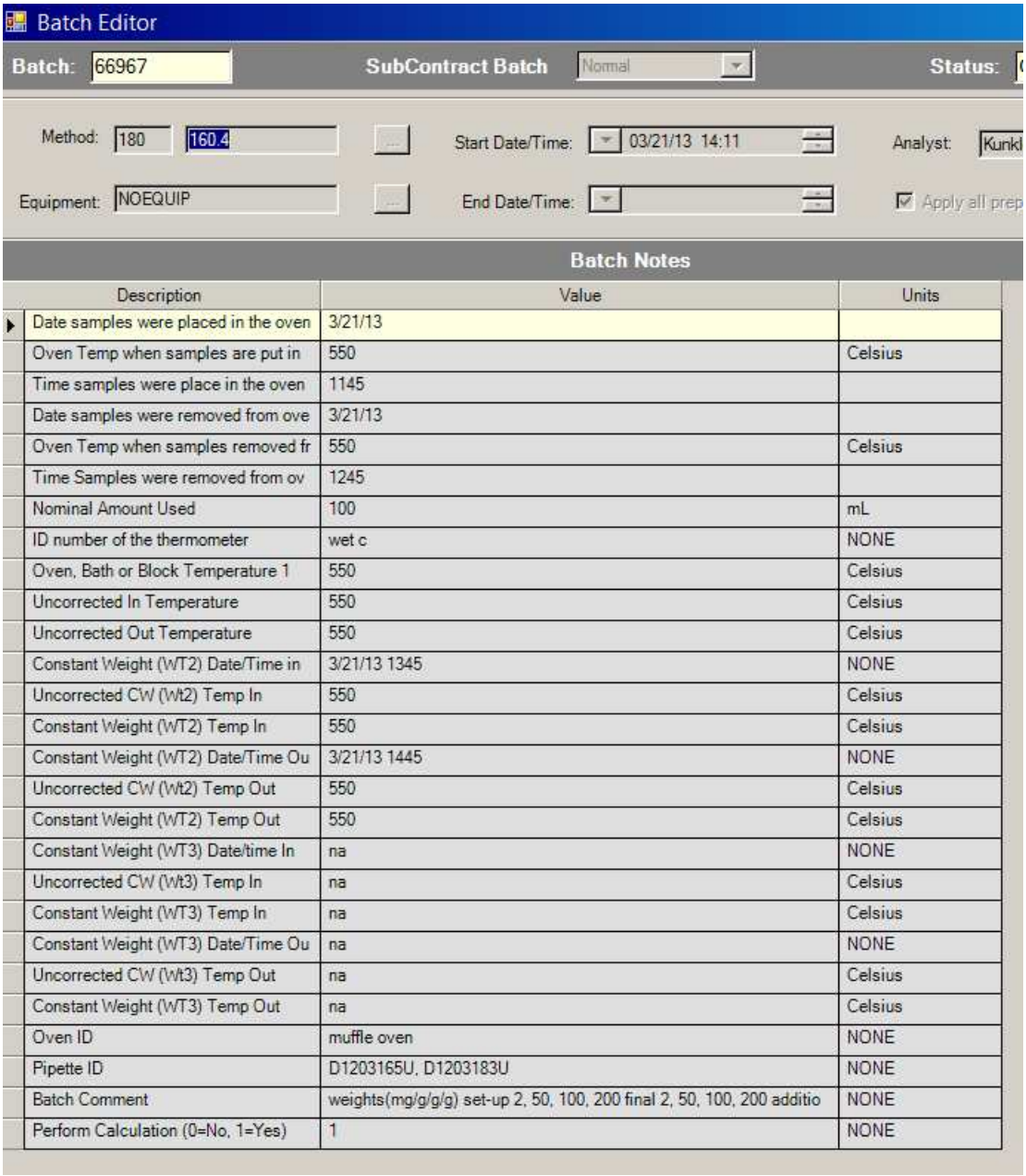


Figure 7 - TALS Batch Information – Method 160.4



Batch Editor

Batch: 66967 SubContract Batch Normal Status:

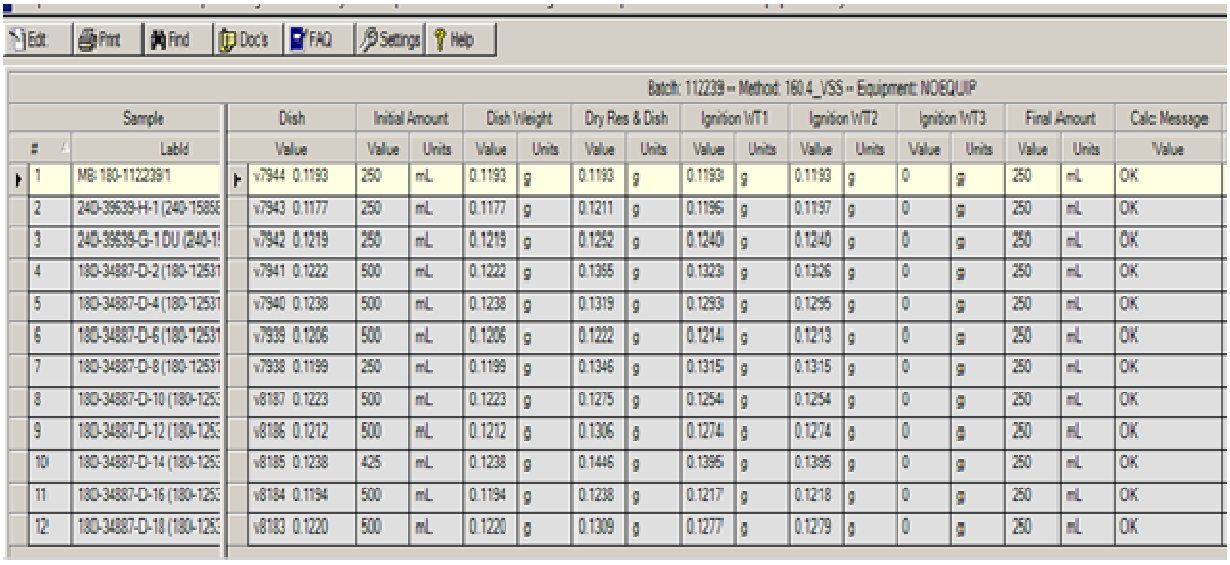
Method: 180 160.4 Start Date/Time: 03/21/13 14:11 Analyst: Kunkl

Equipment: NOEQUIP End Date/Time: Apply all prep

Batch Notes

Description	Value	Units
Date samples were placed in the oven	3/21/13	
Oven Temp when samples are put in	550	Celsius
Time samples were place in the oven	1145	
Date samples were removed from ove	3/21/13	
Oven Temp when samples removed fr	550	Celsius
Time Samples were removed from ov	1245	
Nominal Amount Used	100	mL
ID number of the thermometer	wet c	NONE
Oven, Bath or Block Temperature 1	550	Celsius
Uncorrected In Temperature	550	Celsius
Uncorrected Out Temperature	550	Celsius
Constant Weight (WT2) Date/Time in	3/21/13 1345	NONE
Uncorrected CW (Wt2) Temp In	550	Celsius
Constant Weight (WT2) Temp In	550	Celsius
Constant Weight (WT2) Date/Time Ou	3/21/13 1445	NONE
Uncorrected CW (Wt2) Temp Out	550	Celsius
Constant Weight (WT2) Temp Out	550	Celsius
Constant Weight (WT3) Date/time In	na	NONE
Uncorrected CW (Wt3) Temp In	na	Celsius
Constant Weight (WT3) Temp In	na	Celsius
Constant Weight (WT3) Date/Time Ou	na	NONE
Uncorrected CW (Wt3) Temp Out	na	Celsius
Constant Weight (WT3) Temp Out	na	Celsius
Oven ID	muffle oven	NONE
Pipette ID	D1203165U, D1203183U	NONE
Batch Comment	weights(mg/g/g/g) set-up 2, 50, 100, 200 final 2, 50, 100, 200 additio	NONE
Perform Calculation (0=No, 1=Yes)	1	NONE

Figure 8 - TALS Batch Worksheet – Method 160.4



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Batch: 112239 -- Method: 160.4_VSS -- Equipment: NOEQUIP

	Sample	Dish	Initial Amount		Dish Weight		Dry Res & Dish		Ignition WT1		Ignition WT2		Ignition WT3		Final Amount		Calc Message
#	LabId	Value	Value	Units	Value	Units	Value	Units	Value	Units	Value	Units	Value	Units	Value	Units	Value
1	MB-180-1122391	v7944 0.1193	250	mL	0.1193	g	0.1193	g	0.1193	g	0.1193	g	0	g	250	mL	OK
2	240-39639-H-1 (240-1585	v7943 0.1177	250	mL	0.1177	g	0.1211	g	0.1196	g	0.1197	g	0	g	250	mL	OK
3	240-39639-G-1 DU (240-1	v7942 0.1219	250	mL	0.1219	g	0.1252	g	0.1240	g	0.1240	g	0	g	250	mL	OK
4	180-34887-D-2 (180-1253	v7941 0.1222	500	mL	0.1222	g	0.1355	g	0.1323	g	0.1326	g	0	g	250	mL	OK
5	180-34887-D-4 (180-1253	v7940 0.1238	500	mL	0.1238	g	0.1319	g	0.1293	g	0.1295	g	0	g	250	mL	OK
6	180-34887-D-6 (180-1253	v7939 0.1206	500	mL	0.1206	g	0.1222	g	0.1214	g	0.1213	g	0	g	250	mL	OK
7	180-34887-D-8 (180-1253	v7938 0.1199	250	mL	0.1199	g	0.1346	g	0.1315	g	0.1315	g	0	g	250	mL	OK
8	180-34887-D-10 (180-125	v8187 0.1223	500	mL	0.1223	g	0.1275	g	0.1254	g	0.1254	g	0	g	250	mL	OK
9	180-34887-D-12 (180-125	v8186 0.1212	500	mL	0.1212	g	0.1306	g	0.1274	g	0.1274	g	0	g	250	mL	OK
10	180-34887-D-14 (180-125	v8185 0.1238	425	mL	0.1238	g	0.1446	g	0.1395	g	0.1395	g	0	g	250	mL	OK
11	180-34887-D-16 (180-125	v8184 0.1194	500	mL	0.1194	g	0.1238	g	0.1217	g	0.1218	g	0	g	250	mL	OK
12	180-34887-D-18 (180-125	v8183 0.1220	500	mL	0.1220	g	0.1309	g	0.1277	g	0.1279	g	0	g	250	mL	OK

STANDARD OPERATING PROCEDURE

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION FOR PCB/PESTICIDES USEPA METHOD 3510C

APPROVALS:

Barbara Ball

10/17/12

QA Officer Date

Maya Mushaben

10/17/12

Technical Director Date

Number	Description of Change	Date
001-009	Previous changes were not documented	
010	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
011	Updated to correct 2012 Internal Audit findings.	04/17/12
012	pH check requirement added based NY NELAP Assessment	10/17/12
013		
014		
015		
016		
017		
018		
018		
020		

1.0 SCOPE AND APPLICATION

This SOP is a procedure for isolating organic compounds from aqueous samples. This SOP is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures, specifically polychlorinated biphenyls (PCBs) and Pesticides. These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

A measured volume of sample, up to 1 liter, is extracted with methylene chloride using a separatory funnel. The extract is concentrated and exchanged into hexane solvent, which is also compatible with the cleanup procedures utilized for PCBs. Clean glassware and matrix cleanup procedures are used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. Degradation of PCBs, as well as more complex matrices (e.g., oil, tar, sulfur, etc.), can interfere with the “clarity” of the chromatograms.

4.0 APPARATUS AND MATERIALS

Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

Evaporation tubes, 250-ml volume, Zymark with end point of 0.5 ml.

Zymark Turbo Vap II Concentration Station with temperature control water bath.

Vials – 4 ml, glass with PTFE-lined screw caps.

pH indicator paper - pH range including the desired extraction pH.

Glass beakers, 250 ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

Syringe - 5-mL NIST certified.

Graduated cylinder - 1-liter.

250 mL Erlenmeyer flasks.

Pipettors.

Automated Shakers.

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades can be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

Deionized (DI) water.

Sodium sulfate (granular, anhydrous), Na_2SO_4. (precleaned with Methylene Chloride)

Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

- Methylene chloride, CH_2Cl_2, boiling point 49°C
- Hexane, C_6H_{14}, boiling point 68.7°C
- Ethyl ether (6%)
- Nonchromix, used when contamination is detected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All aqueous samples for the analysis of Pesticides and PCBs must be stored in Amber glass containers only. Approximately 1L volume of sample is needed for extraction. Refrigerate at $4^o \pm 2°$ C. The holding time for samples is 7 days from collection until extraction and 40 days until analysis.

Note: If samples contain significantly less volume then 1L, Quality Assurance Manager & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP # GEN-002.

2. Mark the level of sample on the outside of the bottle. Pour the sample into the 2 liter separatory funnel. After step 5, find the original volume of the sample by pouring tap water into the sample container to the mark. Pour the water into a 1000 ml graduated cylinder, and record the volume in the extraction logbook and label. Check the pH of the sample (5 - 9) with wide-range pH paper and adjust the pH if necessary. Do not place pH paper directly into sample container.

3. Pipette 1.0 ml of the surrogate spiking solution into the funnel and swirl the sample. For matrix spike samples and LCS, add 1ml surrogate and 1 ml matrix spike standard.

4. Add 60 ml of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel.

5. Venting prior to the 3 minute shake: Place cap on funnel, tip up/down five to 10 times, release vent into paper towel (to prevent cross contamination). Initial venting must be done immediately after the separatory funnel has been sealed and shaken once. Seal the separatory funnel and shake vigorously for 3 minutes on a horizontal placement at a motor speed 70 in accordance with Table 1 shake program. The separatory funnel must be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample. *Note: If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and can include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.*

6. Drain the extract through a filter filled with approximately 10g of Na_2SO_4 into a 250-ml glass Zymark evaporation tube.

7. Repeat step 6 twice more with 60 ml methylene chloride each in accordance with Table 1 shake program.

8. After all of the extract solvent has been collected, place the evaporation tube into the Turbo Vap II evaporation station, with the bath water at 48°C ± 2°C and 29 psi. Allow the sample to evaporate down to 0.5 ml methylene chloride or until the evaporation station signals completion.

9. Add 30 ml hexane and evaporate down to 0.5 ml final volume under the same conditions as above.

10. Transfer the final volume into a pre-calibrated 4-ml glass vial, rinse the evaporation tube with clean Hexane and bring to 1 ml. If the final volume is over 1ml, use compressed air to evaporate to the 1 ml mark.

11. Final 1 ml adjustment: if the transfer is greater than 1 ml, use compressed air to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.

12. The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.

13. Follow with clean-up procedures as appropriate for PCB analysis. See Document # ORL-002 for details.

- Sulfuric Acid Clean-up
- Sulfur Clean-up
- Alumina Column Clean-up.

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch there must be a blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples must be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.03 mg/l.

The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike must be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.05 ppm.

New lot blanks are analyzed to ensure the purity of the materials and reagents.

Note: The working standards are prepared every six months or when evidence of bias or trends are observed to show that the standards need to be replaced.

For DoD projects the MS/MSD and LCS spike solution must contain ALL target compounds.

All pertinent information is entered into an extraction bench sheet (Figure 1).

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in Document #'s ORL-001 and ORL-002. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Methylene chloride is harmful if swallowed, inhaled or absorbed through skin. Methylene chloride affects central nervous system, liver, cardiovascular system, and blood. Also, it can cause irritation to skin, eyes, and respiratory tract. Risk of cancer depends on level and duration of exposure. Vapor may form flammable mixture in atmosphere that contains a high percentage of oxygen. Sealed containers may rupture when heated. Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a flame or hot surface to form toxic gas phosgene and corrosive mists of hydrochloric acid. Carbon dioxide and carbon monoxide may form when heated to decomposition.

- Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: An organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, *Quality Systems Manual for Environmental Laboratories* (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on NELAC Voted Revision 5 June 2003, Version 4.1, April 22, 2009.

USEPA, SW-846, Revision 3; Method 3510C.

Table 1. Extraction Funnel Shake Program

Stage	Solvent Volume	pH	Funnel Position	Shaker Time	Shaker Intensity
1a	60 ml	5-9	Vertical/open	5 to 10 times	to vent
1b			horizontal/closed	3 min	70
2	60 ml	5-9	horizontal/closed	3 min	70
3	60 ml	5-9	horizontal/closed	3 min	70

(1) Solvent – Methylene chloride.

(2) *Funnel Position* indicates whether the funnel is horizontally or vertically situated in the automatic shaker and whether the stopcock is open or closed.

(3) *Shaker Time* is the timer setting on the shaker unit. The funnel is vented at the end of every time interval (*i.e.* 1, 2, or 3 minutes).

(4) *Shaker Intensity* is the dial setting on the automatic shaker unit. A higher number indicates a more vigorous shake.

Figure 1: PCB/Pesticide Extraction

$MeCl_2$_____ | Analyst: _____
Hexane_____ | Date _____
Na_2SO_4 _____ | Time Started _____
H_2SO_4_____ | Time Ended _____
SSD# _____ Ether/Hexane_____ | Prep Batch ID#_____
PCB MS ID#_____ Pest MS ID#_____

PCB/Pesticide Extraction
Method 3510C

#	Merit #	Matrix	Sample Vol (ml)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	pH	Alumina Cleanup	Dioxin Cleanup	Turbo Vap ID	Sep Funnel ID	Notes
Initial Q.C.	BLANK	D.I.		$MeCl_2$/Hex	180	1	1							
	LCS	D.I.						1						
	LCSD	D.I.						1						
	MS													
	MSD													
1														
2														
3														
4														
5														
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Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.

STANDARD OPERATING PROCEDURE

ULTRASONIC EXTRACTION FOR PCBS/PESTICIDES USEPA METHOD 3550C

APPROVALS:

Barbara Ball

09/29/16

QA Officer — Date

Maya Mushaly

09/29/16

Technical Director — Date

Number	Description of Change	Date
001-008	Previous changes were not documented	
009	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
010	Updated to address 2012 internal audit findings.	04/17/12
011	Wipe extraction procedure added	10/10/12
012	Updated to follow Method 3550C	08/27/13
013	Updated based on NELAC Audit findings	09/29/16
014		
015		
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

This SOP is used for extracting polychlorinated biphenyls (PCBs) and pesticide organic compounds from solids such as soils, sludges, wipes and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. The PCB extracts are cleaned up prior to analysis. These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

For most samples, 1g - 30g of sample (depending on the matrix; typically 0.3g for oils and 20g for soils) or wipe (100 cm^2) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Add acetone/hexane (1:1) and extract three times using ultrasonic extraction. The extract is separated from the sample by centrifugation or through a filter paper. The extract is separated from the sample and concentrated. The extract is ready for cleanup and analysis. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. Degradation of PCBs, as well as more complex matrix (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

Apparatus for grinding/crushing solid waste samples (i.e. drill press or hammer).

Ultrasonic device – Branson Sonifier, Model 450.

Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.

- 3/4" horn
- Sonabox – (Ultrasonics #432B).

Zymark Evaporation Station.

Evaporation tubes.

Water bath - Heated, capable of temperature control (± 5ºC).

Balance - capable of accurately weighing to the nearest 0.01 g.

Vials – 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.

Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

Tongue depressors, disposable.

Drying column - 50ml Pyrex chromatographic column with Pyrex glass wool at bottom.

Syringe - 5-mL NIST Certified.

Beakers – 250 ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

250 mL Erlenmeyer flasks.

Pipettors.

4 oz glass sample bottles

100 cm^2 wipe

100 cm^2 wipe template

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades must be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

Deionized (DI) water.

Sodium sulfate (granular, anhydrous), Na_2SO_4. (Heated to 400 ºC for 4 hours or precleaned with Methylene Chloride)

Extraction - All solvents must be pesticide quality or equivalent.

- Methylene chloride, CH_2Cl_2, boiling point 49°C
- Hexane, C_6H_{14}, boiling point 68.7°C
- Ethyl Ether (6%)
- Acetone
- Nonchromix used when contamination is detected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All soil samples for the analysis of Pesticides and PCBs must be stored in non-preserved glass containers only. Approximately 0.3g to 30g (depending on the matrix) of sample is needed for extraction. Wipe samples for PCB analysis must be collected using a 100 cm^2 wipe moistened with Hexane and wiped over a sample area of 100 cm^2 using wipe template. Wipe samples are stored in non-preserved glass containers. Refrigerate at 4º ± 2°C. Holding Time for solid samples is 14 days from collection to extraction and 40 days after extraction until analysis.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP #GEN-002.

2. The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.

   - The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument.
   - Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.
   - Three extractions are performed with 60ml acetone/hexane (1:1) solvent for 3 minutes each.
   - Extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
   - Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. Observe such mixing at some point during the extraction process to ensure that the placement of the horn is correct.

3. Sample handling

   - Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

- ♦ Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

- ♦ Solid waste samples amenable to grinding - Drill or hammer until uniform matrix is achieved.

- ♦ Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.

4. Extraction method

- Weigh approximately 0.3 - 30 g of sample (depending on the matrix) into a 250-ml beaker. Typically, on a standard soil, 20 grams of sample is used. Record the weight to the nearest 0.1 g.

- Add 1.0 ml of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.

- For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution.

    - Note: Add surrogates and matrix spiking compounds to the sample aliquot prior to mixing the sample with the sodium sulfate drying agent. Spiking the sample first increases the contact time of the spiked compounds and the actual sample matrix. It should also lead to better mixing of the spiking solution with the sample when the sodium sulfate and sample are mixed to the point of free-flowing.

- Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate can be added. After addition of sodium sulfate, the sample must be free flowing.

- Add 60 ml of Acetone/Hexane (1:1) to the beaker.
- Place the bottom surface of the tip of the 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

- Extract ultrasonically for 3 minutes, with output control knob set at 6 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).

- Decant through a conical gravity filter (Whatman No. 41 filter paper or equivalent) and sodium sulfate to catch any excess water into an evaporation tube.

- Repeat the extraction two more times with an additional 60 ml portion of acetone/hexane (1:1). Pour off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample onto the filter with extraction solvent.

5. Wipe samples

- ♦ Take 4 oz container containing wipe.

- ♦ Add 1.0 ml of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.

- ♦ For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution.

- ♦ Add 60 ml of Acetone/Hexane (1:1) to the 4 oz container.

- ♦ Shake 4 oz container and let stand for a few minutes (~5 minutes).Pour sample through sodium sulfate into evaporation tube.

- ♦ Repeat the extraction two more times with an additional 60 ml portion of acetone/hexane (1:1).

6. Evaporation method

- ♦ Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath @ 48ºC ± 2°C, 29 psi, until 0.5 ml final volume.

- ♦ Transfer the sample extract to a 4 ml vial rinse evaporation tube with 0.5 ml Hexane. Adjust up to 1 ml final volume.

- Final 1 ml adjustment: if the transfer is greater than 1 ml, use the compressed air to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.
    - The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.
- Follow with clean–up procedures as appropriate for PCB analysis. See Document # ORL-002 for details.
    - Sulfuric Acid Clean-up
    - Sulfur Clean-up
    - Alumina Column Clean-up.

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch there must be a blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples must be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample amount to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.03 mg/l.

The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike must be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.5 ppm.

The MS/MSD and LCS spikes contain a mixture of Pesticides. This spike must be prepared at a concentration at or below the medium level of the Pesticide curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.1 ppm.

New lot blanks are analyzed to ensure the purity of the materials and reagents.

For DoD projects, the MS/MSD and LCS spike solution must contain ALL target compounds.

All pertinent information is entered into an extraction bench sheet (Figure 1).

Note: The working standards are prepared every six months or when evidence of bias or trends are observed to show that the standards need to be replaced.

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in SOPs #ORL-001 and #ORL-002. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument. When cavities are observed, horns are cleaned and/or replaced.

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€

and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.0, July 2013.

USEPA, SW-846, Revision 3, Method 3550C.

Figure 1: PCB/Pesticide Extraction Bench Sheet

Acetone_____
Hexane_____
Ether/Hexane_____
Na_2SO_4 _____
H_2SO_4_____
SSD# _____
PCB MS ID#_____Pest MS ID#_____

PCB/Pesticide Extraction Method 3550C

Analyst _____
Date _____
Time Started _____
Time Ended _____
Prep Batch ID#_____
Balance ID#_____

#	Merit #	Matrix	Sample Wt. (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Alumina Cleanup	Dioxin Cleanup	Turbo Vap ID	Notes
Initial Q.C.	BLANK			Acetone/Hexane	180	1	1					
	LCS							1				
	LCSD							1				
	MS								☐	☐		
	MSD								☐	☐		
1									☐	☐		
2									☐	☐		
3									☐	☐		
4									☐	☐		
5									☐	☐		
6									☐	☐		
7									☐	☐		
8									☐	☐		
9									☐	☐		
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19									☐	☐		
20									☐	☐		

Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.

EXT-F05 Effective Date 9/29/2016

STANDARD OPERATING PROCEDURE

ULTRASONIC EXTRACTION FOR BNAS/PNAS/DRO EPA METHOD 3550C

APPROVALS:

Barbara Ball

09/29/16

QA Officer Date

Maya Mushaly

09/29/16

Technical Director Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
007	Reference to analysis SOPs added	10/17/12
008	Updated to follow Method 3550C	08/27/13
010	Additional of water miscible solvent	08/19/14
011	Updated based on NELAC Audit findings	09/29/16
012		
013		
014		
015		
016		
017		

1.0 SCOPE AND APPLICATION

This SOP is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA), polynuclear aromatic hydrocarbon (PNA) and diesel range organics (DRO) organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

For most of samples, 0.5g - 30g sample (depending on the matrix; 30g is typical for a soil) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Extract with methylene chloride/acetone (1:1) mixture using ultrasound. The extract is separated from the sample and concentrated. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. Degradation of sample matrix (i.e. oil, tar, sulfur, etc.), can interfere with the “clarity” of the chromatograms.

4.0 APPARATUS AND MATERIALS

Apparatus for grinding/crushing solid waste samples (i.e. drill press or hammer).

Ultrasonic device - Branson Sonifier, Model 450.

Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.

- 3/4" horn
- Sonabox - (Ultrasonics #432B).

Zymark Evaporation Station.

Evaporation tubes.

Water bath - Heated, capable of temperature control (± 5ºC).

Balance - capable of accurately weighing to the nearest 0.01 g.

Vials - 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.

Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

Tongue depressors, disposable.

Beakers - 250ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

Syringe - 5-mL NIST certified.

250mL Erlenmeyer flasks.

Pipettors.

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades can be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

Sodium sulfate (granular, anhydrous), Na_2SO_4. (Heated to 400 ºC for 4 hours or precleaned with Methylene Chloride)

Extraction - All solvents must be pesticide quality or equivalent.

- Methylene Chloride, CH_2Cl_2.
- Acetone
- Nonchromix, used when contamination is detected.

Surrogate and matrix spiking solutions are prepared as listed in Table 2. The detailed list of compounds for each stock mixture is given in Table 1.

Deionized (DI) Water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All soil samples for the analysis of BNAs/PNAs/DRO are stored in non-preserved glass containers only. Approximately 0.5 to 30 g (depending on the matrix) of sample is needed for extraction. Oils are weighed

out to 0.5 ml. Refrigerate at 4º±2°C. Holding Time for solid samples is 14 days from collection to extraction and 40 days after extraction until analysis.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP # GEN-002.

2. The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.

   - The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument.
   - Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.
   - Three extractions are performed with 60ml of Methylene Chloride/Acetone (1:1) solvent mixture for 3 minutes each.
   - Extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
   - Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. Observe such mixing at some point during the extraction process to ensure that the placement of the horn is correct.

3. Sample handling.

   - Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.
   - Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

- Solid waste samples amenable to grinding - Drill or hammer until uniform matrix is achieved.

- Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.

4. Extraction method

- Weigh approximately 0.5-30 g of sample (depending on the matrix) into a 250-ml beaker. Record the weight to the nearest 0.1 g.

    - The default weight used is 30g for a soil sample.

    - If the sample is a solvent or an oil matrix, approximately 0.5 ml of neat sample is weight out and brought up to 2 ml with solvent put into a 4ml screw cap vial and given to the GC/MS analyst. No extraction is performed due to the exceptionally high chromatographic response of these sample types. These samples are diluted by a factor of 400:1 and analyzed directly (see SOP: ORL-004). The relative response of this base dilution may result in a final analysis of the sample at a higher or lower net dilution.

- a) For BNA extraction: Add 1.0 ml of the BNA surrogate standard solution to all samples, spiked samples, QC samples, and blanks (see Table 2).

    b) For PNA extraction: Add 1.0 ml of the PNA surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 2).

    c) For DRO extraction: Add 1.0 ml of the DRO surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 2).

- For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution (BNA, PNA, or DRO, as appropriate, see Table 2).

    - Note: Add surrogates and matrix spiking compounds to the sample aliquot prior to mixing the sample with the sodium sulfate drying agent. Spiking the sample first increases the contact time of the spiked compounds and the actual sample matrix. It

should also lead to better mixing of the spiking solution with the sample when the sodium sulfate and sample are mixed to the point of free-flowing.

- Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with a maximum 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

- Place the bottom surface of the tip of the 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

- Extract ultrasonically for 3 minutes, with output control knob set at 6 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).

- Decant through a conical gravity filter (Whatman No. 41 filter paper or equivalent) and sodium sulfate to catch any excess water into an evaporation tube.

- Repeat the extraction with an additional 60 ml portion of methylene chloride/acetone (1:1) solvent mixture. Pour off the solvent after the ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample onto the filter with extraction solvent.

5. Evaporation method

- Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath at 47+/2°C, 21 psi, until the extract reaches a 0.5 ml final volume.

- Transfer the sample extract to a 4 ml pre-calibrated vial. Adjust to 1 ml final volume with methylene chloride.

- Final 1 ml adjustment: if the transfer is greater than 1 ml, use compressed air to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.

- After extraction, samples are analyzed by following SOP ORL-004 (SVOCs) or SOP ORL-11 (DRO).

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch, there must be a Blank, LCS, MS, and MSD/DUP depending on the clients' request. All the reagent blanks, matrix spikes, or replicate samples must be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

The Base/Neutral surrogate standard must contain the compounds listed in Table 1. The Acid surrogate standard must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. [the Acid surrogate standard is N/A for the PNA method.] The surrogate standard is prepared according to Table 2.

The Base/Neutral MS/MSD and LCS spikes must contain the compounds listed in Table 1. The Acid MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 2.

The PNA MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike must be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 2.

The DRO MS/MSD and LCS spikes contain neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 2.

For DoD projects, the MS/MSD and LCS spike solution must contain ALL target compounds.

New lot blanks are analyzed to ensure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

All pertinent information is entered into an extraction bench sheets (Figure 1 and 2).

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in SOP # ORL-004 and ORL-012. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument. When cavities are observed horns are cleaned and/or replaced.

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Methylene chloride is harmful if swallowed, inhaled or absorbed through skin. Methylene chloride affects central nervous system, liver, cardiovascular system, and blood. Also, it can cause irritation to skin, eyes, and respiratory tract. Risk of cancer depends on level and duration of exposure. Vapor may form flammable mixture in atmosphere that contains a high percentage of oxygen. Sealed containers may rupture when heated. Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a flame or hot surface to form toxic gas phosgene

and corrosive mists of hydrochloric acid. Carbon dioxide and carbon monoxide may form when heated to decomposition.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

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Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is

to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.0, July 2013.

USEPA, SW-846, Revision 3, Method 3550C.

Table 1: Surrogate/LCS/MS Compounds

Standard Type	Compound	CAS #	Concentration	Supplier
Base/Neutral Surrogate	Nitrobenzene-d5	4165-60-0	5000 ug/ml	RESTEK
	2-Fluorobiphenyl	321-60-8	5000 ug/ml	RESTEK
	p-Terphenyl-d14	1718-51-0	5000 ug/ml	RESTEK
Acid Surrogate	2-Fluorophenol	367-12-4	10000 ug/ml	RESTEK
	Phenol-d6	13127-88-3	10000 ug/ml	RESTEK
	2,4,6-Tribromophenol	118-79-6	10000 ug/ml	RESTEK
Base/Neutral MS/MSD/LCS Spike	Acenaphthene	83-32-9	5000 ug/ml	RESTEK
	1,4-Dichlorobenzene	106-46-7	5000 ug/ml	RESTEK
	2,4-Dinitrotoluene	121-14-2	5000 ug/ml	RESTEK
	N-nitroso-di-n-propylamine	621-64-7	5000 ug/ml	RESTEK
	Pyrene	129-00-0	5000 ug/ml	RESTEK
	1,2,4-Trichlorobenzene	120-82-1	5000 ug/ml	RESTEK
Acid MS/MSD/LCS Spike	4-Chloro-3-methylphenol	59-50-7	10000 ug/ml	RESTEK
	2-Chlorophenol	95-57-8	10000 ug/ml	RESTEK
	4-Nitrophenol	100-02-7	10000 ug/ml	RESTEK
	Pentachlorophenol	87-86-5	10000 ug/ml	RESTEK
	Phenol	108-95-2	10000 ug/ml	RESTEK
PNA MS/MSD/LCS Spike	Naphthalene	91-20-3	2000 ug/ml	RESTEK
	2-Methylnaphthalene	91-57-6	2250 ug/ml	RESTEK
	Acenaphthylene	208-96-8	2000 ug/ml	RESTEK
	Acenaphthene	83-32-9	2000 ug/ml	RESTEK
	Fluorene	86-73-7	2000 ug/ml	RESTEK
	Phenanthrene	85-01-8	2000 ug/ml	RESTEK
	Anthracene	120-12-7	2000 ug/ml	RESTEK
	Fluoranthene	206-44-0	2000 ug/ml	RESTEK
	Pyrene	129-00-0	2000 ug/ml	RESTEK
	Benzo(a)anthracene	56-55-3	2000 ug/ml	RESTEK
	Chrysene	218-01-9	2000 ug/ml	RESTEK
	Benzo(b)fluoranthene	205-99-2	2000 ug/ml	RESTEK
	Benzo(k)fluoranthene	207-08-9	2000 ug/ml	RESTEK
	Benzo(a)pyrene	50-32-8	2000 ug/ml	RESTEK
	Indeno(1,2,3-cd)pyrene	193-39-5	2000 ug/ml	RESTEK
	Dibenzo(ah)anthracene	53-70-3	2000 ug/ml	RESTEK
	Benzo(ghi)perylene	191-24-2	2000 ug/ml	RESTEK

Table 2. Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L:
- 97 ml of Acetone
- 1 ml of 10,000 mg/L Acids surrogate
- 2 ml of 5,000 mg/L B/N surrogate

BNA MS/MSD/LCS Spike:

For 20 ml total solution at 50 mg/L:
- 19.7 ml of Acetone
- 100 ul of 10,000 mg/L Acids spike
- 200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L:
- 98 ml of Acetone
- 2 ml of 5,000 mg/L B/N surrogate

PNA MS/MSD/LCS Spike:

For 20 ml total solution at 50 mg/L:
- 19.1 ml of Acetone
- 500 ul of 2,000 mg/L PNA stock
- 444 ul of 2250 mg/L 2-Methylnapthalene stock

DRO MS/MSD/LCS Spike:

For 20 ml total solution at 1000 mg/L;
- 20.0 ml of Acetone
- 20.0 mg of neat Diesel Fuel (gravimetric preparation)

Figure 1: SVOC Extraction Bench Sheet

Methylene Chloride Lot #: _____ Analyst: _____
Acetone Lot #: _____ Date: _____
Na2SO4 Lot #: _____ SVOC Solid Extraction Log Time Started: _____
SSD #: _____ Method 3550 C Time Ended: _____
MS/LCS #: _____ Batch ID#: _____

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Turbo VAP ID	Notes	
Initial Q.C.	BLANK	Sand	30.0 g	Acetone/Methylene Chloride	180	1	1	---			
	LCS	Sand	30.0 g					1			
	LCSD	Sand	30.0 g					1			[ ]
	MS							1			[ ]
	MSD							1			
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Reviewed by: _____ On: _____ Balance ID: _____ Prepared by: Merit Laboratories, Inc.

EXT-F07 Effective Date 9/29/2016

Figure 2: PNA/DRO Extraction Bench Sheet

Methylene Chloride Lot #: _____ Analyst: _____

Acetone Lot #: _____ Date: _____

Na2SO4 Lot #: _____ PNA/DRO Solid Extraction Log Time Started: _____

SSD #: _____ Method 3550 C Time Ended: _____

MS/LCS #: _____ Batch ID#: _____

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Turbo VAP ID	Notes	
Initial Q.C.	BLANK	Sand	30.0 g	Acetone/Methylene Chloride	180	1	1	---			
	LCS	Sand	30.0 g					1			
	LCSD	Sand	30.0 g					1			[ ]
	MS							1			[ ]
	MSD							1			
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Reviewed by: _____ On: _____ Balance ID: _____ Prepared by: Merit Laboratories, Inc.

EXT-F06 Effective Date 9/29/2016

STANDARD OPERATING PROCEDURE

SEPARATORY FUNNEL EXTRACTION FOR BNAS/PNAS/TCLP/DRO EPA METHOD 3510C

APPROVALS:

Barbara Ball

09/29/16

QA Officer — Date

Mayer Mushaly

09/29/16

Technical Director — Date

Number	Description of Change	Date
001-006	Previous changes were not documented	
007	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
008	Reference to analysis SOPs added	10/17/12
009	Additional Basic extraction added	8/19/14
010	Updated based on NELAC findings	09/29/16
011		
012		
013		
014		
015		
016		
017		

1.0 SCOPE AND APPLICATION

This SOP is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA) polynuclear aromatic hydrocarbon (PNA), and diesel range organics (DRO) organic compounds from aqueous samples. This SOP is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures. The following BNA method is congruent with Toxicity Characteristic Leaching Procedure (TCLP) and Total Toxic Organics (TTO) procedures in their entirety and can also be used with PNA (with the omission or addition of appropriate steps). These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

A measured volume of sample, up to 1 liter, at a specific pH is extracted with methylene chloride using a separatory funnel. The extract is concentrated. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides can de-chlorinate, phthalate esters can exchange, and phenols can react to form tannates.

4.0 APPARATUS AND MATERIALS

Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

Evaporation tubes, 250-ml volume, Zymark with end point of 0.5-ml.

Zymark Turbo Vap II Concentration Station with temperature control water bath.

Vials – 4-ml, glass with PTFE-lined screw caps.

pH indicator paper - pH range including the desired extraction pH.

Glass beakers, 250-ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

Syringe - 5-mL NIST certified.

Graduated cylinder - 1-liter.

250 mL Erlenmeyer flasks.

Pipettors.

Automated Shakers.

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades can be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

Deionized (DI) water.

Sodium sulfate (granular, anhydrous), Na_2SO_4. (Heated to 400 ºC for 4 hours or precleaned with Methylene Chloride)

Sulfuric acid, concentrated, as well as solution (1:1 v/v), H_2SO_4. Slowly add 500 ml of H_2SO_4 to 500 ml of DI water.

Sodium Hydroxide solution (10 N), NaOH. Slowly add 1 Liter of DI water to 400 g of NaOH crystals.

Extraction/exchange solvents. All solvents must be of pesticide quality or equivalent.

- Methylene chloride, CH_2Cl_2, boiling point 49°C.
- Acetone, C_3H_6O.

Surrogate and matrix spiking solutions are prepared as listed in Table 2. The detailed list of compounds for each stock mixture is given in §9 and Table 1.

Nonchromix, used when contamination is detected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All aqueous samples for the analysis of BNAs, PNAs, and DRO must be stored in Amber glass containers only. Approximately 1-L volume of sample is needed for extraction. Refrigerate at 4º ± 2° C. The holding time for samples is 7 days until extraction and 40 days thereafter for analyses.

Note: If samples contain significantly less volume then 1L, Quality Assurance Manager & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP #GEN-002.

2. Mark the level of sample on the outside of the bottle. After step 6, pour the sample into the 2-liter separatory funnel. Find the original volume of the sample by pouring tap water into the sample container to the mark. Pour the water into a 1000 ml graduated cylinder, and record the volume in the extraction logbook and label.

3. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH < 2 using H_2SO_4. Do not place pH paper directly into sample container.

4. For all samples, spikes, and blanks, pipette 1.0-ml of the appropriate surrogate spiking solution (see Table 2 and §9.2) into the funnel and swirl. For matrix spike samples (including the LCS), add 1ml surrogate and 1-ml matrix spike standard (see Table 2 and §9.3).

5. Add 10-ml of Acetone into the separatory funnel and swirl the sample (applicable for BNAs).

6. Add 35-ml (for PNAs, DRO and phenols), or 30 ml (for BNA/TCLP) of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel.

7. Venting prior to the 3 minute shake: Place cap on funnel, tip up/down 5 to 10 times, release and vent into paper towel (to prevent cross contamination). Initial venting must be done immediately after the separatory funnel has been sealed and shaken once. Seal the separatory funnel and shake vigorously for 3 minutes on a horizontal placement at a motor speed 70 in accordance with Table 3 shake program. The separatory funnel must be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample.

Note: If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and can include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

8. Drain the extract through a filter filled with approximately 10g of Na_2SO_4 into a 250-ml glass Zymark evaporation tube.

9. Repeat step 6 two more times with 35 ml (PNA/DRO) or 30 ml (BNA) methylene chloride each in accordance with Table 3 shake program [PNA and DRO samples are done after 4 shakes].
Note: Samples requiring PNA and/or DRO analysis may be extracted in an analytical batch for BNAs, using the additional procedural steps and surrogate compounds, without loss of generality.

10. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH > 12 using NaOH [BNA only].

11. Repeat step 6 three times at three minutes each in accordance with Table 3 shake program [BNA only].

12. Rinse the funnel and Na_2SO_4 with a squirt of Methylene chloride into the collected sample in between shakes.

13. After all of the extract solvent has been collected, place the evaporation tube into the Turbo Vap II evaporation station, with the bath water at 47°C ± 2°C and 21 psi. Allow the sample to evaporate down to 0.5ml methylene chloride or until the evaporation station signals completion.

14. Transfer the final volume into a pre-calibrated 4-ml glass vial, rinse the evaporation tube with clean methylene chloride and bring to 1-ml. If the final volume is over 1ml, use compressed air to evaporate to the 1-ml mark.

15. Final 1 ml adjustment: if the transfer is greater than 1 ml, use compressed air to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.

16. After extraction, samples are analyzed by following SOP ORL-004 (SVOCs) or SOP ORL-11 (DRO).

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Samples are extracted in batches of 20 samples or less. For every batch there must be a Blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples must be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

The Base/Neutral surrogate standard must contain the compounds listed in Table 1. The Acid surrogate standard must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. The Acid surrogate standard is N/A for the PNA and DRO methods. The surrogate standard is prepared according to Table 2.

The Base/Neutral MS/MSD and LCS spikes must contain the compounds listed in Table 1. The Acid MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike must be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 2.

The PNA MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike must be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 2.

The DRO MS/MSD and LCS spikes contains neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 2.

New lot blanks are analyzed to insure the purity of the materials and reagents.

- *Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.*

For DoD projects the MS/MSD and LCS spike solution must contain ALL target compounds.

All pertinent information is entered into an extraction bench sheets (Figure 1, 2, and 3).

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- Methylene chloride is harmful if swallowed, inhaled or absorbed through skin. Methylene chloride affects central nervous system, liver, cardiovascular system, and blood. Also, it can cause irritation to skin, eyes, and respiratory tract. Risk of cancer depends on level and duration of exposure. Vapor may form flammable mixture in atmosphere that contains a high percentage of oxygen. Sealed containers may rupture when heated. Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a flame or hot surface to form toxic gas phosgene and corrosive mists of hydrochloric acid. Carbon dioxide and carbon monoxide may form when heated to decomposition.

- Concentrated sulfuric acid is toxic and damaging to skin and mucus membranes. If eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.

- Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

- Acetone is an extremely flammable liquid and vapor, vapor may cause flash fire. Hexane is harmful or fatal if swallowed or inhaled, causes irritation to skin, eyes and respiratory tract, and can affect the central nervous system. May cause coughing, dizziness, dullness, and headache. Higher concentrations can produce central nervous system depression, narcosis, and unconsciousness. Carbon dioxide and carbon monoxide may form when heated to decomposition.

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	Phenol-d6	13127-88-3	10000 ug/ml	RESTEK
	2,4,6-Tribromophenol	118-79-6	10000 ug/ml	RESTEK
Base/Neutral MS/MSD/LCS Spike	Acenaphthene	83-32-9	5000 ug/ml	RESTEK
	1,4-Dichlorobenzene	106-46-7	5000 ug/ml	RESTEK
	2,4-Dinitrotoluene	121-14-2	5000 ug/ml	RESTEK
	N-nitroso-di-n-propylamine	621-64-7	5000 ug/ml	RESTEK
	Pyrene	129-00-0	5000 ug/ml	RESTEK
	1,2,4-Trichlorobenzene	120-82-1	5000 ug/ml	RESTEK
Acid MS/MSD/LCS Spike	4-Chloro-3-methylphenol	59-50-7	10000 ug/ml	RESTEK
	2-Chlorophenol	95-57-8	10000 ug/ml	RESTEK
	4-Nitrophenol	100-02-7	10000 ug/ml	RESTEK
	Pentachlorophenol	87-86-5	10000 ug/ml	RESTEK
	Phenol	108-95-2	10000 ug/ml	RESTEK
PNA MS/MSD/LCS Spike	Naphthalene	91-20-3	2000 ug/ml	RESTEK
	2-Methylnaphthalene	91-57-6	2250 ug/ml	RESTEK
	Acenaphthylene	208-96-8	2000 ug/ml	RESTEK
	Acenaphthene	83-32-9	2000 ug/ml	RESTEK
	Fluorene	86-73-7	2000 ug/ml	RESTEK
	Phenanthrene	85-01-8	2000 ug/ml	RESTEK
	Anthracene	120-12-7	2000 ug/ml	RESTEK
	Fluoranthene	206-44-0	2000 ug/ml	RESTEK
	Pyrene	129-00-0	2000 ug/ml	RESTEK
	Benzo(a)anthracene	56-55-3	2000 ug/ml	RESTEK
	Chrysene	218-01-9	2000 ug/ml	RESTEK
	Benzo(b)fluoranthene	205-99-2	2000 ug/ml	RESTEK
	Benzo(k)fluoranthene	207-08-9	2000 ug/ml	RESTEK
	Benzo(a)pyrene	50-32-8	2000 ug/ml	RESTEK
	Indeno(1,2,3-cd)pyrene	193-39-5	2000 ug/ml	RESTEK
	Dibenzo(ah)anthracene	53-70-3	2000 ug/ml	RESTEK
	Benzo(ghi)perylene	191-24-2	2000 ug/ml	RESTEK

Table 2: Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L;
- 97 ml of Acetone
- 1 ml of 10,000 mg/L Acids surrogate
- 2 ml of 5,000 mg/L B/N surrogate

BNA MS Spike:

For 20 ml total solution at 50 mg/L;
- 19.7 ml of Acetone
- 100 ul of 10,000 mg/L Acids spike
- 200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L;
- 98 ml of Acetone
- 2 ml of 5,000 mg/L B/N surrogate

PNA MS Spike:

For 20 ml total solution at 50 mg/L;
- 19.1 ml of Acetone
- 500 ul of 2,000 mg/L PNA stock
- 444 ul of 2,250 mg/L 2-Methylnapthalene stock

DRO MS Spike:

For 20 ml total solution at 1000 mg/L;
- 20.0 ml of Acetone
- 20.0 mg of neat Diesel Fuel (gravimetric preparation)

Table 3: Automated Extraction Funnel Shaking Procedure.

Stage	Solvent Volume (BNA/PNA DRO)	pH	Funnel Position	Shaker Time	Shaker Intensity	BNA Extraction	PNA/DRO Extraction
1a	30 ml/ 35 ml	<2	vertical/open	5 to 10 times	to vent	☑	☑
1b			horizontal/closed	3 min.	70		
2	30 ml/ 35 ml	<2	horizontal/closed	3 min.	70	☑	☑
3	30 ml/ 35 ml	<2	horizontal/closed	3 min.	70	☑	☑
4	30 ml	>12	horizontal/closed	3 min.	70	☑	☐
5	30 ml	>12	horizontal/closed	3 min.	70	☑	☐
6	30 ml	>12	horizontal/closed	3 min.	70	☑	☐

Notes: (1) Solvent – Methylene Chloride

(2) Funnel Position indicates whether the funnel is horizontally or vertically situated in the automatic shaker and whether the stopcock is open or closed.

(3) *Shaker Time* is the timer setting on the shaker unit. The funnel is vented at the end of every time interval (*i.e.* 1, 2, or 3 minutes).

(4) Shaker Intensity is the dial setting on the automatic shaker unit. A higher number indicates a more vigorous shake.

(5) BNA/PNA/DRO Extraction indicates whether the extraction stage is appropriate for the given class of analytes.

Figure 1: SVOC Extraction Bench Sheet

Methylene Chloride Lot #: _____ Analyst: _____

Na2SO4 Lot #: _____ SVOC Liquid Extraction Log Date: _____

Acid #: _____ Method 3510 C Time Started: _____

SSD #: _____ Time Ended: _____

MS/LCS #: _____ Base #: _____ Batch ID#: _____

Acetone Lot #: _____

#	Merit #	Matrix	Sample Volume (ml)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Turbo VAP ID	Initial pH	Notes	
Initial Q.C.	BLANK	D.I.	1000 ml	Acetone/Methylene Chloride	180	1	1	---				
	LCS	D.I.	1000 ml					1				
	LCSD	D.I.	1000 ml					1				[ ]
	MS							1				[ ]
	MSD							1				
1												
2												
3												
4												
5												
6												
7												
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20												

Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.

EXT-F03 Effective Date 9/29/2016

Figure 2: PNA/DRO Extraction Bench Sheet

Methylene Chloride Lot #: _____ Analyst: _____

Na2SO4 Lot #: _____ PNA/DRO Liquid Extraction Log Date: _____

Acid #: _____ Method 3510 C Time Started: _____

SSD #: _____ Time Ended: _____

MS/LCS #: _____ Batch ID#: _____

#	Merit #	Matrix	Sample Volume (ml)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Turbo VAP ID	Initial pH	Notes	
Initial Q.C.	BLANK	D.I.	1000 ml	Methylene Chloride	140	1	1	---				
	LCS	D.I.	1000 ml					1				
	LCSD	D.I.	1000 ml					1				☐
	MS							1				☐
	MSD							1				
1												
2												
3												
4												
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Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.

EXT-F02 Effective Date 9/29/2016

Figure 3: TCLP Extraction Bench Sheet

Methylene Chloride Lot #: _____ Analyst: _____
Na2SO4 Lot #: _____ TCLP Extraction Log Date: _____
Acetone Lot #: _____ Method 3510 C Time Started: _____
Acid #: _____ Time Ended: _____
SSD #: _____ Batch ID#: _____
MS/LCS #: _____ Base #: _____

#	Merit #	Matrix	Sample Volume (ml)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Turbo VAP ID	Initial pH	Notes
Initial Q.C.	BLANK	Sol	1000 ml	Acetone/Methylene Chloride	180	1	1	---			
	LCS	Sol	1000 ml					1			
	LCSD	Sol	1000 ml					1			
	TCLP MS							1			
	TCLP BLK							---			
	Daily BLK	Sol	1000 ml					---			[ ]
1											
2											
3											
4											
5											
6											
7											
8											
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20											

Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.
EXT-F08 Effective Date 9/29/2016

STANDARD OPERATING PROCEDURE

FLASH POINT FOR SOLIDS
SW-846 METHOD 1030

APPROVALS:

7/18/11

QA Officer — Date

7/18/11

Technical Director — Date

Number	Description of Change	Date
001-002	Previous changes were not documented	
003	2011 Internal Audit Findings	7/18/11
004		
005		
006		
007		
008		
009		
010		
011		
012		
013		

1.0 SCOPE AND APPLICATION

This SOP is suitable for the determination of the ignitability of solids and is appropriate for soils, pastes, granular materials, solids that can be cut into strips, and powdery substances. Solid Flashpoint is run by SW-846 Method 1030.

2.0 SUMMARY OF METHOD

In a preliminary test, the test material is formed into an unbroken strip or powder train 250mm in length. A blowtorch is applied to one end of the test material to determine whether combustion will propagate along 200mm of the strip within a specified time period. If combustion propagates at a fast enough rate, the test material is subjected to a burning rate test. In this test, the burning time is measured over a distance of 100mm and the rate of burning is determined.

3.0 INTERFERENCES

Large differences in burning rate duplicate runs may occur due to variable conditions (such as variation in the test material). Particle size of the test material can affect the burning rate and the initial ignition of the material. Temperature of some test material such as sulfur powder affects the burning rate. All tests must be performed at approximately the same initial temperature. All tests must be carried out inside a fume hood with the test apparatus situated perpendicular to the direction of flow. Airflow parallel to the test apparatus results in non-reproducible burning rates. The rate of airflow through the fume hood affects the burning rate. The optimum airflow is in the range of 0.7-1 meter per second. Materials that are moisture sensitive (i.e. readily absorb moisture from the air) must be tested as quickly as possible after removal from the sample container.

4.0 APPARATUS AND MATERIALS

Low-heat conducting, non-combustible, impervious ceramic tile

Marker

Blowtorch

Butane lighter

Stop watch

Thermocouple

Anemometer to measure airflow in the fume hood

Ruler

5.0 REAGENTS

Not applicable.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are tested on as-received basis unless requested otherwise. Samples must be tested as soon as possible after removal from the sample container.

7.0 PROCEDURE

1. Preliminary Screening Test.

   - On a clean ceramic tile, clearly mark a 250 mm long test path along the edge of the tile. Make another mark at exactly 200 mm from the start of the sample path.
   - Prepare the test material in its "as received" form by forming an unbroken strip or powder train of sample 250 mm long by approximately 20 mm wide and by approximately 10 mm high.
   - Place the ceramic tile with the loaded sample in a fume hood about 20 cm (about 8 in) from the front of the hood and in an area of laminar airflow. Position the sample perpendicular to the airflow. Measure the air velocity to make sure that it is approximately 0.7 m/s.
   - Light the blowtorch using a butane lighter and adjust the height of the flame to its maximum setting.
   - Measure the temperature of the flame (blue cone on the inside) using the thermocouple to make sure that it is at least 1832ºF (1000ºC).
   - If the sample is nonmetallic, apply the tip of the flame to one end of the sample strip and start the stopwatch.
     - If the sample ignites, watch it and note whether the combustion propagates up to the 200mm mark within 2 minutes.
     - If the sample does not ignite, hold the tip of the flame to the sample for 2 minutes to ensure that combustion does not occur.
   - If the sample is a metal or a metal-alloy powder, apply the tip of the flame to one end of the sample and start the stopwatch.
     - If sample combustion occurs within 5 minutes, re-start the stopwatch and note whether the combustion propagates up to the 200 mm mark within a 20-minute test period.
   - If the sample does not ignite or propagate to the 200 mm mark, the waste is not considered flammable and no further testing is required. The result is "not detected."
   - If the sample propagates burning of 200 mm of the test strip within the 2-minute test period, the material must be evaluated by the burning rate test (Section 7.2).

2. Burning Rate Test

- On a clean ceramic tile, clearly mark a 200 mm long test path. Mark two additional timing marks at 80 mm and 180 mm from the start of the sample path. The distance between the two marks (100 mm) will be used to calculate the rate of burn.
- Prepare the test material in its "as received" form by forming an unbroken strip or powder train of sample 250 mm long by approximately 20 mm wide and by approximately 10mm high, just as was done for the preliminary screening test.
- Place the ceramic tile with the loaded sample in a fume hood about 20cm from the front of the hood.
- Light the blowtorch using a butane lighter and adjust the height of the flame to its maximum setting.
- Measure the temperature of the flame (blue cone on the inside) using the thermocouple to make sure that it is at least 1832ºF.
- Apply the tip of the flame to one end of the sample strip to ignite the test strip.
- When the test strip of powder train has burned up to the 80 mm time marker, begin timing the rate of combustion with a stopwatch. Stop the timer when the burned strip reaches the 180mm mark. Record the amount of time (in seconds) required to burn the 100 mm test strip.
- Calculate the rate of burning by dividing the length of the burn test strip (100 mm) by the total time (seconds). Results of the burn rate test are reported in mm/sec.
    - Samples that have a rate of burning of more than 2.2 mm/sec (or burn time of less than 45 seconds for 100 mm) are considered to have a positive result for ignitability.
    - For metals, this time is 10 minutes or less for 100 mm (or a burn rate of more than 0.17 mm/sec).
- Repeat Burn Rate Test two times to give triplicate runs for the test.
- The result of the test is the average of the 3 triplicate runs

8.0 QUALITY CONTROL

See Table 1 for Quality Control items, frequency and corrective actions. A "blank" must be run at the start of each day or set of 20 samples. This is a piece of regular copy paper vertically folded as many times as possible. A sample duplicate must be run for each set of 20 samples. The burn rate test must be conducted in triplicate if the preliminary screening test is positive. This can count as the sample duplicate for a set of 20 samples. All tests must be performed on a clean ceramic plate at room temperature. All replicate runs must be at the same initial temperature. All replicate tests must be run at approximately the same airflow through the fume hood. Only materials of the same particle size distribution should be used for all replicate tests.

9.0 METHOD PERFORMANCE

All positive results are run in triplicate.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. Maintenance procedures provided in the equipment manual shall be followed. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

Acids and bases should be neutralized before disposal. All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Sample Duplicate: The analyses of the variable of interest performed identically on two subsamples of the same sample. The results of duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory.

14.0 REFERENCES

SW-846 Standard Method 1030: Ignitability of Solids

Table 1. Quality Control Items, Frequency and Corrective Action

QC Item	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Blank (piece of copy paper)	1/20 samples	Not Detected (Negative Preliminary Screening Test Result)	If failed, clean apparatus and repeat.
Sample Duplicate	1/20 samples	0.0-20.0 rpd	If failed, clean apparatus and repeat.
Burn Rate Test in Triplicate	For each sample that has a positive preliminary screening test result.	N/A	

MERIT LABORATORIES, INC.

Figure 1: Preliminary Solid Flashpoint Test

Ambient Temperature: _____^{o}F

Date: _____
Analyst: _____
Hood Flow @ 141 ft.min: YES / NO
Flame Temperature >1832^{o}F YES / NO

Preliminary Screening

	Merit #	Sample Discription	Metal[2] (5/20 min)	Non-Metal[3] (2 min)	Observations	Combustion traveled 200mm within time	Result[4]
Blank[1]	Control	Paper, folded		X		YES / NO	
Dup						YES / NO	
1						YES / NO	
2						YES / NO	
3						YES / NO	
4						YES / NO	
5						YES / NO	
6						YES / NO	
7						YES / NO	
8						YES / NO	
9						YES / NO	
10						YES / NO	
11						YES / NO	
12						YES / NO	
13						YES / NO	
14						YES / NO	
15						YES / NO	
16						YES / NO	
17						YES / NO	
18						YES / NO	
19						YES / NO	
20						YES / NO	

[1] - Clean piece of copy paper folded in half four times with edges of paper on the inside of folds.

[2] - If conbustion occurs within 5 minutes, re-start timing and note if combustion travels 200mm in 20minutes.

[3] - Time for 2 minutes to see if cumbustion travels 200mm.

[4] - Detect or Non-Detect. If detect, run Burn Rate Test.

Figure 2: Burn Rate Bench sheet

Burn Rate Test

Merit #	Metal[5]	Non-Metal[6]	Sample Discription	Burn time of 100mm	Rate: mm/sec	Average Burn Rate	Result[7]

Notes:

Notes:

Notes:

Notes:

Notes:

Notes:

[5] - For metals, the rate of burning is 10 minutes or less for 100mm (Burn rate of more than 0.17 mm/sec) are considered positive.

[6] - For Non-metals, the rate of burning of more than 2.2 mm/sec (burn time of less than 45 seconds for 100mm) are considered positive.

[7] - Positive or Negative. See footnote [5] and [6] for rates.

STANDARD OPERATING PROCEDURE

FLASH POINT FOR LIQUIDS
ASTM D3278

APPROVALS:

7/14/11

QA Officer Date

7/14/11

Technical Director Date

Number	Description of Change	Date
001-002	Previous changes were not documented	
003	2011 Internal Audit Findings	7/14/11
004		
005		
006		
007		
008		
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010		
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012		
013		

1.0 SCOPE AND APPLICATION

This method uses a Stanhope-Seta SetaFlash Series 8 'ActiveCool' Closed-Cup Flash Point Tester to determine the flashpoint of a liquid. The liquid matrix is inclusive of oils, solvents, water, liquids that form a surface film under test conditions and liquids that contain non-filterable, suspended solids. Flashpoint is defined as the lowest temperature, at which application of a test flame causes the vapor of a specimen to ignite under specified conditions of this test.

2.0 SUMMARY OF METHOD

The samples injected into a stainless steel cup, preheated to a determined temperature. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flashpoint is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite.

3.0 INTERFERENCES

Sometimes if a sample has a low boiling point, the sample can bubble up and the liquid can set of the alarm by touching the sensor. This is of particular concern when a sample has high water content. A ramped test of water samples is preferable to a flash/no flash test for this reason. Hood in flash point room must be closed to keep air pressure in room constant.

4.0 APPARATUS AND MATERIALS

Stanhope-Seta SetaFlash Series 8 'ActiveCool' Closed-Cup Flash Point Tester

Reusable glass syringe for standards

Disposable syringes

Disposable Aluminum tins

Watch glass

KimWipes

Paper Towel

Lighter

5.0 REAGENTS

Low Level Standard: p-Xylene Flash Point: 77ºF

Mid Level Standard: n-Butanol Flash Point: 95ºF

High Level Standard: Kerosene: Flash Point 137ºF

Acetone

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples must be stored in glass bottles, preferably at refrigerator temperature (4±2 C). Hold time for samples is 14 days. Samples should not be stored in plastic bottles, the volatile materials in the samples may diffuse through the walls.

7.0 PROCEDURE

1. Turn on the SetaFlash Series 8 flash point machine.
2. Testing a Standard:
    - ♦ Select “Ramp” on the menu.
    - ♦ Adjust the “Set Test Temperature” for the desired beginning temperature of the ramp. For p-xylene standards, start ramp at 60ºF. For n-Butanol, start ramp at 85ºF.
    - ♦ Wait for the temperature to reach the set temperature. It will beep when it’s ready.
    - ♦ Inject 2 mL of the standard with a glass 2 mL syringe into the machine’s sample cup through the injection port.
    - ♦ Push the “Start” button to start the test.
    - ♦ Wait while the machine works.
        - o The machine will ramp up the temperature 2ºC and then test for a flash after each ramp.
    - ♦ When/if the machine detects a flash, it will beep and say “Test Result” on the screen.
    - ♦ Record the “Adjusted Temperature” in the bench book.
    - ♦ Clean the syringe with acetone and then air dry.
    - ♦ Open the lid and clean the sample cup with KimWipes and acetone.
3. Testing a Sample:
    - ♦ FLASH/NO FLASH AT 72ºF (ROOM TEMPERATURE).
        - o Perform this part of the procedure in the hood.
        - o Shake sample before running to obtain a representative sample.
        - o Measure 2 mL of sample using a disposable syringe.
        - o Place 2 mL of sample into disposal aluminum tin.
        - o Place flame from lighter to the sample inside the tin.
        - o Have watch glass on hand to put out sample if sample flashes.

- Record results in bench book.
- If sample flashes, the final result is flash point <72ºF. If sample does not flash, continue on to Flash/No Flash at 180ºF.

♦ FLASH/NO FLASH AT 180ºF

- Select "Menu" then "Flash/No Flash".
- Adjust the "Test Temperature" to 180.0ºF.
- Wait for the machine to heat the sample cup up to the determined temperature. The machine will beep when it's ready.
- Add 2 mL of the sample using disposable syringe directly into the sample cup and immediately close the lid.
  - Note: The sample could change the temperature of the sample cup, so the machine may need time to adjust itself.
- Press the "Start" button.
- Wait while the machine works.
- The machine will wait for 1 minute then it will test for a flash.
- After the test, the machine will give its result ("Flash" or "No Flash")
- Record this result in the bench book.
- Open the lid and clean the sample cup with KimWipes and acetone.
- If the machine recorded a "No Flash", the final result is "Not Detected" and the test is done.
- If the machine recorded a "Flash," continue on to Step Flash/No Flash at 126ºF.
- Clean out cup after each run with KimWipes and acetone. Add new sample volume for each test stage

♦ FLASH/NO FLASH AT 126ºF

- Select "Menu" then "Flash/No Flash".
- Adjust the "Test Temperature" to 126.0ºF.
- Repeat Steps for Flash at 180ºF.
- If the machine recorded a "No Flash", start the ramped temperature test at 126.0ºF. Clean out cup after each run with KimWipes and acetone. Add new sample volume for each test stage.
- If the machine recorded a "Flash", start the ramped temperature test at 72.0ºF. Clean out

cup after each run with KimWipes and acetone. Add new sample volume for each test stage.

4. Ramped Temperature:

- Select “Ramp” on the menu.
- Adjust the “Set Test Temperature” for the desired beginning temperature of the ramp.
- Wait for the temperature to reach the set temperature. It will beep when it’s ready.
- Add 2 mL of the sample directly into the sample cup.
- Push the “Start” button.
- Wait while the machine works.
  - The machine will ramp up the temperature 2ºC and then test for a flash after each ramp.
- When/if the machine detects a flash, it will beep and say “Test Result” on the screen.
  - Note: If the sample has high water content, it is very likely to have triggered a false positive result for a flash at 180.0ºF. If this happened, a flash would not have been detected on the ramp test starting at 126.0ºF. Repeat the Ramp Up Temperature procedure in order to ensure this result.
- Record the “Adjusted Temperature” in the bench book.
- If sample flashes, run duplicate for that sample by repeating the Ramp Up Temperature procedure.
- The final result is the average of the first and second Ramp Up Temperature tests.
- A duplicate needs to be run for every batch of 20 samples. In none of the samples flash, a duplicate is chosen at random.
- Open the lid and clean the sample cup with KimWipes and Acetone

8.0 QUALITY CONTROL

Samples that flash below 180ºF, must be verified by a duplicate analysis. If no samples flash, run one duplicate per batch of 20 samples. Standards must be analyzed with every batch not exceeding 20 samples.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on as needed basis.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer’s procedures. Each instrument is

assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention be paid (but not limited) to

- p-Xylene is harmful or fatal if swallowed and flammable. Contact with strong oxidizers may cause fire. Sensitive to static discharge.
- n-Butanol is harmful if swallowed, inhaled or absorbed through the skin and flammable. Vapors can flow along surfaces to distant ignition source and flash back. Sensitive to static discharge.
- Kerosene is hazardous in case of skin contact, eye contact, ingestion and inhalation. Reactive with oxiding agents and instable under heat and ignition sources.
- Acetone is an extremely flammable liquid. Acetone vapors may cause flash fire. Acetone is harmful if swallowed or inhaled. Vapors can flow along surfaces to distant ignition source and flash back. Contact with strong oxidizers may cause fire. Sealed containers may rupture when heated.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

Acids and bases should be neutralized before disposal. All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 10 samples or less.

Sample Duplicate: The analyses of the variable of interest performed identically on two subsamples of the same sample. The results of duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory.

14.0 REFERENCES

ASTM Standard Method D3278: Standard Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus

Stanhope-Seta SetaFlash Series 8 'ActiveCool' Closed-Cup Flash Point Tester instrument manual

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Item	**Frequency**	**Acceptance Criteria**	**Corrective Action**
p-Xylene Standard	1/20 samples	74°F-80°F	If failed, clean apparatus and repeat. Check the validity of the standard with a cross reference standard.
n-Butanol Standard	1/20 samples	92°F-98°F	If failed, clean apparatus and repeat. Check the validity of the standard with a cross reference standard.
Kerosene Standard	1/20 samples	134ºF-140ºF	If failed, clean apparatus and repeat. Check the validity of the standard with a cross reference standard.
Duplicates	All samples that flash below 180°F, or one per batch of 20 samples or less	±3°F	Repeat the test on the sample. If repeatability is not within the range after a triplicate is performed, flag the results accordingly.

Check Standard 1 - p-Xylene 77°F: Results = _____°F % Accuracy = ___%

Check Standard 2 - 1-Butanol 95°F: Results = _____°F % Accuracy = ___%

Batch #: _____

	MERIT #	Type of Sample*	Observations	room temp check 72°F	flash/no flash @ 180°F	flash/no flash @ 126°F	ramped temp	dup ramped temp	Avg result	Notes
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										

Dup Merit #_____ Result #1: _____ Result #2: _____ % Difference = ____%

Std 3 - Kerosene- °F: Results:_____°F %Acc:_____

STANDARD OPERATING PROCEDURE

OIL AND GREASE EXTRACTION USING HEXANE (GRAVIMETRIC)

EPA METHOD 1664A

APPROVALS:

Barbara Ball

01/10/17

QA Officer Date

Maya Mushahwar

01/10/17

Technical Director Date

Number	Description of Change	Date
001-004	Previous changes were not documented	
005	Required sections added and Internal Audit findings fixed.	8/17/11
006	Quality control items updated	6/21/12
007	Updated instrument method information and constant weight check information added	8/10/12
008	Emergency SOP Amendment Form	01/10/17
009		
010		
011		
012		
013		
014		
015		

1.0 SCOPE AND APPLICATION

This SOP is a procedure for determining the concentration of Oil and Grease from aqueous samples using n-Hexane. It is based on SW846 Third Edition, Method 1664A n-Hexane Extractable Material and Silica Gel Treated n-Hexane Extractable Material by Extraction and Gravimetry Revision 2, February, 1999. Extractable materials that may be determined are relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials. This SOP is not applicable to the measurement of materials that volatilize at temperatures less than 85ºC. Petroleum fuels from gasoline through #2 fuel oil may be partially lost during the solvent removal operation. Some crude oils and heavy fuel oils contain significant percentages of materials that are not soluble in hexane. Recoveries of these materials may be low. This SOP is capable of measuring n-Hexane extractable material (HEM) and n-hexane extractable material that is not adsorbed by silica gel (SGTHEM) in the range of 5 to 1000 mg/L. The MDL for this procedure is 1.4 mg/L and the recommended minimum level of quantitation is 5.0 mg/L.

2.0 SUMMARY OF METHOD

A one liter sample is acidified to pH 2.0 with a 1:1 solution of HCl (or approximately 15 drops of concentrated HCl) and extracted with the SPE-DEX 1000 XL automated extractor system by bypassing the sample through a solid phase extraction (SPE) disk and eluting the analytes with n-hexane. The n-hexane layer of the collected extract is transferred to a Zymark® evaporation tube and evaporated using the Zymark® evaporator. The residue is weighed and reported as HEM. The residue for the HEM determination is re-dissolved in n-hexane and treated with silica gel for SGT-HEM. Methanol cannot come into contact with samples based on January 16, 2009 modification to EPA Method 1664A. “Co-solvents and/or alternate solvents (including methanol) can significantly change the chemistry of Method 1664A.”

3.0 INTERFERENCES

Interferences that affect results can come from solvents, reagents, glassware, and other sample processing hardware. Silica gel has the potential to inflate results for SGT-HEM if it is transferred with the n-hexane into the pan for gravimetric determination. Samples may contain complex matrices containing substances (such as particulate and detergents) that may interfere with the extraction procedure.

4.0 APPARATUS AND MATERIALS

Horizon SPE-DEX 1000 XL Automated Extraction System

Zymark Evaporation Station.

Evaporation tubes, 250 ml volume, Zymark with end point of 0.5 ml.

Aluminum weighing dishes.

Analytical Balance - capable of accurately weighing to the nearest 0.1 mg.

pH indicator paper - pH range including the desired extraction pH.

Horizon Solvent Trap™ Solvent Recovery System

Disks- 90 mm (JT Baker Speedisk™ 50 mm, CPI Nu-Phase™ SPE Disks, Whatman® SPE Oil & Grease , or 3M Empore™ Oil and Grease Extraction Disks).

One liter sample bottles (HCl preserved).

125 mL Erlenmeyer flasks.

5 gallon safety coated water waste recovery bottle.

2.5 L safety coated solvent bottles, 2 for 1000 XL unit.

5 mL glass volumetric pipettes.

Disposable polyethylene pipettes

Glass stir rod

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades must be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Deionized (DI) water.

n-Hexane ACS Reagent Grade-85% minimum purity, 99.0% min. saturated C6 isomers, residues less than 1 mg/L.

Hydrochloric acid, concentrated, as well as solution (1:1 v/v), HCl. Slowly add 50mL of HCl to 50 ml of DI water

Oil & Grease Standard containing 0.4-g Hexadecane and 0.4 g Stearic Acid in 100 ml of Acetone

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples for the analysis of Oil and Grease must be stored in 32oz glass containers and preserved with HCl. Approximately 1L volume of sample is needed for extraction. Note: If significantly less than one liter of sample is supplied, the Project Manager, QA Officer and the client need to be notified. Refrigerate at 4ºC ± 2 ºC. Samples must be extracted and analyzed within 28 days of the sampling date.

7.0 PROCEDURE

1. Standard Preparation.

- Oil & Grease Standard contains 0.4 g of Hexadecane and 0.4 g of Stearic Acid in 100 ml of Acetone. A concentration of 40 mg/L can be achieved by spiking 5 mL of the solution into a 1 L sample.
- Visually inspect the vial for a precipitate, which resembles small particles, indicating that the standard has come out of solution. If a precipitate is detected, gently swirl the vial under warm running water until the Stearic Acid is driven into solution. It is essential to allow the vial to equilibrate to ambient room temperature before spiking. Note: Method 1664A suggests confirmation of the actual weight of the standard (40 mg/L). Pipette 5.0 mL into a tarred aluminum weighing pan and evaporate. The calculated weight should be used to determine percent recoveries in the spiked samples.
- Fill a clean sample bottle with approximately 800 mL to 1000 mL of reagent water. Note the volume on the bench sheet.
- Acidify the water to pH 2.0 with 1:1 HCl solution. Do not over acidify the water as this could cause the disk packing to breakdown. Cap the bottle and shake.
- Pipette 5 mL of the oil and grease standard using a 5 mL Class A glass pipette. Verify that there are no air bubbles in the pipette.
- Touching the tip of the pipette to the inside of the neck of the bottle, allow the standard to slowly flow down the side of the bottle and settle on the water layer. A cloudy precipitate will form on the water. *Avoid shooting the standard into the water or introducing it too quickly. If the standard is not properly floated it can cause flow problems during the sample processing step*.
- Do not shake the bottle. Attach a closed Water Inlet Valve to the bottle. An adapter will be necessary if using a wide mouth bottle or jar.

2. Sample Preparation

- Verify that the pH of the sample is less than 2 using the following procedure:
  - Dip a glass stirring rod into the well mixed sample.
  - Withdraw the stirring rod and allow a drop of the sample to fall on or touch the pH paper.

  NOTE: Do not dip the pH paper into the bottle or touch it to the sample on the lid.

- Rinse the stir rod with a small portion of n-hexane that will be used for extraction (to ensure that no extractable material is lost on the stirring rod). Collect the rinsate in the separatory funnel to be used for sample extraction.

- Acidify the samples to a pH of 2.0 with 1:1 HCl, if not already acidified. Do not over acidify the samples, as this will cause the disk material to break down and result in low recoveries. Cap and invert the sample bottle several times to mix.
- Mark the liquid level on the sample bottles. The sample volume will later be measured and used in the calculation of the oil and grease concentration.
- Prepare a laboratory reagent blank by adding approximately 800 mL to 900mL of reagent water to a bottle. Adjust the pH to 2.0 with 1:1 HCl. Do not over acidify. Invert the bottle several times to mix.
- Attach a closed Water Sample Inlet Valve to the bottle. Use an adapter if necessary.
- The standard, samples and blank are now ready for processing.

3. System Performance Checks

- Empty all waste recovery bottles. Loss of pressure in the bottles will occur if the caps are loose.
- Fill the solvent bottles as follows:
  - Prewet 1: n-hexane connected to Prewet Fitting #1 on Exterior
  - Prewet 2: n-hexane connected to Prewet Fitting #2 on Exterior
  - Rinse 1: n-hexane Connected to Rinse Fitting #1 on Exterior
  - Rinse 2: n-hexane connected to Rinse Fitting #2 on Exterior
  - Secure the caps on the solvent bottles. Loss of pressure in the bottles will occur if the caps are loose.
- Turn on the main power switch on the back of the Controller and allow the Liquid Level Sensor to stabilize for 3 to 5 minutes.
- Turn on the gas source and slowly increase the main gas source pressure while checking for liquid and gas leaks. Adjust the main gas source pressure in increments, checking for leaks as the pressure is increased to a minimum of 60 psi and a maximum of 80 psi.
- Turn on the vacuum pump and check for vacuum leaks. The main vacuum source gauge should read between -25" Hg and -30"Hg.
- Verify that there are no crimped lines that may impede the flow of liquids, gas, or vacuum.

- Free the Elute Check valve using the Check Valve Release Tool. In the center of the platform, below the drain whole, is the Sample Collect Check Valve. Gently insert the needle end straight down into the opening and tap the head several times to free the check valve. This will move the Check Valve Ball off of the seat assembly. An internal spring will gently push the ball back into the sealing position.
- Lift and move the Liquid Sensor/ Prewet Arm into the Disk Holder Base.
- If using a VOA vial as a collection vessel, attach the glass adapter to the vessel by screwing it on using the turquoise cap. Do not screw on the adapter by using the glass part; this may not produce a good seal. Place the collection vessel in position on the Taper of the unit by lifting and twisting to ensure a vacuum tight seal. An adapter is not required for an Erlenmeyer flask with a 19/22 taper.
- Lower the Water Sample Bottle Arm.
- Attach an empty sample bottle to the Water Sample Inlet Valve and place the valve into position on the Water Sample Bottle Arm.
- A Purge sequence is run to remove any air from the solvent lines and to wash the parts of the extractor. Press the STATUS key to display the status for all three stations.
- Select Station #1 by pressing the A-key. Press the DRAIN function key (E-key). Then press the PURGE key (D-key). Press the A-key for YES to begin the purge on Station #1. Run the purge sequence three times to ensure all air has been removed from the lines when first installed or when refilling the solvent bottles.
- If the system is being used for the first time or has not been used for an extended period of time, create a test run using 500 mL of water, no disk or screen, 47 mm size Disk Holder Assembly, and the following conditions:
  - n-Hexane Prewet: 5 sec. Dispense, 1 sec. Saturate, 10 sec. Soak, 0 sec. Drain.
  - Air Dry: 10 sec.
  - Two n-Hexane Rinses: 3 sec. Dispense, 0 sec. Soak, 10 sec. Elute.
- Remove the empty sample bottle and collection vessel. Lift the Liquid Sensor/Prewet Arm and place it outside the Disk Holder Base. Remove the Disk Holder Base from the platform.

4. Evaporation Procedure and Gravimetric Determination

- Sample Extraction.

- Attach the Water Sample Inlet Valve to the bottle. Use an adapter if required.
- Place the screen in the Disk Holder Base. Place the SPE disk on the screen.
- Insert the Riser into the Disk Holder Base over the disk. The Riser holds the disk in place. Screw on the aluminum Locking Ring, load the Disk Holder assembly onto the Extractor platform and place the Liquid Sensor/Prewet Arm in the Disk Holder Assembly. Load the Disk Holder Assembly on the station.
- Place a collection vessel with adapter in position by lifting and twisting to ensure a vacuum tight seal. Use 125 mL flasks for dirty samples.
- Lower the Sample Holder Arm on the extractor.
- Load the sample bottle onto the unit. Minimize the agitation of the standard. With the Water Sample Inlet Valve aluminum shaft facing you, place your right index finger over the solvent rod on the right hand side. This will prevent the sample from leaking out. Gently invert the bottle and place it onto the Holder Arm of the unit. Help guide the Water Sample Inlet Valve shaft onto the actuator key. Firmly press the valve in place.
- Select the appropriate method for the extraction process according to the disk size and type. From the STATUS mode, select the station with sample loaded for processing by pressing the appropriate key. Press the A-key to increase the method number or the B-key to decrease the method number to the one desired.
- Return to the STATUS mode and proceed as using previous step to load the method to the station.
- Return to the STATUS screen and confirm that the station is set to the desired method.
- Press the A-key to start the extraction. Confirm the start of the extraction by pressing the A-key again.
- Start extraction Method #1 (see Table #1).
- After Method #1 has finished, leave the sample bottle and collection vessels on the instrument and change to Method #2 (see Table #2).
- Start extraction Method #2.
    - It may be necessary to squirt a small amount of hexane onto the thermistor when the station is in the Sample Process step. This will

"trick" the thermistor into thinking a sample is present and allow the station to continue.

- Once Method #2 is completed the sample is ready to be evaporated.

♦ Instructions for using JT Baker Speedisk.

- Use the small circular adapter for JT Baker disks. Press the adapter down firmly into the Disk Holder Platform. Next, carefully but firmly, press the Speedisk into the center whole adapter.
- Use a Sensor Arm Clip to properly position the tip of the sensor the correct distance from the surface of the JT Baker Speedisk. Simply snap the clip onto the Stainless Steel rod of the Liquid Sensor Arm Assembly.
- Lift and move the Sensor Arm into the Speedisk, and visually confirm that the sensor tip does not touch the surface of the disk.
- Remove the Sample Inlet Tube from the Water Sample Inlet Valve. The Inlet Tube is pressed into the bottom of the valve. Grab with a twisting motion to pull the Inlet Tube out. Replace the shorter inlet tube.

♦ Gravimetric Determination

- Rinse the collection vessel at least three times with hexane, remove water layer and keep hexane/oil layer by transferring each rinse to the evaporation tube.
- Evaporate the hexane using the TurboVap until the volume is small enough (approximately ½ ml) that it can be transferred to an aluminum weighing pan.
- Continue evaporating the rest of the hexane in the pan under the hood and then in the oven.
- If samples are not dried overnight, samples must be checked for constant weight. Constant weight check is performed by drying the samples in the oven for an additional hour. Constant weight is obtained when weight change is less than 4% of the previous weight or 0.5 mg, whichever is less.
- Once the hexane is evaporated, determine the weight of HEM by subtracting the tare weight from the total weight.

♦ Shut-down procedure for extractors

- Remove the Disk Holder Assembly from the extractor unit and discard the used disks.

- Pour water in the platform cavity of the station. Select the station from the STATUS mode. Press the DRAIN (E-key) function and then the ELUTE (C-key). Repeat for each station. This procedure will remove any residual solvent from the check valve.
- Turn off the vacuum pump and vent by removing the line attached to the waste bottle.
- Turn off the gas supply.
- Turn off the controller power.
- Flush the Water Sample Inlet Valve by manually turning it open and closed while flushing under warm running water. Non-surfactant soap may be used to clean the valve. Make sure to thoroughly rinse it out. Do not scrub using a cleaning brush.
- Leave the Water Sample Inlet Valve in a half open position to allow the water to drain.

5. Calculations

- Standard Recovery: % Recovery= $\frac{W_f - W_i}{40mg} * 100\%$
- Concentration Calculation for HEM and SGT-HEM

  Oil and Grease (mg/L) = $\frac{W_f - W_i}{V}$

  Where: W_f = final weight of dish (mg)

  W_i = initial weight of dish (mg)

  V = sample volume (L)
- Concentration of polar material: $C_P = C_T - C_{NP}$

  Where: C_P=Concentration of polar material

  C_T=Total oil and grease (HEM-oil and grease)

  C_{NP}=Concentration of non-polar material (SGT-HEM)
- Relative Percent Difference $RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$

  Where: S = Initial sample result

  D = Duplicate sample result

8.0 QUALITY CONTROL

Samples are extracted in batches of 10 samples or less. Every batch includes a LCS, Blank and MS/MSD, depending on the client request and when sample volume is available. When MS/MSD sample volume is not

provided, an LCSD is analyzed and evaluated. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed. The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced. Acceptance Criteria for Performance Tests from Method 1664A, February 1999

Acceptance Criterion	Limit (%)
Matrix Spike/Matrix Spike Duplicate	
HEM Recovery	78-114
HEM RPD	18
Silica Gel-HEM Recovery	64-132
Silica Gel-HEM RPD	34
LCS Recovery	
HEM Recovery	78-114
Silica Gel-HEM Recovery	70-130

9.0 METHOD PERFORMANCE

The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
- Methanol is a slight irritant to the mucous membranes, can intoxicate and cause blindness, stable under ordinary conditions of use and storage, incompatible with strong oxidizing agents such as nitrates, perchlorates or sulfuric acid and will attack some forms of plastics, rubber, and coatings.
- Hexane is stable, incompatible with oxidizing agents, chlorine, fluorine, magnesium perchlorate, highly flammable, readily forms explosive mixtures with air, low flash point, may cause impaired fertility, harmful by inhalation, and prolonged exposure may cause serious health damage.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 10 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a

method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

14.0 REFERENCES

SW846 Third Edition, Method 1664A Revision 2, February 1999.
Horizon user manuals.

Table 1: Method #1, 90 mm Pacific Premium Disk

Prewet			
n-Hexane		n-Hexane	
Dispense	10 sec	Dispense	10 sec
Saturate	1 sec	Saturate	1 sec
Soak	1 min	Soak	1 min
Drain	1 min	Drain	1 min
Air Dry			3 min
Rinse	Dispense	Soak	Elute
Hexane	7 sec	45 sec	0 sec
Hexane	7 sec	45 sec	45 sec
Hexane	7 sec	45 sec	0 sec
Hexane	4 sec	45 sec	45 sec

Table 2: Method #2, 90 mm Pacific Premium Disk

Prewet			
n-Hexane		n-Hexane	
Dispense	0 sec	Dispense	4 sec
Saturate	0 sec	Saturate	1 sec
Soak	0 sec	Soak	20 sec
Drain	0 min	Drain	1 sec
Air Dry			0 min
Rinse	Dispense	Soak	Elute
Hexane	4 sec	45 sec	0 sec
Hexane	4 sec	45 sec	30 sec
Hexane	4 sec	45 sec	1 min

Figure 1: Oil & Grease Hexane Extractable Material Bench Sheet

Date: _____ Analyst: _____ Batch I.D._____

Hexane Lot#: _____ Methanol Lot #: _____ O&G STD Lot #: _____

Sodium Sulfate Lot: _____ Instrument ID: _____ Turbo Vap ID: _____

Merit #	Tin #	Sample Volume (ml)	Weight of Tin (g)	Weight of Tin & HEM (g)	Reweigh Weight of Tin & HEM (g)	Weight of HEM (g)	HEM, PPM (mg/L)	Reported Value, PPM	pH	Notes
BLANK										
LCS										% Recovery:
LCS DUP										% Recovery:

Calculation: $\frac{\text{Weight of HEM}}{\text{Sample Vol. (L)}} * 1000 = \text{HEM (mg/L)}$

Spike solution concentration: 4mg/ml

Balance Used: _____ Balance Check, 1g: _____

Reviewed By: _____ On: _____

Figure 2: Silica Gel Treated Hexane Extractable Material Bench Sheet

Analyst: _____

Balance Used: _____ Balance Check, 1g: _____ Instrument ID: _____ Turbo VAP ID: _____

Hexane Lot#: _____ Methanol Lot #: _____ Sodium Sulfate Lot#: _____ O&G STD Lot #: _____

Merit #	Tin #	Sample Volume (ml)	HEM Conc., (mg/L)	Weight of HEM (g)	Dilution of HEM (g/ml)	Vol. Of Dilution used (ml)	Weight of Tin (g)	Weight of Tin & SGT-HEM (g)	Weight of SGT-HEM (g)	SGT-HEM, PPM (mg/L)	Reported Value, PPM	Date	Notes
BLANK													
LCS													% Recovery:
LCS DUP													% Recovery:

Calculations: $\frac{\text{Weight of SGT-HEM}}{\text{Sample Vol. (L)}} * 1000 =$ SGT-HEM (mg/L)

Diluted: $\frac{\text{Weight of SGT-HEM}}{\text{(Dilution of HEM * mls used of Dilution)}} *$ HEM mg/L = SGT-HEM mg/L

Spiking solution Concentration: 4mg/ml for total EM, 2mg/ml for TPH EM

Reviewed By: _____ On: _____

STANDARD OPERATING PROCEDURE

PAINT FILTER SW-846 METHOD 9095

APPROVALS:

7/8/11

QA Officer Date

7/8/11

Technical Director Date

Number	Description of Change	Date
001-002	Previous changes were not documented	
003	2011 Internal Audit Findings	7/8/11
004		
005		
006		
007		
008		
009		
010		
011		
012		
013		

1.0 SCOPE AND APPLICATION

This SOP is used to determine the presence of free liquids in a representative sample of waste. Paint filter test is run by Method 9095. The SOP is used to determine compliance with 40 CFR 264.314 and 265.314.

2.0 SUMMARY OF METHOD

A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the five minute test period, the material is deemed to contain free liquids.

3.0 INTERFERENCES

Filter media were observed to separate from the filter cone on exposure to alkaline materials. This development causes no problem if the sample is not disturbed. Temperature can affect the test results if the test is performed below the freezing point of any liquid in the sample. Tests must be performed above the freezing point and can, but are not required to, exceed room temperature of 25° C.

4.0 APPARATUS AND MATERIALS

Conical paint filter: Mesh number 60 +/- 5% (fine mesh size).

Glass funnel: If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least 1 inch of the filter mesh to protrude must be used to support the filter. The funnel must be fluted or have a large open mouth in order to support the paint filter yet not interfere with the movement, to the graduated cylinder of the liquid that passes through the filter mesh.

Ring stand, or tripod.

Graduated cylinder or beaker: 100 mL.

Cutting Utensil.

Timer/Stopwatch.

5.0 REAGENTS

Not applicable.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples must be collected according to the directions in Chapter 9 of the SW486 manual. Samples are collected in glass or plastic unpreserved containers and stored in refrigerator at 4±2°C. A 100 mL or 100 g representative sample is required for the test. If it is not possible to obtain a sample of 100 mL or 100 g that is sufficiently representative of the waste, the analyst must use larger size samples in multiples of 100 mL or 100

g. However, when larger samples are used, analysts must divide the sample into 100 mL or 100 g portions and test each portion separately. If any portion contains free liquids, the entire sample is considered to have free liquids. If the sample is measured volumetrically, then it must lack major air spaces or voids.

7.0 PROCEDURE

1. Assemble test apparatus as shown in Figure 1.

2. Place sample in the filter. A funnel can be used to provide support for the paint filter. If the sample is of such light bulk density that it overflows the filter, then the sides of the filter can be extended upward by taping filter paper to the inside of the filter above the mesh. Settling the sample into the paint filter can be facilitated by lightly tapping the side of the filter as it is being filled.

3. In order to assure uniformity and standardization of the test, material such as sorbent pads or pillows which do not conform to the shape of the paint filter, must be cut into small pieces and poured into the filter. Sample size reduction can be accomplished by cutting the sorbent material with scissors, shears, knife or other such device so as to preserve as much of the original integrity of the sorbent fabric as possible. Sorbents enclosed in a fabric must be mixed with the resultant fabric pieces. The particles to be tested must be reduced smaller than 1 cm (i.e., should be capable of passing through a 9.5 mm (0.375 inch) standard sieve). Grinding sorbent materials must be avoided as this may destroy the integrity of the sorbent and produce many “fine particles” which would normally not be present.

4. For brittle materials larger than 1 cm that do not conform to the filter, light crushing to reduce oversize particles is acceptable if it is not practical to cut the material. Materials such as clay, silica gel, and some polymers may fall into this category.

5. Allow sample to drain five minutes into the graduated cylinder.

6. If any portion of the test material collects in the graduated cylinder in the five minute period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314.

8.0 QUALITY CONTROL

Duplicate samples must be analyzed every ten samples.

9.0 METHOD PERFORMANCE

Not applicable.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Visually inspect all equipment for damage before use. Assemble the apparatus according to Figure 1.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour

when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Duplicate: The analyses of the variable of interest performed identically on two subsamples of the same sample. The results of duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory.

14.0 REFERENCES

USEPA, SW-846, Method 9095.
USEPA, SW-846, Chapter 9.

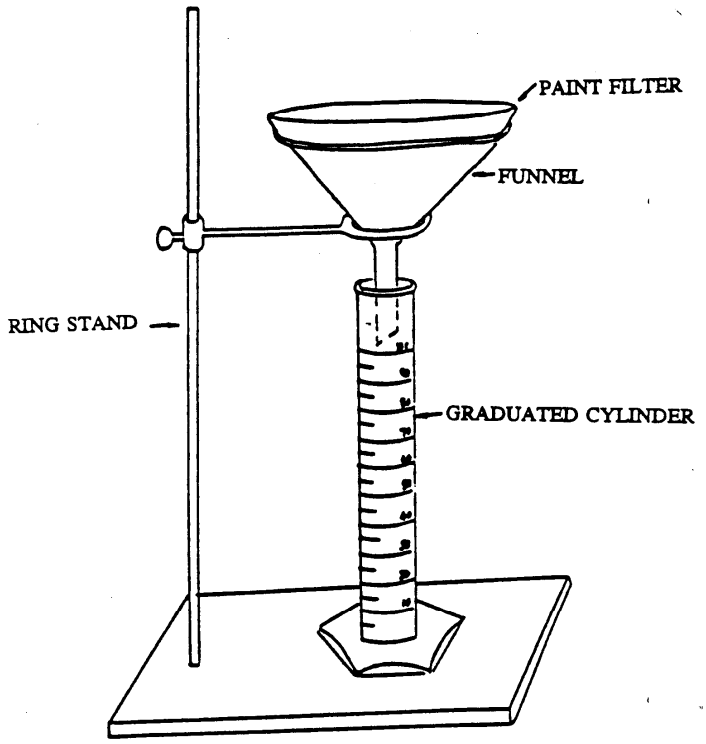
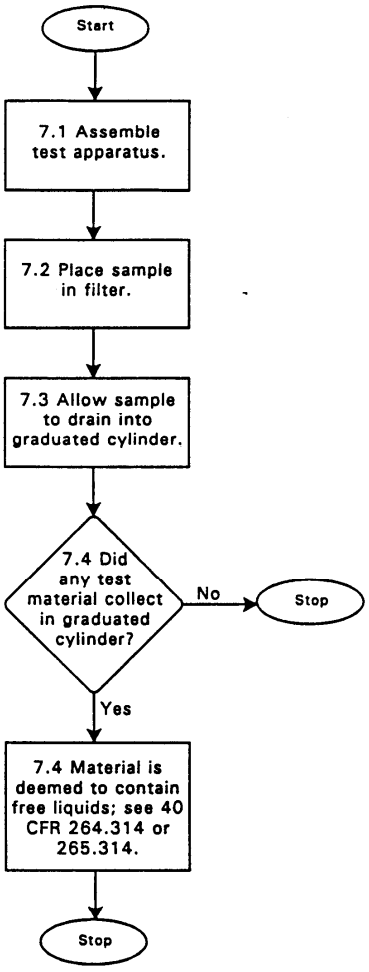


Figure 1. Paint filter test apparatus.

METHOD 9095A
PAINT FILTER LIQUIDS TEST



STANDARD OPERATING PROCEDURE

TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) & SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP) SW-846 METHOD 1311 & METHOD 1312

APPROVALS:

06/08/11

QA Officer — Date

06/08/11

Technical Director — Date

Number	Description of Change	Date
001-007	Previous changes were not documented	
008	Updated to comply with DoD QSM and ISO 17025 standards.	06/08/11
009		
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1.0 SCOPE AND APPLICATION

This SOP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multi-phasic wastes. These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods. For volatile analysis, always use Zero Headspace Extraction (ZHE) extraction.

2.0 SUMMARY OF METHOD

For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP/SPLP extract.

For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 2 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

If compatible (*i.e.*, multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately.

3.0 INTERFERENCES

Potential interferences that can be encountered during analysis are discussed in the individual analytical methods that follow extraction, for both TCLP and SPLP extractions.

4.0 APPARATUS AND MATERIALS

Agitation apparatus: Analytical Testing and Consulting Services, Inc. 4-vessel extractor (DC20S) and 3 Lars Lande Manufacturing 5-vessel extractors (5VRE) (Table 3).

Extraction Vessels.

- Zero-Headspace Extraction Vessel (ZHE) (Figure 2). ZHE devices known to EPA, and used by Merit are listed in Table 4.
    - ZHEs use gas pressure to actuate the ZHE piston. The volatiles procedure (see Section 7.0) refers to pounds per square inch (psi).
- Bottle Extraction Vessel. Borosilicate glass bottles are used. Plastic bottles, other than polytetrafluoroethylene, must not be used if organics are to be analyzed.

- Filter HolderSuitable filter holders known to EPA are shown in Table 5.
- 3 Liter Glass Erlenmeyer Flask.
- TCLP/SPLP Filter Paper, pore size of 0.6 – 0.8 µm, or equivalent (Table 6).
    - ZHE: 110 mm filter paper with a diameter of 90 mm.
    - SVOCs and/or Metals: Filters are acid treated by manufacturer.
    - Positive Pressure Filtration (used for initial solids calculation).
    - Vacuum Filtration (used for SVOCs and Metals extraction filtration).
- Vacuum Filtration is used for SVOC and Metal TCLP/SPLP analyses.
- Positive Pressure Filtration is used for initial solids calculations.

pH Meters: the meter must be accurate to ± 0.05 units at 25 °C.

ZHE Extract Collection Devices: TEDLAR®[2] bags or PTFE gas-tight syringes.

ZHE Extraction Fluid Transfer Devices: ZHE Extraction Vessel (containing non-pressurized sample) and ZHE Extraction Vessel (containing pressurized fluid) are used. Connect the 2 ZHEs with stainless steel tubing to each other. Open the valve on both vessels, forcing the pressurized liquid into the non-pressurized sample. When finished, close the sample ZHE valve.

Laboratory Balance: A laboratory balance accurate to within ± 0.01 grams is used (all weight measurements are to be within ± 0.1 grams).

Beaker or Erlenmeyer flask, glass, 500 mL.

Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

Magnetic stirrer.

Tongue Depressors.

Hot plate/magnetic stir combination.

Scissors.

Thermometer.

Sieve 9.5 mm.

[2] TEDLAR® is a registered trademark of Du Pont.

5.0 REAGENTS

Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Deionized (DI) Water.

Hydrochloric acid (1 N), HCl, made from ACS reagent grade.

Nitric acid (1 N), HNO_3, made from ACS reagent grade.

Sodium hydroxide (10 N), NaOH, made from ACS reagent grade.

Sulfuric acid/nitric acid (H2SO4/HNO2) 60/40 weight percent mixture.

Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

TCLP Extraction fluid:

- Extraction fluid # 1: add 5.7 mL glacial CH_3CH_2OOH to 500 mL of DI water, add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. The pH of this fluid shall be 4.93 $\pm$ 0.05.

- Extraction fluid # 2: dilute 5.7 mL glacial CH_3CH_2OOH with DI water to a volume of 1 liter. The pH of this fluid shall be 2.88 $\pm$ 0.05.

SPLP Extraction Fluid:

- Extraction fluid #1: add the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to DI water until the pH is 4.20 $\pm$ 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained

- Extraction fluid #2: add the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to DI water until the pH is 5.00 $\pm$ 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

- Extraction fluid #3: this fluid is DI water and is used to determine cyanide and volatiles leachability.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Samples are collected in borosilicate glass jars and are stored in refrigerator at 4 ± 2 °C.

Preservatives must not be added to samples before extraction.

Samples can be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) must be extracted.

When the waste is to be evaluated for volatile analytes, care must be taken to minimize the loss of volatiles. Samples must be collected and stored in a manner intended to prevent the loss of volatile analytes. Samples must be opened only immediately prior to extraction.

TCLP/SPLP extracts must be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs. Extracts must be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations must not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Table #1 for acceptable sample and extract holding times.

7.0 PROCEDURE

1. Preliminary Evaluations.

- ♦ Perform preliminary TCLP/SPLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP/SPLP extraction. The preliminary evaluation includes: (1) determination of the percent solids; (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration; (3) determination of whether the solid portion of the waste requires particle size reduction; and (4) determination of which of the extraction fluids are to be used for the nonvolatile TCLP/SPLP extraction of the waste.

  - ● Preliminary determination of percent solids:

    - o If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to the second diamond bullet below.

    - o If the sample is liquid or multi-phasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in number 4 and is outlined below.

    - o Pre-weigh the filter and the container that will receive the filtrate.

    - o Assemble the filter holder and filter. Place the filter on the support screen and secure.

    - o Weigh out a subsample of the waste (100 gram minimum) and record the weight.

- Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid must be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

- Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4° C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in number 1 to determine the weight of the waste sample that will be filtered. Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration. Instantaneous application of high pressure can degrade the glass fiber filter and can cause premature plugging.

- The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

- Determine the weight of the liquid phase by subtracting the weight of the filtrate container from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample.

- Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\%Solids = \frac{Weight\ of\ \ solid}{Total\ \ weight\ of\ \ waste} x100\%$$

♦ If the percent solids determined above is equal to or greater than 0.5%, then proceed either to the next diamond bullet below to determine whether the solid material requires particle size reduction or to the bulleted item directly below if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined above is less than 0.5%, then proceed to number 2 if the nonvolatile TCLP/SPLP is to be performed and to number 3 with a fresh portion of the waste if the volatile TCLP/SPLP is to be performed.

- Remove the solid phase and filter from the filtration apparatus.
- Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution must be taken to ensure that the subject solid will not flash upon heating. The vented drying oven in the total solids labs is used.

- Calculate the percent dry solids as follows:

$$\%drysolids = \frac{(Wt.\ of\ \ dry\ waste + \ filter) - (tared\ \ weight\ of\ \ filter)}{Initial\ \ weight\ of\ \ waste} x100\%$$

- If the percent dry solids are less than 0.5%, then proceed to number 2 if the nonvolatile TCLP/SPLP is to be performed and to number 3 if the volatile TCLP/SPLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP/SPLP is to be performed, determine whether particle size reduction is necessary and determine the appropriate extraction fluid. If only the volatile TCLP/SPLP is to be performed, proceed to number 3.

♦ Determination of whether the waste requires particle size reduction: Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken.

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

- Determination of appropriate extraction fluid:
  - TCLP Extraction Fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents, determine the appropriate fluid for the nonvolatiles extraction as follows:

    NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (number 5). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to number 3.

    - Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.
    - Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to number 2.
    - If the pH from number 1 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.
    - Let the solution cool to room temperature, continue to stir the sample while cooling, and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to number 2.
  - SPLP Extraction Fluid:
    - For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 must be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 must be used.
    - For wastes and wastewater, extraction fluid #1 must be used.
    - For cyanide-containing wastes and/or soils, extraction fluid #3 (DI water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

- If the aliquot of the waste used for the preliminary evaluation was determined to be 100% solid, then it can be used for the non-volatile TCLP/SPLP extraction (assuming at least 100 grams remain), and for the volatile TCLP/SPLP extraction (assuming at least 25 grams remain). If the aliquot was heated, then another aliquot must be used for the volatile extraction procedure. The heated sample can be used for the non-volatile TCLP/SPLP extraction, if there is enough sample remaining. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to the fifth bullet under number 2 of the nonvolatile TCLP/SPLP extraction.

2. Procedure When Volatiles are Not Involved.

   A minimum sample size of 25 grams (solid and liquid phases) is recommended. In some cases a larger sample size is appropriate, depending on the solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids must be used for extraction such that the volume of TCLP/SPLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP/SPLP extraction will not be sufficient to perform all of the analyses, more than one extraction can be performed and the extracts from each combined and aliquoted for analysis.

- If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a subsample of the waste (25 gram minimum) and proceed to the fourth bullet below.

- If the sample is liquid or multi-phasic, liquid/solid separation is required. This involves the filtration device described in number 4 and is outlined in number 1 above.

- If the waste contains <0.5% dry solids, proceed to the fourth bullet below. If the waste contains >0.5% dry solids, and if particle size reduction of the solid was needed, proceed to the next bullet. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase and proceed to the second bullet below.

- Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in the third diamond bullet under number 1. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve is used to avoid contamination of the sample.

- Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$Weight\ \ of\ \ extraction\ \ \ fluid\ = \frac{20 \times \%\ solids\ \times weight\ \ of\ \ waste\ \ \ filtered}{100}$$

Check the extraction fluid for impurities and the pH prior to use. If impurities are found or the pH is not within the above specifications, the fluid must be discarded and fresh extraction fluid prepared.

Slowly add this amount of appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (Teflon tape can be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature must be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure can build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste can evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle can be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

- Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter. For final filtration of the TCLP/SPLP extract, the glass fiber filter can be changed, if necessary, to facilitate filtration.

- Prepare the TCLP/SPLP extract as follows:
  - If the waste contained no initial liquid phase, the filtered liquid material obtained from tumbling is defined as the TCLP/SPLP extract.
  - If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from tumbling with the initial liquid phase of the waste obtained in number 1. This combined liquid is defined as the TCLP/SPLP extract.
  - If the initial liquid phase of the waste, as obtained from number 1, is not compatible with the filtered liquid resulting from tumbling, do not combine these liquids. Analyze these liquids separately.

- Following collection of the TCLP/SPLP extract, the pH of the extract must be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2.

All other aliquots must be stored under refrigeration (4 ± 2°C) until analyzed. The TCLP/SPLP extract must be prepared and analyzed according to appropriate analytical methods.

NOTE: If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses must not be acidified and the extract must be analyzed as soon as possible.

3. Procedure When Volatiles are Involved.

Use the ZHE device to obtain TCLP/SPLP extract for analysis of volatile compounds only.

The ZHE device has approximately a 500 mL internal capacity. The ZHE can accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid can be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Repeated filling of the ZHE is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials must be done when cold (4 °C) to minimize loss of volatiles.

- The containers listed in number 4 are used to move fluid into the pressurized vessel.
- Place the ZHE piston within the body of the ZHE.
- If the waste is 100% solid, weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to the second diamond bullet below.
    - If the waste contains < 5.0% dry solids, the liquid portion of waste, is defined as the TCLP/SPLP extract. Fill a 10 ml syringe with liquid sample and transfer to volatile laboratory. For wastes containing $\geq$ 5.0% dry solids, use the percent solids information obtained in number 1 to determine the optimum sample size to charge into the ZHE. Determine the amount of waste to charge into the ZHE as follows:

$$Weight\ of\ \ waste\ to\ change\ ZHE = \frac{25}{\%\ Solids} \times 100$$

Weigh out a sub sample of the waste of the appropriate size and record the weight.

- If particle size reduction was not required in number 1, proceed to below.

- Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in number 1. Wastes are refrigerated, when possible, to 4 ± 2 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere must be avoided to the extent possible.

NOTE: The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials.

- Quantitatively transfer the 100% solid sample and TCLP/SPLP Extraction Fluid or the entire sample, when sample is between 5 to 100% solid, (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top lid of the device and secure the top flange to the ZHE body. Tighten all ZHE fittings. (gas inlet connector on the bottom/liquid outlet on the top).

NOTE: If possible, weigh the sticky adhereable sample directly into the ZHE.

Attach a gas line to the gas inlet/outlet valve (bottom of ZHE) and, with the liquid inlet/outlet valve (top of ZHE) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. The final pressure inside the ZHE needs to be approximately 15 psi. If the waste is 100% solid, slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to below.

- Attach a TEDLAR bag to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into TEDLAR bag. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the TEDLAR bag.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and can cause premature plugging.

- The material in the ZHE is defined as the solid phase of the waste and the filtrate in the Tedlar bag is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the

material within the filtration device is defined as a solid and is carried through the TCLP/SPLP extraction as a solid.

The liquid phase is stored at 4 ± 2 °C until time of analysis.

♦ Determine the weight of extraction fluid to add to the ZHE as follows:

$$Weight\ of\ extraction\ fluid = \frac{20 \times \%solids \times weight\ of\ waste\ filtered}{100}$$

The following sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. TCLP Extraction fluid #1 is used in all cases for TCLP. SPLP Extraction fluid # 3 is used in all cases for SPLP. Check the extraction fluid for impurities and the pH prior to use. If impurities are found or the pH is not within the above specifications, the fluid must be discarded and fresh extraction fluid prepared.

- To the ZHE, attach a line from the extraction fluid reservoir (i.e., another ZHE vessel containing extraction fluid) to the liquid inlet/outlet valve. The line used must contain fresh extraction fluid and must be pre-flushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.
- After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of extraction fluid. This bleeding must be done quickly and must be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed. Final pressure inside the ZHE needs to be approximately 15 psi.
- Place the ZHE in the rotary agitation apparatus and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature must be maintained at 23 $\pm$ 2 °C during agitation.

♦ Following the 18 $\pm$ 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained,

the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid can be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. If the sample did not have an initial liquid phase, attach a syringe to the liquid valve and collect the filtered sample.

NOTE: An in-line glass fiber filter can be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

- If the original waste contained no initial liquid phase, the filtered liquid material obtained from number 3 is defined as the TCLP/SPLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from number 3 and the initial liquid phase are collectively defined as the TCLP/SPLP extract.

- Following collection of the TCLP/SPLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP/SPLP extract according to the appropriate analytical methods.

- Analyte concentrations in the TCLP/SPLP extract are reported with the levels identified in the appropriate regulations.

8.0 QUALITY CONTROL

A minimum of one blank and one sample duplicate (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

Matrix spikes are added after filtration of the TCLP/SPLP extract and before analyses. Matrix spikes must not be added prior to TCLP/SPLP extraction of the sample.

All quality control measures described in the appropriate analytical methods must be followed.

The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

This SOP strictly follows the guidelines and procedures of SW-846 Methods 1311 and 1312, including the quality control procedures to ensure consistent and reproducible data.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

For the ZHE to be acceptable for use, the piston within the ZHE must be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device must be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP/SPLP analyses and the manufacturer must be contacted. The ZHE must be checked for leaks after every extraction. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer must be contacted.

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing TCLP/SPLP analyses. Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: also referred to as a Laboratory Reagent Blank. An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Percent solids: percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid can be forced out by an applied pressure.

14.0 REFERENCE

DoD Quality Systems Manual Version 4.2, Revision 5 June 2010.

ISO. 2005. *General Requirements for the Competence of Testing and Calibration Laboratories.*

NELAC Standards, Chapters 1–6. June 5, 2003. EPA/600/R-04/003.

USEPA, SW-846 with Update III, Method 1311 Toxicity Characteristic Leaching Procedure, 1998.

USEPA, SW-846, Method 1312 Synthetic Precipitation Leaching Procedure, 1994.

Table 1. Sample Maximum Holding times

Sample Maximum Holding Time (Days)				
Analyses	From: Field collection to TCLP/SPLP Extraction	From TCLP/SPLP extraction until analyses extraction	From extraction to analyses	Total Time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except Mercury	180	NA	180	360

Table 2 TCLP/SPLP Organic Analytes

Analyte List	Compound	CAS Number
Volatiles[1]	Benzene	71-43-2
	Carbon Tetrachloride	56-23-5
	Chlorobenzene	108-90-7
	Chloroform	67-66-3
	1,4-Dichlorobenzene	106-46-7
	1.2-Dichloroethane	107-06-2
	1,1-Dichloroethene	75-35-4
	2-Butanone (MEK)	78-93-3
	Tetrachloroethene	127-18-4
	Trichloroethene	79-01-6
	Vinyl Chloride	75-01-4
Semi-volatiles	o-Cresol	95-48-7
	p,m-Cresol	3/4-Cresol
	Pentachlorophenol	87-86-5
	2,4,5-Trichlorophenol	95-95-4
	2,4,6-Trichlorophenol	88-06-2
	2,4-Dinitrotoluene	121-14-2
	Hexachlorobenzene	118-74-1
	Hexachlorobutadiene	87-68-3
	Hexachloroethane	67-72-1
	Nitrobenzene	98-95-3
	Pyridine	110-86-1
Herbicides	2,4-D	94-75-7
	2,4,5-TP (Silvex)	93-72-1
Pesticides	Chlordane	57-74-9
	Endrin	72-20-8
	Heptachlor	76-44-8
	Lindane	58-89-9
	Methoxychlor	72-43-5
	Toxaphene	8001-35-2
RCRA 8 Metals	Arsenic	7440-38-2
	Barium	7440-39-3
	Cadmium	7440-43-9
	Chromium	7440-47-3
	Lead	7439-92-1
	Mercury	7439-97-6
	Selenium	7782-49-2
	Silver	7440-22-4

1 When testing for volatile analytes, the zero headspace extractor must be used.

Analysis following TCLP extraction is not limited to the analytes listed above; other analytes can be analyzed following TCLP extraction, with prior laboratory approval.

Table 3: Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	5-vessel (5VRE)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Table 4: Zero-Headspace Extractor Vessels[2]

Company	Location	Model No.
Lars Lande Manufacturing[3]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device

[2] Any device that meets the specifications listed in Section 4.0 of the method is suitable.

[3] This device uses a 110 mm filter.

Table 5: Filter Holders[4]

Company	Location	Model/Catalogue No.	Size
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[4] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 6: Suitable Filter Media[5]

Company	Location	Model	Pore Size (µm)
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7

[5] Any filter that meets the specifications in Section 4.0 of the Method is suitable.

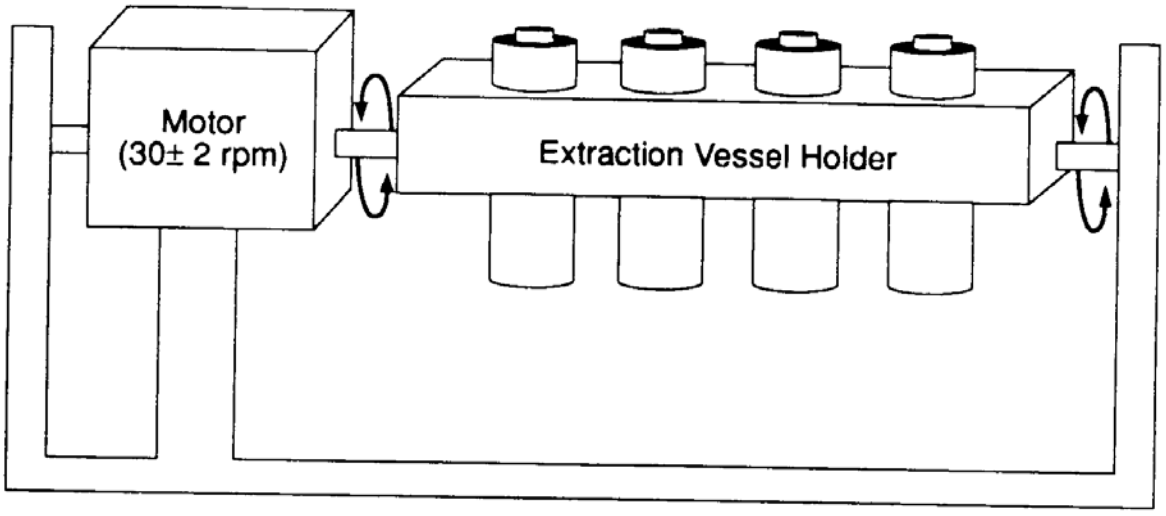


Figure 1. Rotary Agitation Apparatus

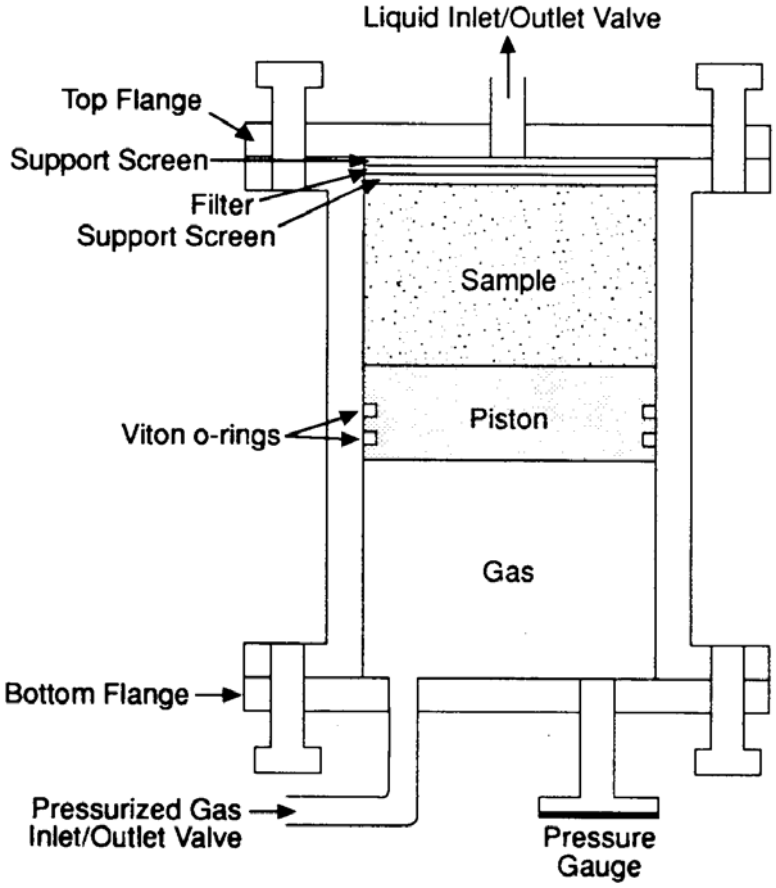
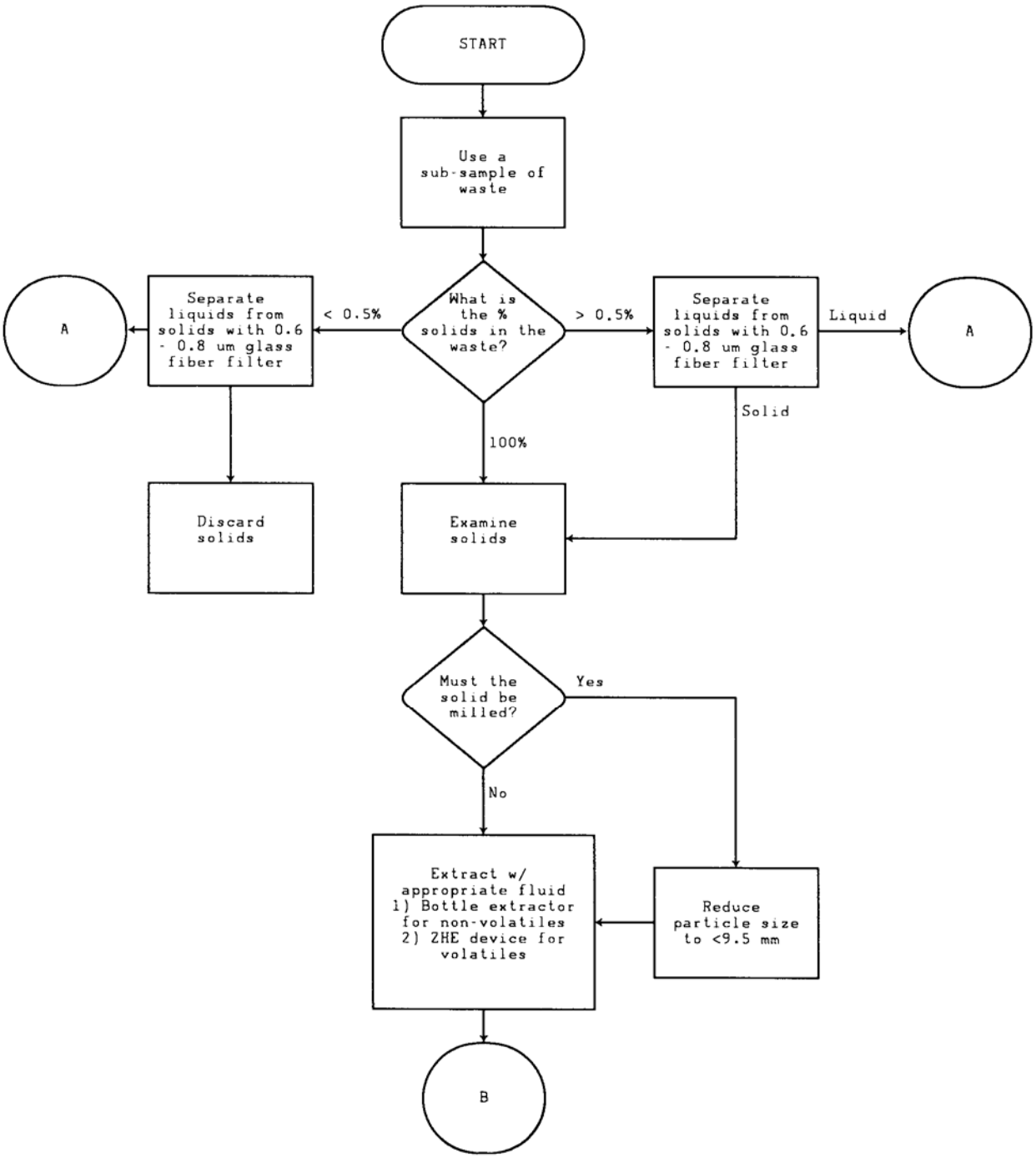


Figure 2. Zero-Headspace Extractor (ZHE)

Figure 3: TCLP/SPLP FLOW DIAGRAM



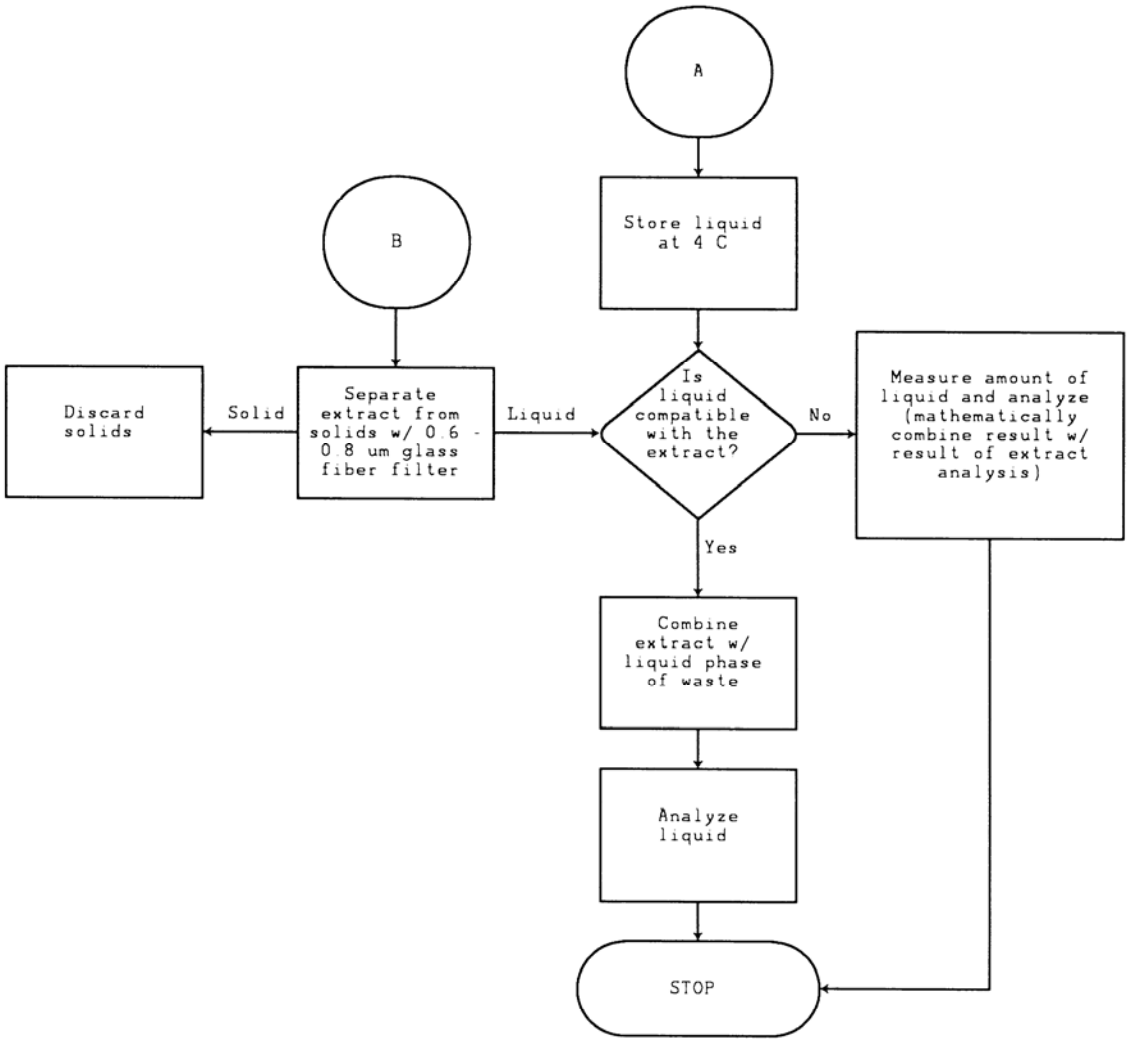

A
B
Store liquid at 4 C
Is liquid compatible with the extract?
No
Measure amount of liquid and analyze (mathematically combine result w/ result of extract analysis)
Yes
Liquid
Separate extract from solids w/ 0.6 - 0.8 um glass fiber filter
Solid
Discard solids
Combine extract w/ liquid phase of waste
Analyze liquid
STOP

Figure 4: TCLP/SPLP Bench Sheet

Merit # : S_____ Rush____ Analyst: _____ Date: _____/_____/_____

Sample Type: -Soil -Sludge -Ind.Solid -Oil -Slurry -Liquid -Wood -Concrete -Oily Waste

Color: -Black -Brown -Gray -White -Clear Other _____

Room Temperature: _____ ^{o}C - TCLP - SPLP - Formaldehyde

- Full extraction - Semi-vol Only - Metals Only | - Tumblers @ 30 RPM

TCLP/SPLP Prep

LIMITED SAMPLE

_____g Solid and Filter
\- _____g Filter weight
= _____g Solid (*S*)
\+ _____g Liquid (*L*)
= _____g Total Sample used (*TotS*)

% Solid: $\frac{S}{TotS} * 100 =$ _____

_____g Solid used * 20 = _____ml Solution

_____ ml Solution used
\+ _____ ml Liquid (*L*)
= _____ Final Volume

- Sample unable to be filtered
% Solid = 100 %

\- 100 g Solid * 20 = 2,000 ml Solution
\- _____ g Solid * 20 = _____ ml Solution

Final Volume: - 2,000 ml or - _____ ml

- Sample is less than 0.5%

Considered a liquid, no extraction needed

pH meter Calibration date: ____/____/____
*see pH benchbook for calibration information for this day

Initial pH of sample: _____ > 5 _____ < 5
Acid-Heat[1] pH: _____ > 5 _____ < 5

Extraction Fluid pH: _____ Solution #1[2]
_____ Solution #2[3]
_____ Acid Leach #1[4]
_____ Acid Leach #2[5]

Time in: _____ : _____ Time out: _____ : _____ Final pH: _____

ZHE Prep

% Solid: _____

Sample Wt: $\frac{25}{\%\ Solid} * 100 =$ _____

Wt of extraction fluid: $\frac{sample\ wt * 20 * \%\ solid}{100} =$ _____

- % Solid: 100%
- Sample Wt: 25 g
- ZHE Fluid 500 g

- Sample is less than 5.0%

Considered a liquid, no extraction needed

pH meter Calibration date: ____/____/____

Extraction Fluid pH: _____ Solution #1[2]
_____ Acid Leach #3[6]

Time in: _____ : _____ Time out: _____ : _____

Notes:

1 - Add 3.5ml 1N HCL, cover, and heat to 50°C, hold temp for 10 minutes, cool to room temp
2 -Solution #1, 5.7ml Acetic Acid + 6.4ml NaOH sol. to 1L of DI water, pH: 4.93 +/- 0.05
3 -Solution #2, 5.7ml Acetic Acid to 1L of DI water, pH: 2.88 +/- 0.05
4 -Acid Leach #1, Sulfuric/Nitric Acid mix to DI water, pH: 4.20 +/- 0.05 (East of Mississippi River)
5 -Acid Leach #2, Sulfuric/Nitric Acid mix to DI water, pH: 4.00 +/- 0.05 (West of Mississippi River)
6 -Acid Leach #3, DI water (for volatile ZHE samples only)

TCLP/Lot #: _____/_____
TCLP/Lot #: _____
TCLP/Lot #: _____
TCLP/Lot #: _____

STANDARD OPERATING PROCEDURE

MICROWAVE EXTRACTION FOR PCBS/PESTICIDES USEPA METHOD 3546

APPROVALS:

Barbara Ball

02/13/19

QA Officer Date

02/13/19

Technical Director Date

Number	Description of Change	Date
001	Emergency SOP Amendment	02/13/19
002		
003		
004		
005		
006		
007		
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

This SOP is used for extracting polychlorinated biphenyls (PCBs) and pesticide organic compounds from solids such as soils, sludges, wipes and wastes. The microwave process ensures intimate contact of the sample matrix with the extraction solvent. The PCB extracts are cleaned up prior to analysis. These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

For most samples, 1g - 30g of sample (depending on the matrix; typically 0.3g for oils and 20g for soils) or wipe (100 cm^2) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Add acetone/hexane (1:1) and extract by microwave. The extract is separated from the sample by centrifugation or through a filter paper. The extract is separated from the sample and concentrated. The extract is ready for cleanup and analysis. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. Degradation of PCBs, as well as more complex matrix (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

Apparatus for grinding/crushing solid waste samples (i.e. drill press or hammer).

Zymark Evaporation Station.

Evaporation tubes.

Water bath - Heated, capable of temperature control (± 5ºC).

Microwave that applies heat at a wattage of 300, 600, 1200

Constant temperature reading using infrared detector and a fiber optic probe to monitor temperature and adjust power accordingly.

Pressure vessel

Disposable glass tube liners

Balance - capable of accurately weighing to the nearest 0.01 g.

Vials – 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.

Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

Tongue depressors, disposable.

Drying column - 50ml Pyrex chromatographic column with Pyrex glass wool at bottom.

Syringe - 5-mL NIST Certified.

Beakers – 250 ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

250 mL Erlenmeyer flasks.

Pipettors.

4 oz glass sample bottles

100 cm^2 wipe

100 cm^2 wipe template

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades must be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

Deionized (DI) water.

Sodium sulfate (granular, anhydrous), Na_2SO_4. (Heated to 400 ºC for 4 hours or precleaned with Methylene Chloride)

Extraction - All solvents must be pesticide quality or equivalent.

- Methylene chloride, CH_2Cl_2, boiling point 49°C
- Hexane, C_6H_{14}, boiling point 68.7°C
- Ethyl Ether (6%)
- Acetone
- Nonchromix used when contamination is detected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All soil samples for the analysis of Pesticides and PCBs must be stored in non-preserved glass containers only. Approximately 0.3g to 30g (depending on the matrix) of sample is needed for extraction. Wipe samples for PCB analysis must be collected using a 100 cm^2 wipe moistened with Hexane and wiped over a sample area of 100 cm^2 using wipe template. Wipe samples are stored in non-preserved glass containers. Refrigerate at $4^o \pm 2°C$. Holding Time for solid samples is 14 days from collection to extraction and 40 days after extraction until analysis.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP #GEN-002.

3. Sample handling

   - ♦ Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

   - ♦ Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

   - ♦ Solid waste samples amenable to grinding - Drill or hammer until uniform matrix is achieved.

   - ♦ Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.

4. Extraction method

   - Weigh approximately 0.3 - 30 g of sample (depending on the matrix) into a disposable glass tube. Typically, on a standard soil, 20 grams of sample is used. Record the weight to the nearest 0.1 g.

   - Add 1.0 ml of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.

- For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution.

    - Note: Add surrogates and matrix spiking compounds to the sample aliquot prior to mixing the sample with the sodium sulfate drying agent. Spiking the sample first increases the contact time of the spiked compounds and the actual sample matrix. It should also lead to better mixing of the spiking solution with the sample when the sodium sulfate and sample are mixed to the point of free-flowing.

- Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate can be added. After addition of sodium sulfate, the sample must be free flowing.

- Add 25 ml of Acetone/Hexane (1:1) to the disposable glass tube.
- Place the tube in a pressure vessel and close cap to manufactures' specifications.
- Run heating program to bring samples up to 100°C in 15 minutes.
- Hold samples at 100°C for 15 minutes.
- Allow samples to cool to room temperature before opening pressure vessel.
- Decant through a conical gravity filter (Whatman No. 41 filter paper or equivalent) and sodium sulfate to catch any excess water into an evaporation tube.
-

5. Wipe samples

    - ♦ Take 4 oz container containing wipe.
    - ♦ Add 1.0 ml of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.
    - ♦ For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution.
    - ♦ Add 60 ml of Acetone/Hexane (1:1) to the 4 oz container.

- Shake 4 oz container and let stand for a few minutes (~5 minutes).Pour sample through sodium sulfate into evaporation tube.

- Repeat the extraction two more times with an additional 60 ml portion of acetone/hexane (1:1).

6. Evaporation method

- Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath @ 48ºC ± 2°C, 29 psi, until 0.5 ml final volume.

- Transfer the sample extract to a 4 ml vial rinse evaporation tube with 0.5 ml Hexane. Adjust up to 1 ml final volume.

- Final 1 ml adjustment: if the transfer is greater than 1 ml, use the compressed air to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.

    - The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.

- Follow with clean–up procedures as appropriate for PCB analysis. See Document # ORL-002 for details.

    - Sulfuric Acid Clean-up
    - Sulfur Clean-up
    - Alumina Column Clean-up.

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch there must be a blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples must be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample amount to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.03 mg/l.

The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike must be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.5 ppm.

The MS/MSD and LCS spikes contain a mixture of Pesticides. This spike must be prepared at a concentration at or below the medium level of the Pesticide curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.1 ppm.

New lot blanks are analyzed to ensure the purity of the materials and reagents.

For DoD projects, the MS/MSD and LCS spike solution must contain ALL target compounds.

All pertinent information is entered into an extraction bench sheet (Figure 1).

Note: The working standards are prepared every six months or when evidence of bias or trends are observed to show that the standards need to be replaced.

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in SOPs #ORL-001 and #ORL-002. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances.

Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.0, July 2013.

USEPA, SW-846, Revision 0, Method 3546.

Figure 1: PCB/Pesticide Extraction Bench Sheet

Acetone_____
Hexane_____
Ether/Hexane_____
Na_2SO_4 _____
H_2SO_4_____
SSD#_____
PCB MS ID#_____ Pest MS ID#_____

PCB/Pesticide Extraction
Method 3546 (Microwave)

Analyst _____
Date _____
Time Started _____
Time Ended _____
Prep Batch ID#_____
Balance ID#_____

#	Merit #	Matrix	Sample Wt. (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Alumina Cleanup	Dioxin Cleanup	Turbo Vap ID	Notes
Initial Q.C.	BLANK			Acetone/Hexane								
	LCS											
	LCSD											
	MS								☐	☐		
	MSD								☐	☐		
1									☐	☐		
2									☐	☐		
3									☐	☐		
4									☐	☐		
5									☐	☐		
6									☐	☐		
7									☐	☐		
8									☐	☐		
9									☐	☐		
10									☐	☐		
11									☐	☐		
12									☐	☐		
13									☐	☐		
14									☐	☐		
15									☐	☐		
16									☐	☐		
17									☐	☐		
18									☐	☐		
19									☐	☐		
20									☐	☐		

Reviewed by: _____ On: _____ Prepared by: Merit Laboratories, Inc.

EXT-F12 Effective Date 4/10/2018

STANDARD OPERATING PROCEDURE

MICROWAVE EXTRACTION FOR BNAS/PNAS/DRO EPA METHOD 3546

APPROVALS:

Barbara Ball

02/13/19

QA Officer Date

Maya Mushaly

02/13/19

Technical Director Date

Number	Description of Change	Date
001	Emergency Amendment Form	02/13/19
002		
003		
004		
005		
006		
007		
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

This SOP is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA), polynuclear aromatic hydrocarbon (PNA) and diesel range organics (DRO) organic compounds from solids such as soils, sludges, and wastes. The microwave process ensures intimate contact of the sample matrix with the extraction solvent. These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

For most of samples, 0.5g - 30g sample (depending on the matrix; 30g is typical for a soil) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Extract with methylene chloride/acetone (1:1) mixture using microwave. The extract is separated from the sample and concentrated. Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate. Degradation of sample matrix (i.e. oil, tar, sulfur, etc.), can interfere with the “clarity” of the chromatograms.

4.0 APPARATUS AND MATERIALS

Apparatus for grinding/crushing solid waste samples (i.e. drill press or hammer).

Zymark Evaporation Station.

Evaporation tubes.

Water bath - Heated, capable of temperature control (± 5ºC).

Microwave that applies heat at a wattage of 300, 600, 1200

Constant temperature reading using infrared detector and a fiber optic probe to monitor temperature and adjust power accordingly.

Pressure vessel

Disposable glass tube liners

Balance - capable of accurately weighing to the nearest 0.01 g.

Vials - 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.

Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

Tongue depressors, disposable.

Beakers - 250ml.

Glass funnel.

Filter paper, coarse grade.

Adhesive labels.

Syringe - 5-mL NIST certified.

250mL Erlenmeyer flasks.

Pipettors.

5.0 REAGENTS

Note: Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades can be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents must be stored in glass to prevent the leaching of contaminants from plastic containers.

Sodium sulfate (granular, anhydrous), Na_2SO_4. (Heated to 400 ºC for 4 hours or precleaned with Methylene Chloride)

Extraction - All solvents must be pesticide quality or equivalent.

- Methylene Chloride, CH_2Cl_2.
- Acetone
- Nonchromix, used when contamination is detected.

Surrogate and matrix spiking solutions are prepared as listed in Table 2. The detailed list of compounds for each stock mixture is given in Table 1.

Deionized (DI) Water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All soil samples for the analysis of BNAs/PNAs/DRO are stored in non-preserved glass containers only. Approximately 0.5 to 30 g (depending on the matrix) of sample is needed for extraction. Oils are weighed

out to 0.5 ml. Refrigerate at 4º±2°C. Holding Time for solid samples is 14 days from collection to extraction and 40 days after extraction until analysis.

7.0 PROCEDURE

1. All glassware must be kept immaculate. Glassware must be cleaned as soon as possible after extraction. Glassware washing procedures are found in SOP # GEN-002.

2. Sample handling.

- Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

- Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

- Solid waste samples amenable to grinding - Drill or hammer until uniform matrix is achieved.

- Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.

3. Extraction method

- Weigh approximately 0.5-30 g of sample (depending on the matrix) into a 250-ml beaker. Record the weight to the nearest 0.1 g.

    - The default weight used is 30g for a soil sample.
    - If the sample is a solvent or an oil matrix, approximately 0.5 ml of neat sample is weight out and brought up to 2 ml with solvent put into a 4ml screw cap vial and given to the GC/MS analyst. No extraction is performed due to the exceptionally high chromatographic response of these sample types. These samples are diluted by a factor of 400:1 and analyzed directly (see SOP: ORL-004). The relative response of this base dilution may result in a final analysis of the sample at a higher or lower net dilution.

- a) For BNA extraction: Add 1.0 ml of the BNA surrogate standard solution to all samples, spiked samples, QC samples, and blanks (see Table 2).

  b) For PNA extraction: Add 1.0 ml of the PNA surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 2).

  c) For DRO extraction: Add 1.0 ml of the DRO surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 2).

- For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution (BNA, PNA, or DRO, as appropriate, see Table 2).

  - Note: Add surrogates and matrix spiking compounds to the sample aliquot prior to mixing the sample with the sodium sulfate drying agent. Spiking the sample first increases the contact time of the spiked compounds and the actual sample matrix. It should also lead to better mixing of the spiking solution with the sample when the sodium sulfate and sample are mixed to the point of free-flowing.

- Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with a maximum 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

- Add 25 ml of Acetone/Methylene Chloride (1:1) to the disposable glass tube.

- Place the tube in a pressure vessel and close cap to manufactures' specifications.

- Run heating program to bring samples up to 100°C in 15 minutes.

- Hold samples at 100°C for 15 minutes.

- Allow samples to cool to room temperature before opening pressure vessel.

- Decant through a conical gravity filter (Whatman No. 41 filter paper or equivalent) and sodium sulfate to catch any excess water into an evaporation tube.

5. Evaporation method

- Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath at 47+/2°C, 21 psi, until the extract reaches a 0.5 ml final volume.

- Transfer the sample extract to a 4 ml pre-calibrated vial. Adjust to 1 ml final volume with methylene chloride.

- Final 1 ml adjustment: if the transfer is greater than 1 ml, use compressed air to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.

- After extraction, samples are analyzed by following SOP ORL-004 (SVOCs) or SOP ORL-11 (DRO).

8.0 QUALITY CONTROL

Samples are extracted in batches of 20 samples or less. For every batch, there must be a Blank, LCS, MS, and MSD/DUP depending on the clients' request. All the reagent blanks, matrix spikes, or replicate samples must be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

The Base/Neutral surrogate standard must contain the compounds listed in Table 1. The Acid surrogate standard must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. [the Acid surrogate standard is N/A for the PNA method.] The surrogate standard is prepared according to Table 2.

The Base/Neutral MS/MSD and LCS spikes must contain the compounds listed in Table 1. The Acid MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 2.

The PNA MS/MSD and LCS spikes must contain the compounds listed in Table 1. The concentrations listed are those in the stock spiking solutions. MS/MSD spike must be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 2.

The DRO MS/MSD and LCS spikes contain neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 2.

For DoD projects, the MS/MSD and LCS spike solution must contain ALL target compounds.

New lot blanks are analyzed to ensure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

All pertinent information is entered into an extraction bench sheets (Figure 1 and 2).

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in SOP # ORL-004 and ORL-012. The MDLs and PQLs can be found in Merit's LIMS system are from the most recent detection limit studies.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Methylene chloride is harmful if swallowed, inhaled or absorbed through skin. Methylene chloride affects central nervous system, liver, cardiovascular system, and blood. Also, it can cause irritation to skin, eyes, and respiratory tract. Risk of cancer depends on level and duration of exposure. Vapor may form flammable mixture in atmosphere that contains a high percentage

of oxygen. Sealed containers may rupture when heated. Emits highly toxic fumes of phosgene when heated to decomposition. Decomposes in a flame or hot surface to form toxic gas phosgene and corrosive mists of hydrochloric acid. Carbon dioxide and carbon monoxide may form when heated to decomposition.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Surrogate: an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is

to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.0, July 2013.

USEPA, SW-846, Revision 0, Method 3546.

Table 1: Surrogate/LCS/MS Compounds

Standard Type	Compound	CAS #	Concentration	Supplier
Base/Neutral Surrogate	Nitrobenzene-d5	4165-60-0	5000 ug/ml	RESTEK
	2-Fluorobiphenyl	321-60-8	5000 ug/ml	RESTEK
	p-Terphenyl-d14	1718-51-0	5000 ug/ml	RESTEK
Acid Surrogate	2-Fluorophenol	367-12-4	10000 ug/ml	RESTEK
	Phenol-d6	13127-88-3	10000 ug/ml	RESTEK
	2,4,6-Tribromophenol	118-79-6	10000 ug/ml	RESTEK
Base/Neutral MS/MSD/LCS Spike	Acenaphthene	83-32-9	5000 ug/ml	RESTEK
	1,4-Dichlorobenzene	106-46-7	5000 ug/ml	RESTEK
	2,4-Dinitrotoluene	121-14-2	5000 ug/ml	RESTEK
	N-nitroso-di-n-propylamine	621-64-7	5000 ug/ml	RESTEK
	Pyrene	129-00-0	5000 ug/ml	RESTEK
	1,2,4-Trichlorobenzene	120-82-1	5000 ug/ml	RESTEK
Acid MS/MSD/LCS Spike	4-Chloro-3-methylphenol	59-50-7	10000 ug/ml	RESTEK
	2-Chlorophenol	95-57-8	10000 ug/ml	RESTEK
	4-Nitrophenol	100-02-7	10000 ug/ml	RESTEK
	Pentachlorophenol	87-86-5	10000 ug/ml	RESTEK
	Phenol	108-95-2	10000 ug/ml	RESTEK
PNA MS/MSD/LCS Spike	Naphthalene	91-20-3	2000 ug/ml	RESTEK
	2-Methylnaphthalene	91-57-6	2250 ug/ml	RESTEK
	Acenaphthylene	208-96-8	2000 ug/ml	RESTEK
	Acenaphthene	83-32-9	2000 ug/ml	RESTEK
	Fluorene	86-73-7	2000 ug/ml	RESTEK
	Phenanthrene	85-01-8	2000 ug/ml	RESTEK
	Anthracene	120-12-7	2000 ug/ml	RESTEK
	Fluoranthene	206-44-0	2000 ug/ml	RESTEK
	Pyrene	129-00-0	2000 ug/ml	RESTEK
	Benzo(a)anthracene	56-55-3	2000 ug/ml	RESTEK
	Chrysene	218-01-9	2000 ug/ml	RESTEK
	Benzo(b)fluoranthene	205-99-2	2000 ug/ml	RESTEK
	Benzo(k)fluoranthene	207-08-9	2000 ug/ml	RESTEK
	Benzo(a)pyrene	50-32-8	2000 ug/ml	RESTEK
	Indeno(1,2,3-cd)pyrene	193-39-5	2000 ug/ml	RESTEK
	Dibenzo(ah)anthracene	53-70-3	2000 ug/ml	RESTEK
	Benzo(ghi)perylene	191-24-2	2000 ug/ml	RESTEK

Table 2. Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L:
- 97 ml of Acetone
- 1 ml of 10,000 mg/L Acids surrogate
- 2 ml of 5,000 mg/L B/N surrogate

BNA MS/MSD/LCS Spike:

For 20 ml total solution at 50 mg/L:
- 19.7 ml of Acetone
- 100 ul of 10,000 mg/L Acids spike
- 200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L:
- 98 ml of Acetone
- 2 ml of 5,000 mg/L B/N surrogate

PNA MS/MSD/LCS Spike:

For 20 ml total solution at 50 mg/L:
- 19.1 ml of Acetone
- 500 ul of 2,000 mg/L PNA stock
- 444 ul of 2250 mg/L 2-Methylnapthalene stock

DRO MS/MSD/LCS Spike:

For 20 ml total solution at 1000 mg/L;
- 20.0 ml of Acetone
- 20.0 mg of neat Diesel Fuel (gravimetric preparation)

Figure 1: SVOC Extraction Bench Sheet

Methylene Chloride Lot #: _____ Analyst: _____
Acetone Lot #: _____ Date: _____
Na2SO4 Lot #: _____ SVOC Solid Extraction Log Time Started: _____
SSD #: _____ Method 3546 (Microwave) Time Ended: _____
MS/LCS #: _____ Batch ID#: _____

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Turbo VAP ID	Notes	
Initial Q.C.	BLANK	Sand		Acetone/Methylene Chloride							
	LCS	Sand									
	LCSD	Sand									[ ]
	MS										[ ]
	MSD										
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											

Reviewed by: _____ On: _____ Balance ID: _____ Prepared by: Merit Laboratories, Inc.
EXT-F14 Effective Date 4/11/2018

Figure 2: PNA/DRO Extraction Bench Sheet

Methylene Chloride Lot #: _____ Analyst: _____

Acetone Lot #: _____ Date: _____

Na2SO4 Lot #: _____ PNA/DRO Solid Extraction Log Time Started: _____

SSD #: _____ Method 3546 (Microwave) Time Ended: _____

MS/LCS #: _____ Batch ID#: _____

#	Merit #	Matrix	Sample Weight (g)	Solvent	Solvent Vol (ml)	Final Vol (ml)	SSD Vol (ml)	MS Vol (ml)	Turbo VAP ID	Notes
Initial Q.C.	BLANK	Sand		Acetone/Methylene Chloride						
	LCS	Sand								
	LCSD	Sand								[ ]
	MS									[ ]
	MSD									
1										
2										
3										
4										
5										
6										
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Reviewed by: _____ On: _____ Balance ID: _____ Prepared by: Merit Laboratories, Inc.

EXT-F13 Effective Date 4/11/2018

STANDARD OPERATING PROCEDURE

PYRIDINE-PYRAZALONE COLORIMETRIC METHOD FOR ANALYZING CYANIDE USING THE DR/4000 HACH SPECTROPHOTOMETER METHOD EPA 335.4 AND STANDARD METHOD 4500-CN-E

APPROVALS:

Barbara Ball

01/10/18

QA Officer Date

Mayur Mushahary

01/10/18

Technical Director Date

Number	Description of Change	Date
001-009	Previous changes were not documented	
010	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
011	Updated MS QC Criteria and Cyanide Standard Disposal information	7/25/12
012	Linear Calibration Range Check added	8/19/14
013	Updated to comply with DoD QSM 5.0 standards.	03/10/16
014	Updated to comply with DoD QSM 5.1 standards.	01/10/18
015		
016		
017		
018		
019		
020		

1.0 SCOPE AND APPLICATION

This SOP determines cyanide in drinking, surface, ground, and sea water; domestic and industrial wastes and solids using a colorimetric method after full distillation using the Lachat micro-dist system. The reporting limit for water samples using a double distillation is 0.005 mg/l and 0.5 mg/kg for solids.

2.0 SUMMARY OF METHOD

Cyanide is analyzed after distillation using the DR-4000 Hach spectrophotometer, Method Code 8027. Three separate reagents are added to a distilled neutralized sample. The pyridine-pyrazolone indicator that is used gives an intense blue color if cyanide is present (starts out as pink then goes blue). Reaction time after adding reagents is 30 minutes.

3.0 INTERFERENCES

If the display flashes 0.200, the upper limit of the pre-calibrated range has been exceeded and a sample dilution is needed. A flashing value of –0.020 indicates the sample has a negative absorbance value relative to the blank. This negative value indicates a possible interference in the water sample or a procedure error by the user. Small negative values probably are due to small variations between sample cells or amounts of reagent added and should be treated as a concentration value of zero. Delaying the addition of the CyaniVer 5 Reagent Pillow for more than 0.5minutes after addition of CyaniVer 4 will give lower test results. It is not essential that the entire CyaniVer 4 reagent be dissolved before proceeding with the addition of CyaniVer 5. Too much chlorine will cause a milky white precipitate after addition of CyaniVer 5. See CN- Lachat Distillation SOP IRL-013 for pre-distillation treatment of samples.

4.0 APPARATUS AND MATERIALS

DR/4000 Hach Spectrophotometer (wavelength knob to 612 nm)
10 mL sample cells
10 mL sample cells adapter
25 mL clear glass vials

5.0 REAGENTS

CyaniVer 3 powder pillows for 10 mL sample. (Contains: Sodium Phosphate Dibasic, Halane, & Potassium Phosphate, Monobasic). Shelf life for CyaniVer 3, 4 & 5 is 5 years at 10-30 degrees C.

CyaniVer 4 powder pillows for 10 ml sample. (Contains: Ascorbic Acid, Pyridine-3-nitrophthalic acid, & Sodium Sulfate).

CyaniVer 5 powder pillows for 10ml sample. (Contains: Potassium Phosphate, Monobasic, Sodium Sulfate, 3-Methyl-1-phenyl-2pyrazolin-5-one, & Sodium Phosphate Dibasic).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Water samples are collected in plastic containers and preserved with NaOH to a pH ≥ 12 and cooled to 4 ±2 °C. Soil samples are collected in a non preserved glass container and cooled to 4 ±2 °C. Holding time for cyanide is 14 days from the time of sampling.

7.0 PROCEDURE

1. Allow for DR/4000 warm-up (approximately 15 min).

2. All samples including QC samples having been distilled, neutralized, and brought to final volume (10 mL) in the 15ml glass vials are now ready to be analyzed. It is possible to do two samples at a time. Start with method blank, which is used to zero instrument.

3. Add the contents of one CyaniVer 3 reagent pillow to each sample vial, stopper and shake for 0.5 minutes—press: 0.5 timer. When timer goes off, reset timer for 0.5 and allow samples to stand undisturbed.

4. After the timer sounds, add the contents of a CyaniVer 4 reagent pillow to each sample re-stopper and shake for 0.1 minute--press timer. When timer sounds, immediately add CyaniVer 5 reagent pillow and shake vigorously to dissolve. Set timer for 30 minutes. Repeat procedure for all the samples. *See 3.0*.

5. The cyanide calibration curve needs to be entered in the DR/4000.

6. Select user program **175**; calibration curve & wavelength 612 nm are then auto selected. Place the 10 mL vial adapters into cell compartment making sure openings are aligned with light path in compartment.

7. When 30-minute reaction period is over pour method blank into 10ml sample cell, cap the cell and place into cell compartment with letter on cell facing the front.

8. Press: **Zero** Absorbance so displays reads 0.000. Enter the entire calibration curve.

9. Press 0.000 Std 1, which is Absorbance, then Press 0.000 Std 2, which is the corresponding concentration to that Absorbance.

10. Repeat this procedure with the 6 calibration distillates of the curve. Once the curve is entered, press: **Best Fit Calculate** and then press: **Conc**. The Cyanide Calibration curve is now ready. A calibration coefficient of 0.999 or greater is required for the working standard curve. If less than 0.999; rerun standards.

11. Pour samples into 10ml cell and place into cell compartment and read samples mg CN-/L directly from display. Record reading in Cyanide bench book.

12. Calculations :

Calculate cyanide in sample as follows:

$$mg\,CN^{-} = \frac{mg}{L}\ from display\ x \frac{Final Volume(ml)}{Sample Volume or Weight(ml/g)}$$

Example = spectro reading 0.041 mg/L x 10 mL/5 mL = 0.082 mg/L

Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 and Table 2 for DoD projects. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

Linear Calibration Range Check (LCR) – The linear calibration check needs to be verified every 6 months with minimum of a blank and three concentrations. The verification curve must not exceed 10% of the initial curve. If the verification exceeds 10% of the initial curve, a new full calibration curve must be redone.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.). Method Detection Limit studies are performed every six months.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

- Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Cyanide standards must be disposed of using Potassium Permanganate ($KMnO_4$) as an oxidizing agent. For each kilogram of cyanide to be oxidized, 4.5 kg of $KMnO_4$ is required. To enhance the cyanide oxidation rate a catalytic amount of Cu(II) salt is used.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Initial Calibration (ICAL): set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Lachat Instrument Micro-Dist Distillation System Reference and Methods Manual.

USEPA, Method for the Chemical Analysis of Water and Wastes; Method 335.4.

Standard Methods for Examination of Water and Wastewaters, Twentieth Edition; 4500 CN-E

Table 1. Quality Control Items, Frequency, and Corrective Action

QC Items	Frequency	Acceptance Criteria	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	One per batch	<RL or 1/10 Regulatory limit	Remove contamination and re-digest samples.	Notify client. Flag data.
Laboratory Control Sample (LCS)	One for every 10 samples	90%-110%	Re-digest the sample set.	Notify client. Flag data.
Continuing Calibration Verification (CCV)	One for every 10 samples	90% - 110%	All samples bracketed by CCV outside the acceptable control limits must be re-digested and re-analyzed.	Notify client. Flag data.
Matrix Duplicate	1/ 20 samples 1/10 samples for drinking water samples	RPD<20%	Re-digest samples and QC.	Notify client. Flag data.
Matrix Spike	1/ 20 samples 1/10 samples for drinking water samples	90%-110%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	One for every 20 samples for Level 3 and DoD	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Dilution & Rerun	If result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.
Linear Calibration Range Check	One blank and 3 standards every 6 months	±10%	Re-calibration	Re-calibration

Table 2. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL)	Daily ICAL prior to sample analysis.	$R^2 \geq 0.99$.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum three standards and a reagent blank. No samples shall be analyzed until ICAL has passed.
Distillation Verification	Once after each ICAL, with two distilled ICAL standards; prior to sample analysis. Not required if all ICAL standards are distilled.	Within ± 10% of nondistilled std value.	Correct problem, rerun distilled standards or repeat ICAL.	Flagging is not appropriate.	One high and one low distilled ICAL standard. No samples shall be analyzed until distillation technique has been verified.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	Within ± 10% of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for cyanide in all samples since the last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Method Blank (MB)	One per preparatory batch.	The absolute values of all analytes must be <1/2 LOQ or 1/10th the amount measured in any sample.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field sample processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all cyanide results in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Non-detects associated with positive blank infractions may be reported. Sample results > 10X the LOQ associated with negative blanks may be reported. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV.	The absolute values of all analytes must be <1/2 LOQ or 1/10th the amount measured in any sample.	ICB: Correct problem and repeat ICV/ICB analysis. If that fails, rerun ICAL. All samples following the last acceptable	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. Non-detects associated with positive blank infractions may be reported.

			Calibration Blank must be reanalyzed. CCBs may not be reanalyzed without reanalysis of the associated samples and CCV(s).		Sample results > 10X the LOQ associated with negative blanks may be reported. For CCB, failures due to carryover may not require an ICAL.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to the source of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) and Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes $\leq 20\%$ (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits

Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
57-12-15	Cyanide	76	120

Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
57-12-15	Cyanide	83	116

Figure 1: Cyanide Benchsheet

Analysis:*Total Cyanide* **Batch ID:_____** ***CAL ID#*** _____
Analyst:_____ **Method #**335.4/ 8027(Hach) **Program #**175HACH DR/4000 Spec.
Date Run:_____ **Detection Limit:**0.005 mg/l **Wavelength**612 nm

ID	Merit #	Dilution	(mg/l) Conc.	ABS	%S	(mg/l) Result	(mg/l) Spike	%Rec	STD ID / Tag	(Run) Time
	Blank	10/10								
	Blank Spike	10/0.5ml 1ppm					0.050			
	Control								ERA	
	LCS	10/1.0ml 1ppm					0.100			

(Manufac. Date)

Notes:**Lachat micro-distillation / sample prep. ; double distillation for lower detection limit / Dist. tubes**

User fill ID# _____

Releasing Solution ID_____CyaniVer3 lot_____ **CyaniVer4 lot _____** **CyaniVer5 lot _____**

Peer Review: _____ **CN- Stock ID_____** **Chlorine chk _____**

Beginning Distillation block temp: _____ **End Distillation block temp:_____**

Distillation time:_____ **Balance ID:_____**

STANDARD OPERATING PROCEDURE

LACHATCN SOP FOR TOTAL CYANIDE DISTILLATION (LACHAT MICRO-DIST)
METHOD EPA 335.4 AND STANDARD METHOD 4500-CN-E

APPROVALS:

Barbara Ball

01/10/18

QA Officer Date

Maya Mushaly

01/10/18

Technical Director Date

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Number	Description of Change	Date
001-004	Previous changes were not documented	
005	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
006	2012 Internal Audit Findings	6/12/12
007	Updated MS QC Criteria and Cyanide Standard Disposal information	7/26/12
008	Updated to comply with DoD QSM 5.0 standards.	03/10/16
009	Updated to comply with DoD QSM 5.1 standards.	01/10/18
010		
011		
012		
013		
014		
015		

1.0 SCOPE AND APPLICATION

This method is applicable to drinking, surface, groundwaters, treated mixed wastewater, soils, sludges, and some industrial process waters. The method is suitable for distilling samples containing from 0.002 to 5.0 mg Free and Combined Cyanide / L with the Micro-Dist distillation apparatus.

2.0 SUMMARY OF THE METHOD

This SOP is a procedure for cleanup of liquid and soil samples for the determination of total cyanide. The Micro-Dist system was developed for the analytical distillation of samples which are largely aqueous. The system strips analytical distillation down to its bare essentials. The sample is pipetted into a sample tube and sealed to a collector tube. This assembly is placed in a special heating block which fits very tightly, allowing the poorly-conducting polypropylene to be heated rapidly yet locally. As the sample boils, its vapors rise within the tube and pass through a hydrophobic, porous membrane. The vapors condense above the membrane to form droplets, which pool over the membrane, but cannot pass back through it. The short, vertical path of distillation is possible because of the physical separation of distilling sample and distillate by the hydrophobic membrane. See SOP for Total Cyanide Pyridine-Pyrazalone Colorimetric for testing the distillate for Total Cyanide.

3.0 INTERFERENCES

Oxidizing agents can destroy cyanides during storage.
Sulfide can complex with cyanide in sample or distillate.
Fatty acids cause interference during distillation.
Carbonate causes interference during distillation.
Aldehydes cause interference during distillation.
Glucose/sugars cause interference during distillation.
Sulfur-containing compound causes interference during distillation by forming free sulfide that is captured in distillate.

4.0 APPARATUS AND MATERIALS

Micro-Dist Heating Block, 120 VAC transformer.
Blue sample tube rack, 72 tube capacity.
White Collector tube rack, 40 tube capacity.
A pair of heat-resistant gloves.
50 ml polyethylene centrifuge tubes.
Red Micro-Dist assembly press.
Pipettor.

100 ml Pyrex beaker.

Cyanide-1 Collector tubes with sample tubes (0.25 M NaOH) Shelf life / 1 yr. (1.5 ml 1N NaOH and 0.5 ml Deionized water added to each collector tube; membrane added; capped; ready for distillation)

Volumetric flasks

Thermometer

15 ml glass vials for colorimetric analysis.

5.0 REAGENTS

Deionized (DI) water.

CN- Releasing Solution, $MgCl_2$ / H_2SO_4: **Make up in hood.** In 100 ml Pyrex beaker, Dissolve 8.05 g of $MgCl_2$ in 27.7 ml of DI water and add slowly while mixing 19 ml of Concentrated H_2SO_4. Let cool. Pour into 125 ml amber glass container. *See CN- Releasing Solution Prep Log*. Shelf life is 2 months. $MgCl_2$ / Hach H_2SO_4 / VWRBrand.

Sulfamic Acid, NH_2SO_3H. / Hach Shelf life 5 years.

2.5 N HCl (250/52 ml concentrated HCl) *See Wet Chem Reagent Prep Log*. Shelf life 1 year.

1.0 N NaOH (200/8 g NaOH pellets). *See Wet Chem Reagent Prep Log*. Shelf life 1 year.

Phenolphthalein - Weigh 0.125 g of phenolphthalein into a 25 ml volumetric flask, pipette 12.5 ml DI & 12.5 ml Isopropyl alcohol into flask and dissolve. *See Wet Chem Reagent Prep Log*. Shelf life 1 year.

Potassium iodide – starch test paper. Hach.

Acetate buffer solution, pH 4.6; Hach shelf life 1 year.

Sodium Thiosulfate Pentahydrate ACS grade Hach Shelf life 5 years.

Zinc Acetate 2 N. Hach Shelf life 2 years.

Lead acetate test paper. Hach.

6.0 SAMPLE HANDLING AND PRESERVATION

Liquid samples must be collected in polyethylene containers preserved with NaOH (pH >12) and refrigerated at 4 ± 2ºC. Soil samples are collected in non-preserved glass containers and refrigerated at 4 ± 2ºC. Samples must be run within 14 days of collection.

7.0 PROCEDURE

1. Preliminary Treatment of Sample
    I. Oxidizing agents, like chlorine, decompose most cyanide. Test sample by placing a drop on a strip of potassium iodide paper previously moistened with acetate buffer

solution, pH 4.6. If paper turns blue, add sodium thiosulfate, adding less than 0.1g $Na_2S_2O_3$/L.

II. Oxidized products of sulfide convert CN- to SCN- rapidly, especially at high pH. Test for sulfide by placing a drop of sample on lead acetate test paper previously moistened with acetate buffer solution, pH 4.6. Darkening of the paper indicates presence of sulfide. Add 3 drops of zinc acetate 2N per 100ml sample to settle out sulfide, let settle for 30min. Pour off supernatant into another bottle leaving sulfide precipitate behind. Run supernatant for total cyanide.

III. Sulfamic acid is added in the distillation process to avoid nitrite (NO_2-) interference.

2. Standard & QC Preparation

I. Blanks: Method blank follows the entire procedure including digestion. 5 ml of DI water. Then follow steps 7.5-7.18.

II. LCS (0.1 ppm): Laboratory control sample follows entire procedure including digestion. 5 ml of DI water plus 0.1 ml of 10 ppm of working standard (Working standard: 49.5 ml DI water plus 0.5 ml of stock standards @ 1000 ppm) Then follow steps 7.5-7.18.

III. MS/MSD (0.1 ppm): matrix spike/matrix spike duplicate follows entire procedure including digestion. 5 ml of sample plus 0.1 ml of 10 ppm of working standard (Working standard: 49.5 ml DI water plus 0.5 ml of stock standards @ 1000 ppm) Then follow steps 7.5-7.18.

IV. Prepare a set of six standards ranging from 0.005 – 0.200 mg/l.

i. Prepare Stock Cyanide solution as follows: Dissolve 0.2 g NaOH and 0.251 g KCN in 100 ml DI = 1,000 ppm.

ii. Prepare a 1 ppm working standard: Pipet 0.1 ml into a 100 ml volumetric flask and bring to volume. *See Cyanide Standards Prep Log.*

iii. Prepare a Blank, 0.005, 0.01, 0.02, 0.05, 0.100 & 0.200 mg/l standard solutions for 10 ml final volume.

iv. Distill standards in the same manner as the samples following steps 7.5-7.19.

3. Set dial of distillation block to 120 degrees C. Allow the heater block to warm up. This will take about 40 minutes.

4. Put as many collector tubes into the white rack as you have samples; up to 21 maximum for block. Number tubes from 1 – 21 with a marker. Re-seal the foil pack after removing the tubes if there are any left to avoid evaporation of NaOH solution in tubes.

5. Put as many sample tubes into the blue rack as you have samples, matching up with the number of collector tubes.

6. With sample numbers corresponding to tube numbers recorded on bench sheet begin pipetting 5 ml of liquids into sample tubes. (When distilling solids use 0.1-0.5 g of sample and 3 ml DI water)

7. When all sample tubes are filled with sample for each set, add 2 small crystals of Sulfamic acid into each sample tube. Add, 0.7 ml of releasing solution using an automatic pipettor to sample tube (1 at a time then cap). **Do this in a hood.**

8. Immediately push the uncapped bottom end of corresponding collector tube over the end of the sample tube to start seal. Then place the assembly in the press, putting the sample tube through the hole in the white base. Press down on the handle until the stop ring on the sample tube hits the bottom of the collector tube.

9. Push each tube all the way into the heater block pre-heated to 120 degrees C so that the collector stop ring touches the block.

10. For water samples, set timer and leave in block for 30 minutes. For solids or sludges, set timer and leave in block for 30 minutes.

11. When time is up, put on heat resistant gloves. Remove the first tube from the block and immediately pull off its sample tube by twisting it back-and-forth while pulling down. Dispose of sample tube and hot solution left in it by dropping it into the sink or waste bucket. Place each collector tube into the white rack.

12. Allow tubes to cool for about 10 minutes at least.

13. For each collector tube, hold the tube horizontally and rinse its walls with the distillate in order to homogenize it. Then, slowly roll the distillate around in the tube to gather all droplets clinging to the tube walls into the bulk of the distillate. Slowly return collector tube to an upright position and lightly tap tube to get all distillate to bottom of tube.

14. Break away the top section of the collector tube by pulling hard towards yourself to break, then twisting and tearing off the top.

15. Gently pour distillate into 15ml glass vial. Keep sample below 10ml, so sample can be neutralized before analysis.

16. Add 1 drop of Phenolpthlalein, sample should turn pink (pH > 8.3)

17. Add 2.5N HCl drop wise to sample until it just goes clear. A 0.5N HCl solution may be used when color change is close to keep from going too acidic. Sample pH should around 7 before reagents are added.

18. Bring all samples to 10 ml final volume using calibrated 15ml glass vial.

19. Samples are now ready for cyanide analysis using Merit's SOP #033354.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

This method is evaluated by testing a laboratory control sample and duplicate samples.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention be paid (but not limited) to:

a. Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in

contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

b. Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Cyanide standards must be disposed of using Potassium Permanganate ($KMnO_4$) as an oxidizing agent. For each kilogram of cyanide to be oxidized, 4.5 kg of $KMnO_4$ is required. To enhance the cyanide oxidation rate a catalytic amount of Cu(II) salt is used.

13.0 DEFINITIONS

Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): A Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: Aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Initial Calibration (ICAL): Set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Lachat Instrument Micro-Dist Distillation System Reference and Methods Manual.

USEPA, Method for the Chemical Analysis of Water and Wastes; Method 335.4.

USEPA, *SW-846*, Revision 3; Method 9010B.

USEPA, *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Method 4500-CN-E, Cyanide, Residual, for Cyanides Amenable to Chlorination after Distillation, Colorimetric.

Table 1. Quality Control Items Frequency, and Corrective Action

QC Items	**Frequency**	**Acceptance Criteria**	**Corrective Action**	**Corrective Action after Reanalyzing**
Method (preparation) Blank	One per batch	<RL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	One for every 10 samples	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	1/ 20 samples 1/10 samples for drinking water samples	RPD<20%	Rerun entire set	Notify client. Flag data.
Matrix Spike	1/ 20 samples 1/10 samples for drinking water samples	90%-110%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	One for every 20 samples for Level 3 and DoD	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Dilution & Rerun	If result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.

Table 2. Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL)	Daily ICAL prior to sample analysis.	$R^2 \geq 0.99$.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum three standards and a reagent blank. No samples shall be analyzed until ICAL has passed.
Distillation Verification	Once after each ICAL, with two distilled ICAL standards; prior to sample analysis. Not required if all ICAL standards are distilled.	Within ± 10% of nondistilled std value.	Correct problem, rerun distilled standards or repeat ICAL.	Flagging is not appropriate.	One high and one low distilled ICAL standard. No samples shall be analyzed until distillation technique has been verified.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	Within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	Within ± 10% of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since last successful CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for cyanide in all samples since the last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Method Blank (MB)	One per preparatory batch.	The absolute values of all analytes must be <1/2 LOQ or $1/10^{th}$ the amount measured in any sample.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field sample processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all cyanide results in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Non-detects associated with positive blank infractions may be reported. Sample results > 10X the LOQ associated with negative blanks may be reported. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV.	The absolute values of all analytes must be <1/2 LOQ or $1/10^{th}$ the amount measured in any sample.	ICB: Correct problem and repeat ICV/ICB analysis. If that fails, rerun ICAL. All samples following the last acceptable Calibration Blank	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. Non-detects associated with positive blank infractions may be reported. Sample results > 10X the LOQ associated with negative blanks may be reported.

			must be reanalyzed. CCBs may not be reanalyzed without reanalysis of the associated samples and CCV(s).		For CCB, failures due to carryover may not require an ICAL.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to the source of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) and Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
57-12-15	Cyanide	76	120

Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
57-12-15	Cyanide	83	116

Figure 1: Cyanide Distillation Bench Sheet

Analysis: ***Total Cyanide*** **Batch ID:_____** **CAL ID#** _____
Analyst:_____ **Method #**335.4/ 8027(Hach) **Program #**175 HACH DR/4000 Spec.
Date Run:_____ **Detection Limit:** 0.005 mg/l **Wavelength:** 612 nm

ID	Merit #	Dilution	(mg/l) Conc.	ABS	%S	(mg/l) Result	(mg/l) Spike	%Rec	STD ID/Tag	(Run) Time
	Blank	10/10								
	Blank Spike	10/.5ml of 1ppm					0.050			
	Control									
	LCS	10/1.0ml of 1ppm					0.100			

(Manufac. Date)

Notes:**Lachat micro-distillation / sample prep. ; double distillation for lower detection limit / Dist. tubes**

User fill ID# _____

Releasing Solution ID_____**CyaniVer3 lot**_____ **CyaniVer4 lot** _____ **CyaniVer5 lot** _____

Peer Review: _____ **CN- Stock ID**_____ **Chlorine chk** _____

Beginning Distillation block temp: _____ **End Distillation block temp:**_____

Distillation time:_____ **Balance ID:**_____

STANDARD OPERATING PROCEDURE

ION CHROMATOGRAPHY FOR ANALYZING ANIONS (CHLORIDE, FLUORIDE, NITRATE, NITRITE, BROMIDE & SULFATE) USING THE DX-100 DIONEX ION CHROMATOGRAPH EPA METHOD 300.0

APPROVALS:

Barbara Ball

01/12/18

QA Officer Date

Maya Mushaly

01/12/18

Technical Director Date

Number	Description of Change	Date
001-006	Previous changes were not documented	
007	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
008	Linear calibration range check	8/19/14
009	Updated to comply with DoD QSM 5.0 standards.	03/10/16
010	Recipes for standards added to section 7	06/27/17
011	Updated to comply with DoD QSM 5.1 standards.	01/12/18
012		
013		
014		
015		
016		
017		

1.0 SCOPE AND APPLICATION

This method covers the determination of inorganic anions and is applicable to drinking, surface, ground waters, treated mixed wastewater and some industrial process waters, such as boiler water and cooling water as long as samples are filtered through a 0.5 micron filter. (Metrigard, Glass Fiber Filter, 47mm /GE Water & Process Technologies).

The anion reporting limits are as follows:
Bromide – 1 mg/l
Chloride – 1 mg/l
Fluoride – 0.2 mg/l
Nitrate-N – 0.1 mg/l
Nitrite-N – 0.1 mg/l
Sulfate – 1 mg/l.

2.0 SUMMARY OF THE METHOD

This SOP is a procedure for evaluating Anions (Chloride, Sulfate, Nitrate-N, Nitrite-N, Fluoride & Bromide) in liquid samples. A water sample is injected into a stream of carbonate-bicarbonate eluent and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affraction for a low capacity, strongly basic anion exchanger (guard & separator columns). The separated anions are directed onto a strongly acidic cation exchanger (suppressor). The anions are then converted to their highly conductive acid forms and the eluent is converted to weakly conductive carbonic acid. The separated anions are then measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height.

3.0 INTERFERENCES

Any substance that has a retention time coinciding with that of any anions to be determined will cause interferences. Some low-molecular-weight organic acids interfere with chloride and fluoride. High concentration of any one ion also interferes with the resolution of others. Sample dilution overcomes many interferences. To resolve uncertainties of identification use the method of known addition. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.0 APPARATUS & MATERIALS

Ion Chromatograph (DX-100 Dionex).

Ion Chromatograph (ICS-1100 Dionex).

Anion separator column, resolves Br-; Cl-; SO_4; NO_3-; NO_2-; F- and PO_4 (not run with this method).

Guard column, protects separator column.

Self-Regenerating suppressor, converts eluent and separated anions to their acid forms.

5 ml polyvials with filtercaps.

50 ml centrifuge tubes with screw caps.

Filtering apparatus & 0.5 micron filters (Metrigard, Glass Fiber Filter, 47mm /GE Water & Process Technologies).

Auto-pipettors (.05 – 1 mL).

5.0 REAGENTS

Deionized (DI) water.

Stock Eluent, sodium bicarbonate – sodium carbonate: Dissolve 1.908g Na2CO3 and 1.428g NaHCO3 in water and dilute to 100ml. Prepared every 2 months or when stock eluent bottle starts running low.

Working eluent: Pipet 10ml of stock eluent to a 1 L volumetric flask and dilute to volume. Made up fresh when eluent bottle runs low.

Control ERA.

Standard Anion solutions:

- Chloride (Hach Std) 1,000ppm. Expiration listed on standard bottle.
- Sulfate (Hach Std) 1,000ppm Expiration listed on standard bottle.
- Fluoride (Hach Std) 100ppm Expiration listed on standard bottle.
- Nitrate-N (Hach Std) 100ppm Expiration listed on standard bottle.
- Bromide (KBr) (Hach) 1,000ppm Dissolve: 0.1489g KBr in water and dilute to 100ml, *See stock solutions prep log,* Prepared fresh every 3 months. KBr shelf life is 5 years.

- Nitrite-N ($NaNO_2$) (Hach) 100ppm Dissolve: 0.0498g $NaNO_2$ in water and dilute to 100ml, *See stock solutions prep log.* Prepared fresh every 48 hours as need. $NaNO_2$ shelf life is 5 years.

6.0 SAMPLE HANDLING AND PRESERVATION

Samples must be collected in unpreserved high-density polyethylene containers. All bottles purchased by Merit are pre-cleaned certified. Analyze samples needing Nitrite and/or Nitrate as soon as possible, not exceeding 48 hours. Maximum holding time for water samples from the time of sampling is 28 days for Chloride, Sulfate, Fluoride, & Bromide. Sample must be refrigerated at 4±2 degrees C.

7.0 PROCEDURE

1. Standard Preparation

I. Blank Spike - Standard Preparation using Inorganic Ventures Stds / Hach Sodium Nitrite Primary Lot A9364 (Prep ID# 04105SNO2)

II. Stock Std

a. Fluoride 1,000ppm cat # ICF1 exp 1 year

b. Nitrate-N 1,000ppm cat# ICNNO31 exp 1 year

c. Chloride 1,000ppm cat# ICCL1 exp 1 year

d. Sulfate 1,000ppm cat# ICSO41 exp 1 year

e. Bromide 1,000ppm cat# ICBR1 exp 1 year

f. Nitrite-N 100ppm Sodium Nitrite HACH Lot A9364 (Prep ID# 04105SNO2) exp 48 hrs

i. Tare 50ml centrifuge tube on scale.

ii. Add 48.975ml reagent water to tube.

iii. Using calibrated pipettors add 0.375ml of SO4 std; 0.25ml of Cl- std; 0.25ml of Nitrite-N std; 0.1ml of Br- std; 0.025ml of Fluoride std and 0.025ml of Nitrate-N std.

iv. Prep every 48 hrs or as needed.

III. LCS Standard Preparation using Hach Stds / Fisher Sodium Nitrite Primary Lot 080939 (Prep ID# 03105CNO2)/ Aldrich Potassium Bromide Primary Lot MKBB7709 (Prep ID# 0408CBR).

IV. Stock Std

a. Fluoride 100ppm cat # 232-49 exp 4 years

b. Nitrate-N 100ppm cat# 194749 exp 5 years

c. Chloride 1,000ppm cat# 18349 exp 5 years

d. Sulfate 1,000ppm cat# 2175749 exp 2 years

e. Bromide 500ppm Potassium Bromide Aldrich Lot MKBB7709 (Prep ID# 0408CBR) exp 1 year

f. Nitrite-N 100ppm Sodium Nitrite Fisher Lot 080939 (Prep ID# 03105CNO2) exp 48 hrs

i. Tare 50ml centrifuge tube on scale.

ii. Add 47ml reagent water to tube.

iii. Using calibrated pipettors add 0.5ml of SO4 std; 0.5ml of Cl- std; 0.5ml of Nitrite-N std; 0.5ml of Br- std; 0.5ml of Fluoride std and 0.5ml of Nitrate-N std.

iv. Prep every 48 hrs or as needed.

2. System Startup and Test

I. Turn the system power on and set the *Control* button on the system Panel to Relay. Make sure computer, printer and autosampler are also on.

II. Confirm system air is working and pressure is between 50 and 60 psi.

III. Confirm that the eluent container is at least half full before a run. If not, make up working eluent: Add new working eluent as follows.

a. Turn eluent pressure switch to off (should be set at 5psi).

b. Take cap off eluent container and slowly add working eluent, replace cap and swirl to mix.

c. Re-pressurize eluent container by turning eluent switch to on.

d. Open valve below Pulse Damper and allow to bleed for 1 minute.

IV. Ensure pump flow rate adjustment is correct (180 = 1.8 ml/min).

V. Make sure detector range is set to operating range 30 uS.

VI. Check waste container, if close to full empty before startup.

VII. Open Run program. Click on Load / Method / norm.met. Instrument will begin startup. After approximately 20 seconds, open up valve below pulse damper again to rid any air and to reprime pump. Close valve again before system pressure drops to zero (around 8 seconds).

VIII. Let system equilibrate for at least 45 minutes before running samples (Conductivity reading should be between 15 and 17).

IX. Set Low Limit pressure switch to on.

3. Running the Analysis

I. All samples must be filtered through 0.5 micron filters prior to being analyzed.

II. All Anion runs begin with a Blank, Blank Spike, ERA Control and LCS.

III. Fill polyvial with 5ml of sample to be tested.

IV. Place filtercap on polyvial and push to top of vial with filtercap tool.

V. The sample can now be placed in autosampler tray.

VI. Open schedule program; Double-click to setup IC run.

VII. Type in sample ID under **Sample Name**; Norm.met under **Method**; the date of run under **Data File**, ex.(090501); & dilution factor under **Dil**.

VIII. Click on **File; Save As** (type in date); click **ok.**

IX. Go to Run program, click on **Load**; **Schedule,** scroll through to find schedule just set and click **ok.**

X. Push **Run** button on autosampler the 1st tray will then load.

XI. Push green **Run** button on Computer Interface. The scheduled run will now begin.

4. Calibration

I. Inject calibration standards containing a mixture of all anions and determine approximate retention times. Approximate times: Fluoride (0.97min), Chloride (1.53min), Nitrite-N (1.85min), Bromide (2.87min), Nitrate-N (3.30min), and Sulfate (6.80min). This is always the order of retention.

II. Next, prepare 5 different calibration standards for each anion all in one mixture, (See Section 5.4).

III. Run these 5 calibration standards with a blank proceeding the run, following the procedure in 7.2.2 through 7.2.10

IV. A calibration coefficient of 0.999 or greater is necessary for working calibration curve. If less than 0.999, then rerun.

V. A calibration curve can now be plotted in the **Cal Plot / Norm.Meth** program. Open the Cal Plot program by double clicking on icon, click on **File**, double-click on **norm.meth,** click on **Edit,** click on **component table**.

VI. From the component table each anions calibration curve can now be plotted by entering the peak height and area against the concentration.

VII. Recalibration must be done when changing columns, changing any detector settings, when retention times begin to shift, when QC samples begin to fall outside the methods limits, or every 6 months.

5. Calculations

I. Calculate sample results using the following equation:

C = H x F x D

Where:

C = mg anion / L

H = peak area,

F = response factor = concentration of standard / area of standard, and

D = dilution factor for those samples requiring dilution.

Note: This calculation is automatically performed by software when sample is run, so the result on chromatograph for each anion is final result as long as dilution factor was entered before run.

II. Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result

D = Duplicate sample result

III. Spike Recovery Percent Recovery: $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result

SR = Sample (unspiked) result

SA = Spike added

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1and 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

The retention time window width is set per manufacturer settings with the exception of DoD samples, which are set based on the retention time window study. See Table 2 for DoD QC requirements.

Linear Calibration Range Check (LCR) – The linear calibration check needs to be verified every 6 months with minimum of a blank and three concentrations. The verification curve must not exceed 10% of the initial curve. If the verification exceeds 10% of the initial curve, a new full calibration curve must be redone.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on as needed basis.

Method Detection Limit studies are performed every 6 months.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Blank Spike: a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes at a concentration in the bottom half of the calibration.

Control Standard: the control standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The control standard involves the analysis of all target analytes each time the initial calibration is performed.

Initial Calibration (ICAL): set of operations that establish, under specific conditions, the relationship between values of quantities indicating by a measuring instrument, or values represented by a material measure or a reference material, and the corresponding values realized by standards. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of the target anions. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Dionex DX-100 Ion Chromatograph Instrument Manual.

US EPA *Determination of Inorganic Anions by Ion Chromatography*, Method 300.0, Revision 2.2, 1999.

Table 1. Quality Control Items, Frequency and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	One per batch	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Blank Spike	One every 10 for drinking Water and DoD/ One every 20 for solids and wastewaters	90%-110%	Re-prep blank spike and rerun	Re-calibration and reanalyze
Control Standard (mid range check standard)	One every 20 sample	90%-110%	Reanalyze	Discontinue sample analysis, determine cause and/or in case of drift, recalibrate. Reanalyze all samples following last acceptable control.
Laboratory Control Sample (LCS) Soluble or insoluble	One every 10 for drinking Water / One per batch	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Every 10 drinking Water / One per batch	RPD<15%	Rerun entire set	Notify client. Flag data.
Matrix Spike	Every 10 drinking Water / One per batch	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Level 3 One every 10 samples	80%-120% RPD<15%		Notify client. Flag data.
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.
Linear Calibration Range Check	One blank and 3 standards every 6 months	±10%	Re-calibration	Re-calibration

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration (ICAL) for all analytes	ICAL prior to sample analysis.	$R^2 \geq 0.99$.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Minimum 3 standards and a calibration blank. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per multipoint calibration.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte.
Retention Time (RT) window width	At method set-up and after major maintenance (e.g., column change).	RT width is ± 3 times standard deviation for each analyte RT over a 24-hour period.	NA.	NA.	Calculated for each analyte.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within established RT windows. All reported analytes within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging criteria are not appropriate.	Freshly prepared ICV. No samples shall be analyzed until calibration has been verified.
Continuing Calibration Verification (CCV)	Before sample analysis; after every 10 field samples; and at the end of the analysis sequence.	All reported analytes within established retention time windows. All reported analytes within ± 10% of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails of if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all affected samples since the last acceptable CCV. Alternatively, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. Retention time windows are updated per the method.
Method Blank	One per	No analytes	Correct problem. If	If reanalysis	Results may not be

(MB)	preparatory batch.	detected > 1/2 LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for all reported analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Follow project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all reported analytes. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 15% (between MS and MSD or sample and MD).	Follow project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all reported analytes. The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.

DoD Appendix C LCS Limits
Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
24959-67-9	Bromide	86	116
16887-00-6	Chloride	87	115
16984-48-8	Fluoride	73	128
14797-55-8	Nitrate	87	111
14797-65-0	Nitrite	86	115
14265-44-2	Phosphate	91	114
14808-79-8	Sulfate	87	115

Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
24959-67-9	Bromide	91	110
16887-00-6	Chloride	87	111
16984-48-8	Fluoride	88	112
14797-55-8	Nitrate	88	111
14797-65-0	Nitrite	87	111
14265-44-2	Phosphate	80	116
14808-79-8	Sulfate	87	112

MERIT LABORATORIES, INC.

STANDARD OPERATING PROCEDURE

pH ON WATER MATRIX STANDARD METHOD 4500-H^+ B
pH ON SOLID MATRIX EPA SW-846 METHOD 9045D

APPROVALS:

Barbara Ball — 01/04/16

QA Officer — Date

Maya Mushaly — 01/04/16

Technical Director — Date

Number	Description of Change	Date
001-006	Previous changes were not documented	
007	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
008	Updated to include pH 12 buffer	8/8/12
009	Updated to include Martini instrument specifics and additional probe cleaning instructions	01/04/16
010		
011		
012		
013		
014		
015		
016		
017		

1.0 SCOPE AND APPLICATION

This SOP is used to measure pH in water samples, solids, sludges, or non-aqueous liquid samples.

2.0 SUMMARY OF METHOD

This SOP is designed to measure the pH of water samples and solid and soil samples by mixing the sample with reagent water and measuring the pH of the resulting aqueous solution. The procedure in this method is written for the Hach SensION2 and Martini Mil60 Laboratory pH Meters. This SOP follows EPA method 4500 H^+ B and EPA method 9045D.

3.0 INTERFERENCES

Temperature can be an interference. Temperature can change the acid-base equilibrium constant.

Carbon Dioxide absorption from the atmosphere. This can form carbonic acid in water, which can cause interferences.

A pH above 10 can have sodium interference.

Coated electrodes can cause errors.

4.0 APPARATUS AND MATERIALS

Hach SensION pH3 Laboratory pH Meter
Martini Instruments Mil60 pH Meter
Platinum Series Combination pH Electrode with Temperature.
Milwaukee MA918 pH Electrode
Potassium Chloride Electrolyte Cartridge.
Stir Plate.
Magnetic Stir Bar.
Plastic Cup.
Paper Towel.
Beakers
Analytical Balance
Tongue Depressors
50 mL Centrifuge Tubes.

5.0 REAGENTS

pH, 4.00, color-coded red, prepared according to manufacturer's instructions.

pH, 7.00, color-coded yellow, prepared according to manufacturer's instructions.

pH, 10.00, color coded blue, prepared according to manufacturer's instructions.

pH, 5.00, color coded clear (Laboratory Control Sample), prepared according to manufacturer's instructions.

pH, 2.00, color coded clear, prepared according to manufacturer's instructions.

pH, 12.00, color coded clear, prepared according to manufacturer's instructions.

3M KCl electrode storage solution (HACH SensION2)

Milwaukee MA9015 Storage Solution (Martini)

Milwaukee MA9011 Reference Electrolyte Solution (Martini)

Milwaukee MA9016 Cleaning Solution (Martini)

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

pH analyses must be run as soon as possible after sample collection. The samples must be stored in an unpreserved plastic container.

7.0 PROCEDURE

1. HACH SensIon2 Meter Calibration

- Turn on the meter.
- Inspect the Potassium Chloride Electrolyte Gel Cartridge to ensure that it is not empty. If it is empty, replace it.
- Prime the electrode by pushing the dispenser until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet with DI water.
- Press the <CAL> button on the meter. The display will prompt for Standard 1 (pH= 7.00).
- Place the electrode into fresh pH=7 buffer. Then press <Read/Enter> and stir until the display reads "pH STD 2." "Fresh" is defined as prepared within 7 days of calibration.
- Remove the electrode from the pH=7 buffer and rinse it well with DI water.

- Place the electrode into pH=4 buffer. Stir and press <Enter>. Wait until the display prompts for STD 3.
- Remove the electrode from the pH=4 buffer and rinse it well with DI water.
- Place the electrode into pH=10 buffer. Stir and press <Enter>.
- The Slope and "Store" will appear. If the slope is –58 ±3mV/ph unit, record the slope on the benchsheet. If the slope is out of this range press <Exit> and recalibrate. Press <Read/Enter> to save the calibration.
- Remove the electrode from the buffer and rinse well with DI water. The display will now automatically switch to the pH reading mode (i.e. "4.00 pH").
- Calibration is performed daily or when calibration verifications fail.

2. Martini Mil60 Meter Calibration

- Turn on the meter.
- Rinse electrode with DI water. Make sure all the bridges are clean.
- Hit CAL button on meter. Place electrode in buffer indicated on meter. Meter will flash ready when standard is stabilized. Press GLP/ACCEPT button to lock in standard.
- Rinse probe and repeat with the two remaining buffer standards.
- Meter will automatically change to measure mode when all three standards are completed.
- To retrieve slope information, press GLP/ACCEPT followed by ▲ (up) twice. Slope will be displayed as percentage (%).
- Calibration is performed daily or when calibration verifications fail.

3. Calibration Verification

- Place the electrode into pH=4 buffer, stir and wait until the reading is stable. Record reading on the bench sheet, as well as the temperature on the pH bench sheet (Figure 1). Rinse probe after reading.

- Place the electrode into pH=7 buffer, stir and wait until the reading is stable. Record reading on the bench sheet as well as the temperature on the pH bench sheet (Figure 1). Rinse probe after reading.

- Place the electrode into pH=10 buffer, stir and wait until the reading is stable. Record reading on the bench sheet as well as the temperature on the pH bench sheet (Figure 1). Rinse probe after reading.

- Place the electrode into pH=5 (LCS) buffer, stir and wait until the reading is stable. Record reading on the bench sheet as well as the temperature on the pH bench sheet (Figure 1). Rinse probe after reading.

- If any of the readings are outside the acceptable range, recalibrate until all verification readings are within acceptable range.

- When sample results are outside the calibration rage (4 to 10), calibration checks of buffer 2 and/or 12 are required depending on which side of the range the sample results fell outside of.

4. Soil Prep

- Combine 20 g or more of soil sample and add equivalent mls of reagent water in a 50-ml beaker, stir continuously for 5 minutes on stir plate.

- Let soil suspension stand for about 1 hour to allow most of the soil to settle out or centrifuge off the aqueous phase for pH measurement.

- Read only aqueous phase of samples.

5. Analysis

- Remove the electrode and rinse well with DI water. Place the electrode into the liquid sample and stir. Wait until the display shows a stable pH reading and the sample has a temperature near ($\pm$ 5^{o}C), the buffers (room temperature).

- Rinse the probe and replace the sample with a new aliquot and repeat to perform sample duplicate.

- Rinse probe between each sample. If using the HACH SensIon2, clean with electrode gel cartridge when needed.

6. Storage/Cleaning of pH Electrode

- Rinse electrode with DI water.

- HACH SensION2 electrode is stored in a 3M KCl solution when electrode is not in use.

- Martini Mil60 electrode is stored in manufacturer provided storage solution when electrode is not in use.

- For HACH SensION2 electrode, use Potassium Chloride electrolyte cartridge to clean when needed. Paper towel can be used to wipe off residue from the electrode tip.

- For Martini Mil60 electrode, clean using manufacturer cleaning solution or 50% dish soap and tap water. Do not wipe electrode with paper towel.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

This method is evaluated by testing a laboratory control sample and duplicate samples.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment must be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument must not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing pH analyses. Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100 percent fresh air exchange system. This system exchanges 100 percent of the air in the laboratory area with air from outside six times per hour and 30 times per hour when the emergency purge button is hit

A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; a sample batch consists of 10 samples or less.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Laboratory Control Spike: Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability to generate acceptable precision and bias, to verify the analytical system's performance, and to document method accuracy for each matrix.

14.0 REFERENCES

Hach SensION2 Laboratory pH Meter Manual.

Martini Instruments Mil60 Laboratory pH Meter Manual

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 4500-H^+ B.

USEPA, SW-846, Revision 4, Method 9045D.

TABLE 1: QUALITY CONTROL ITEMS, FREQUENCY, AND CORRECTIVE ACTION

Batch = 10 samples

Quality Control Item	**Frequency**	**Acceptance Range**	**Corrective action**
Calibration with three Std buffers (pH=4, 7 & 10)	1/day and when calibration check is outside acceptance range	± 0.05 of pH Slope = -58=±3mV/pH unit	1. Clean electrode and reference junction. Then recalibrate. 2. Prepare new buffers and recalibrate. 3. Call for service.
Laboratory Control Sample pH 5.00	1 per batch	Within certified range	Same as for calibration above.
Temperature of samples and Buffers	Record with each pH reading	Within ± 5^{o}C of the buffers (room temperature	Hold at room temperature until within acceptable range.
Calibration check buffer pH 2.00 and pH 12.00	When sample results are outside the calibration range	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check.
End calibration check Read one standard	1 per batch	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check
Sample Duplicate	1 per batch	± 0.05 pH units	Report with qualification when outside criteria

FIGURE 1: PH BENCH SHEET

Date:	Analyst(s):	Batch:
Lab:	Meter/Probe #:	Electrode:

Buffers

	Buffer - 4	Buffer - 7	Buffer - 10	Buffer - 5 (LCS)	Low Level - 2	High Level - 12	Date Made:	
Lot #							Use Until:	

Calibration

	Buffer	Reading	Temp. (°C)	Slope	Notes:
Std 1	4				
Std 2	7				
Std 3	10				

Standard Verification

LCS	5				
Low Level	2				
High Level	12				

Analysis

	Merit #:	Reading	Temp.	Limits	Matrix:	Time	Notes
1.							
DUP				+/- 0.05 STD units			
2.							
3.							
4.							
5.							
6.							
7.							
8.							
9.							
10.							
End Check: Buffer =				+/- 0.05 STD units			

Reviewed by: _____ Date: _____

STANDARD OPERATING PROCEDURE

TOTAL SUSPENDED SOLIDS (TSS) AND TOTAL VOLATILE SUSPENDED SOLIDS (TVSS) STANDARD METHOD 2540D (TSS), EPA 160.4 (TVSS)

APPROVALS:

Barbara Ball

01/10/17

QA Officer Date

Maya Mushaben

01/10/17

Technical Director Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	Updated to comply with DoD QSM and ISO 17025 standards.	5/27/11
007	2013 Internal Audit Findings	6/04/14
008	2016 Internal Audit Findings	01/10/17
009		
010		
011		
012		
013		
014		
015		
016		

1.0 SCOPE AND APPLICATION

This SOP determines non-filterable residue in drinking, surface, and saline waters; domestic and industrial wastes (TSS); and the weight of solid material combustible at 550 °C (TVSS). The reporting limit is 3 mg/l for TSS and 3 mg/l for TVSS.

2.0 SUMMARY OF METHOD

An aliquot of sample is taken from a stirred/shaken sample and filtered through a pre-weighed filter. After rinsing the solids retained on the filter, the filter is dried and weighed. The weight of solids on the filter represents the TSS. If TVSS are also requested, the dried filter containing the solids is burned at 550 °C and reweighed. The difference in the weight of the solids represents the TVSS.

3.0 INTERFERENCES

Poor shaking or stirring can lead to incorrect results.

Solids larger than ¼ inch in diameter should be excluded from the test.

Improper drying of the solids (not to constant weight) will give higher results than the true value.

The principal source of error in the determination is the failure to obtain a representative sample.

The test is subject to many errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

4.0 APPARATUS AND MATERIALS

Proweigh filters Note: if TVSS are to be analyzed, TVSS pre-primed filters must be used or the TSS filter can be primed at 550^{o} C.

Vacuum filtering apparatus compatible with 47 mm glass fiber filters.

25 disposable pipettes.

Graduated cylinders 50 mL, 100 mL.

Stir Bar.

Tweezers.

Vacuum.

Magnetic Stir Plate

Beaker.

Oven, 103 ± 2 ^{o}C.

Muffle Furnace.

Thermometer.

Desiccators.

Analytical Balance, capable of weighing to 0.1 mg.

5.0 REAGENTS

Deionized (DI) Water.
Laboratory Control Sample (LCS)

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

The sample is usually a composite sample collected in a plastic or glass liter bottle with no preservation other than refrigeration at 4±2^{o}C. The holding time is 7 days from sample collection.

7.0 PROCEDURE

1. Record the date and time of analysis as well as your initials as the analyst on the bench sheet (Figure 1) and in the appropriate batch for TSS and TVSS. A batch is defined as 10 samples of the same or similar matrix.
2. Record the tin number and the filter weight of a preweighed 47 mm glass fiber filter on the bench sheet on the line indicating "Blank." Using tweezers, place the filter in the filter holder with the wrinkled side up.
3. Place the filter holder assembly in the side arm flask with the vacuum hose attached to the side arm.
4. Turn on the vacuum and filter 100 ml of DI water through the filter until all of the water is drawn through. This is the Blank.
5. Record the 100 ml volume on the bench sheet for the Blank. Remove the filter from the filter holder and place it back in its tin.

6. Record on the bench sheet the tin number and the filter weight for another filter and place the preweighed filter in the filter holder assembly with the wrinkled side up, apply vacuum, and wet the filter with a little DI water to ensure adhesion to the holder.

7. Turn on the vacuum and filter 50 ml of LCS through the filter until all of the sample is drawn through. Rinse graduated cylinder and filter apparatus with DI water. This is the LCS.

8. Record the Merit sample number on the bench sheet, vigorously shake and quickly pour the sample (50 to 100mls) from the bottle into a graduated cylinder. When using this method, pour the sample onto the filter from the cylinder.

    - ♦ If sample requires more mixing , mix a sample by shaking it violently and quickly pouring about 150 ml to 250 ml into a beaker.
    - ♦ Place a teflon-covered, magnetic stirring bar in the beaker and place the beaker on top of a magnetic stirrer. Stir for 1 minute or more.
    - ♦ Using a 25 ml serological pipette with a wide opening, remove 25 ml of well mixed sample from halfway into the cup and halfway between the mixing vortex and the side of the cup. Drain the pipette onto and through the filter.
    - ♦ Repeat pipetting until there are enough solids to weigh or 100 ml has been filtered. Usually 50 ml will be enough for most wastewater samples. High suspended solids (cloudy samples after shaking) will require less sample (e.g., 1 ml to 25 ml).

9. Record the volume you filtered on the bench sheet.

10. Remove the filter from the filter holder; place it back in its tin.

11. Dry tin in a 103 ^{o}C oven for 1 hour or more. Note: if filters are dried for more than 4 hours, you can be confident they are dried to a constant weight.

12. Remove the tin containing the filter from the oven and cool it to room temperature in a Desiccator. Carefully remove the filter from the tin and weigh it on an analytical balance to 0.1 mg.

13. Record the weight on the bench sheet (Figure 1).

14. Check the dryness of the sample by drying it for another 15 minutes. Then reweigh. The sample is dried to a constant weight if the two weights differ by no more than four percent or 0.5 mg, whichever is less.

15. If TVSS are needed, mark the tin on the bottom by pressing with a ballpoint pen to crease symbols into the metal in order to identify it. This is done because the label on the tin will burn off at 550 ^{o}C.

16. Place the filter in its tin into the muffle furnace at 550 ^{o}C for 30 minutes.

17. Cool in a Desiccator and weigh.

18. Record the weight on the bench sheet.

19. Calculate TSS as follows:

$$TotalSuspendedSolids = \left(\frac{A - B}{volumeofsample} \right) x1000000$$

- Where A = final weight of sample & dish
- B = original weight of dish

20. Record the TSS on the bench sheet.

21. Repeat number six through 14 for each sample.

22. Calculate TVSS as follows:

$$TotalVolatileSuspendedSolids = \left(\frac{A - B}{volumeofsample} \right) x1000000$$

- Where A = final weight of sample & dish before 550
- B = final weight of sample & dish after 550

26. Other Calculations:

Relative Percent Difference $RPD = \frac{(S - D)}{\left[\frac{S + D}{2} \right]} \times 100$

Where: S = Initial sample result

D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result

SR = Sample (unspiked) result

SA = Spike added

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

This method is evaluated by testing a LCS and duplicate samples.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment must be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument must not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing solids analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100 percent fresh air exchange system. This system exchanges 100 percent of the air in the laboratory area with air from outside six times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Non-filterable residue: solids which are retained by a glass fiber filter and dried to a constant weight at 103-105 ^{o}C.

Sample Batch: samples of the same or similar matrix; a sample batch consists of 10 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike: Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability to generate acceptable precision and bias, to verify the analytical system's performance, and to document method accuracy for each matrix.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

EPA Method 160.4 *Residue, Volatile (Gravimetric, Ignition at 550°C.*

Standard Methods for the Examination of Water and Wastewater, 20th Edition, Method 2540D, *Total Suspended Solids Dried at 103-105℃.*

Table 1: Quality Control Items, Frequency, and Corrective Action

QC Sample	**Frequency**	**Acceptable Limits**	**Corrective Action**	**Follow up Corrective Action**
Blank	1/10 samples	-3 to +3 mg/l	Redry and Reweigh	Reset the entire set of samples with new filters
Laboratory Control Sample-	1/10 samples	Within Supplier's Limits	Redry and Reweigh	Reset the entire set of samples with new filters
Sample Duplicate	1/10 Samples	± 5 % of average	Reset sample duplicates	Footnote non-homogeneity
Analytical Balance Check with "S" Weights	1/day	± 0.1% or ± 0.5 mg; whichever is greater	Recalibrate Balance and Reweigh	Call for Service
Constant Weight Verification	1/10 samples	4 % or 0.5 mg whichever is less	Dry longer and reweigh.	Dry longer and reweigh.

Figure 1: TSS Bench Sheet

Total Suspended Solids

TSS: VLIMS Code: 4630; EPA Method: 2540D

Date Started:_____ Date Finished:_____

Time Started:_____ Time Finished:_____

Analyst:_____ Reviewed by:_____

Batch ID:_____ Review Date:_____

Temperature:_____ Balance ID: _____

Time in Oven: _____ Oven ID: _____

Merit #	Tin #	MLs sample	g. Filter	g. dry solids + filter 103°C	g. reweigh 15 min. 103°C	TSS mg/L	TVSS Y/N	TVSS Tin #
Blank								
LCS Lot								
Dup								

LCS value =_____ Acceptance Criteria (mg/L): _____

% Rec =_____ Acceptance Criteria (%): _____

% RPD =_____ Acceptance Criteria: ± 5% of average

Figure 2: TVSS Bench Sheet

Total Volatile Suspended Solids

TVSS: VLIMS Code: 4640; EPA Method: 160.4

Date Started:_____ Date Finished:_____

Time Started:_____ Time Finished:_____

Analyst:_____ Reviewed by:_____

Batch ID:_____ Date Reviewed:_____

Temperature:_____ Balance ID: _____

Time in Oven: _____ Oven ID: _____

Merit #	Tin #	sample (mls)	Primed Filter (grams)	dry solids + filter 103°C (grams)	Ash + Filter 550°C (grams)	TSS (mg/L)	TVSS (mg/L)
Blank							
LCS Lot							
Dup							

LCS value =_____

% Rec =_____ Acceptance Criteria:_____

% RPD =_____ Acceptance Criteria: ± 5% of average

STANDARD OPERATING PROCEDURE

SPECIFIC CONDUCTANCE BY EPA 120.1/
SALINITY BY STANDARD METHOD 2520B

APPROVALS:

Barbara Ball

8/06/12

QA Officer Date

8/06/12

Technical Director Date

Number	Description of Change	Date
001-002	Previous changes were not documented	
003	Required sections added and Internal Audit findings fixed.	2/9/12
004	Salinity method added and higher standard	8/6/12
005		
006		
007		
008		
009		
010		
011		
012		
013		

1.0 SCOPE AND APPLICATION

This SOP is applicable to drinking, surface, and saline water, domestic and industrial wastes, and acid rain (atmospheric deposition). Conductivity is run by EPA Method 120.1. Salinity is run by Standard Method 2520B.

2.0 SUMMARY OF METHOD

This SOP is a procedure for evaluating Conductivity and Salinity in liquid samples. The specific conductance of a sample is measured by use of a self-contained conductivity meter. Samples are preferably analyzed at 25ºC. Field measurements with comparable instruments are reliable.

3.0 INTERFERENCES

Not applicable.

4.0 APPARATUS AND MATERIALS

Hach Conductivity/TDS Meter

1 L Volumetric flask

Plastic 50 mL Centrifuge tubes

Clean plastic cup

Pipette

Graduated Cylinder

Analytical Balance

5.0 REAGENTS

Deionized (DI) water

Sodium Chloride (NaCl)

Conductivity Standard

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Maximum holding time for water samples is 14 days when refrigerated at 4º C ± 2ºC. Samples must be provided in unpreserved plastic bottles. Analyses can be performed either in the field or laboratory.

7.0 PROCEDURE

1. PREPARATION OF STANDARD SOLUTIONS, PREPARED FRESH EVERY 2 MONTHS.

    - For a 180-µmhos/cm standard, dissolve 0.0214 g NaCl in 250 mL of DI water. The 180-µmhos/cm standard is used for blank spike.

    - For a 1,990-µmhos/cm standard, dissolve 0.25 g NaCl in 250 mL of DI water. The 1,990-

µmhos/cm standard is used for Laboratory Control Sample (LCS).

- For a 7,960-µmhos/cm standard, dissolve 1.0 g NaCl in 250 mL of DI water. The 7,960-µmhos/cm standard is used for standard.

2. Turn on meter and place probe in a plastic cup filled with DI water.
3. For a blank, pour 15 mL DI water in a centrifuge tube.
4. Rinse off probe then place in tube. Make sure to eliminate all air bubbles around the tube. Record value displayed.
5. Place probe back in cup containing clean DI water.
6. Pour 15 mL of Blank Spike into centrifuge tube and read conductivity displayed on meter. Rinse off probe between each sample.
7. Pour 15 mL of LCS into centrifuge tube and read conductivity displayed on meter. Rinse off probe between each sample.
8. Pour 15 mL of Control, ERA standard, into centrifuge tube and read conductivity displayed on meter. Rinse off probe between each sample.
9. Pour 15 mL of sample into centrifuge tube and read conductivity displayed on meter. Rinse off probe between each sample.
10. If Salinity is needed, press the SAL key on the meter. Read salinity as displayed on the meter. Rinse off probe between each sample.
11. Calculations:

- Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result

D = Duplicate sample result

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Precision and accuracy studies are performed on as needed basis.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

Acids and bases should be neutralized before disposal. All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

EPA Water NPDES, Method 120.1, EPA Test Methods, Revision 1982, Conductance (Specific Conductance, µmhos at 25ºC).

Standard Methods for Examination of Water and Wastewater, 20th edition, Method 2520B, Salinity by Electrical Conductivity Method

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Blank Spike	Yes One every 10 samples	90%-110%	Rerun	Notify client. Flag data.
Control	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify client. Flag data
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	Notify client. Flag data.

Analysis: Conductivity/Salinity **Batch ID:** _____

Analyst: _____ **Method #** 120.1/2520B **Program #** _____

Date Run: _____ **Detection Limit:** N/A **Wavelength** _____

ID	Merit #	Dilution	umhos/cm	%S	umhos/cm Result	Salinity Result	umhos/cm Spike	%Rec	Lot / Source	(Run) Time
	Blank									
	Blank Spike						180			
	Control									
	LCS						1,990			
	Standard						7,960			

Notes: Samples tested at 25 degrees Celsius Peer Review: _____

STANDARD OPERATING PROCEDURE

MICROWAVE ASSISTED ACID DIGESTION OF SOLID SAMPLES USEPA METHOD 3050B

APPROVALS:

Barbara Ball

01/15/18

QA Officer Date

Maya Mushaly

01/15/18

Technical Director Date

Number	Description of Change	Date
001-008	Previous changes were not documented	
009	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
010	Emergency SOP Amendment Form updates	2/9/16
011	Updated to comply with DoD QSM 5.0 standards.	03/10/16
012	Updated to comply with DoD QSM 5.1 standards.	01/15/18
013		
014		
015		
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

This digestion procedure is used for the preparation of soils and solid samples for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced within this SOP is the EPA SW-846 Method 3050B.

This method is not a total digestion technique for most samples. The method is a very strong acid digestion that will dissolve almost all elements that could become environmentally available. By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment. Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

Metal (Symbol)	CAS#:
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
*Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
*Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
*Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
*Tin (Sn)	7440-31-5
*Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

* Not approved for DoD work

2.0 SUMMARY OF METHOD

For the digestion of samples, a representative 0.05-2.0 gram (wet weight) sample is digested with nitric acid (HNO_3) using microwave heating. The resultant digestate is diluted to a final volume of 50 ml. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis. If required, a separate sample aliquot is reserved for the determination of percent total solids.

3.0 INTERFERENCES

Addition of nitric acid to samples that contain organics could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. Sludge samples can contain diverse matrix types, each of which can present its own analytical challenge. Spiked samples and any relevant standard reference material must be processed in accordance with the quality control requirements given in Section 8.0. Samples that are highly reactive or contaminated may require dilution before analysis. If samples are diluted, then any dilutions must be accounted for in all subsequent calculations. Highly reactive samples may also require pre-digestion in a hood to minimize the danger of thermal runaway and excessively vigorous reactions.

4.0 APPARATUS AND MATERIALS

Microwave Digestion System CEM–Model MDS-81D and MARSX Model # 907600.

- The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to ensure uniform microwave heating

- The MARSX consists of a microwave drying system with an operator selectable power output of 0 – 1200 watts, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

- Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

Glass Fiber Filter paper, 0.45 μm.

Membrane Filter paper, 0.45 μm.

Analytical balances, 510 g capacity, minimum accuracy ± 0.001 g, and 250g capacity, minimum accuracy ±0.0001g.

Filter funnel, glass, or disposable polypropylene.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Disposable Polypropylene vessels, 50 ml, compatible with centrifuge.

Plastic containers to support minimum of 200 ml.

Disposable tongue depressors for sample handling.

Disposable Pasteur pipettes.

Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.

Centrifuge (IEC Centra GP8).

5.0 REAGENTS

Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM standard criteria.

Concentrated nitric acid, HNO_3, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank (LRB).

Standards added to digestion:

- Spiking Solutions:
  - Multi-element standard solution **WS1** (Figure 1), contains 10 µg/ml (ppm) each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Sr, Sn, Ag, Tl, Ti, V, and Zn. The spiking solution is made by diluting the WS1, 2 to 1 (5 µg/ml). The 5 µg/ml spiking solution is added to the QC samples accordingly, 1.0 ml is added to MS/MSD samples and 0.5 ml is added to the laboratory control sample (LCS), using the Eppendorf automatic pipette.
  - Multi-element standard solution **HM** (Figure 1) contains 100 µg/ml each of Ca, K, Mg, and Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), using the Eppendorf automatic pipette or by weighing the amounts (1.0 g or 0.50 g) on the scale.
  - Spiking solutions are prepared according to the Standard Prep Log (Figure 1). The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard

made, expiration and unique ID of any working standards used are recorded in the standard prep log.

- All standards are NIST traceable.

♦ Internal Standards (after digestion):

- Lithium 6, 1000 μg/ml stock solution.
- Scandium, 1000 μg/ml stock solution.
- Yttrium, 1000 μg/ml stock solution.
- Rhodium, 1000 μg/ml stock solution.
- Rhenium, 1000 μg/ml stock solution.

NOTE: The manufacturer provides the stock solutions with a certificate of analyses and MSDS sheets.

- Internal Standard working solution (**IS-WS**): From the above stock solution, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the bottle will be 2.5 μg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ± 2° Celsius. Holding times for metals are 6 months from the date of sampling, with the exception of Mercury which is not covered in this SOP.

7.0 PROCEDURE

1. The Microwave Accelerated Reaction Systems are equipped with a temperature feedback control system. Microwaves are calibrated once a year according to the manufacturer's operation manual.

2. All digestion vessels are disposable and are used only once. This allows for better sample control and prevents cross contamination.

3. Sample Digestion.

CAUTION: - Toxic nitrogen oxide fumes may evolve; therefore all work must be performed in a properly operating ventilation system.

- *Loss of sample through splattering inside the microwave system needs to be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.*

- Homogenize sample by chopping and mixing sample with a tongue depressor or spatula. Remove any foreign object such as sticks, leaves, or rocks. Transfer 0.2 to 0.3 grams sample (wet weight) for a soil matrix or 0.05 to 2 grams sample (wet weight) for liquidly sludges and other various solid matrices to a digestion vessel, and record the weight on the digestion log (Figure 2), to a minimum of 0.001 g.

- For every sample batch, prepare a Laboratory Reagent Blank (LRB) and Laboratory Control Sample (LCS) by transferring 0.25 grams sand to the digestion vessel. Record the weight on the digestion log (Figure 2) to a minimum of 0.001 g. Additionally, designate a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) or Duplicate (Dp) prepared as per 7.3.1.

- For all metals, except Ca, Mg, K, and Na, add 0.50 ml of the QC spiking solution to the LCS, and 1.0 ml to the MS/MSD samples. For Ca, Mg, K and Na, add 0.5 ml of the **HM** solution to the LCS, and 1.0 ml to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the digestion log. The spike solution for MS/MSD is added before digestion.

- Add 1 ± 0.1 mL of concentrated nitric acid to each conical vessel in the fume hood. Mix the slurry, then wait 5-10 minutes for any reaction to occur.

- Loosely cap the vessel and place into the carousel.

- Samples are slowly ramped in the microwave to 95 ±5 degrees Celsius over the course of a few minutes and maintained at this temperature for 5 minutes without boiling.

- Allow samples to set for 5 minutes then repeat previous step.

- After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood. When the vessels have cooled to near room temperature, determine if the microwave vessels and caps are intact. If the sample vessel look compromised (i.e. cap is not on, sides of the vessel are wet), then the sample is considered compromised and the sample must be re-digested.

- Add 1 ml of the Internal Standard working solution to each sample and QC sample using an Eppendorf automatic pipettor. Dilute to the 50 ml mark with DI Water, into a calibrated (per lot) digestion vessel.

- A post-digestion spike is performed as necessary and prepared as follows: take a 25 ml aliquot of the sample designated for MS/MSD and add to it 0.50 ml of the QC spiking solution (for all elements except Ca, Mg, K, and Na). For Ca, Mg, K, and Na add 0.5 ml of the **HM** solution.

- If the digested sample contains particulate matter, which may clog the nebulizer, the sample may be centrifuged, allowed to settle over night, or filtered.

    - Centrifugation: centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.

    - Settling: allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

    - Filtering: the filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 μm filter paper and transfer the liquid to a new vessel. Glass fiber filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

- Calculations

Dilution factor(DF:

$$DF = \frac{Final\ Volume\ (50)}{Sample\ amount}\ x\ \frac{100}{\%\ Total\ solids}$$

Relative Percent Difference: $RPD = \frac{(S-D)}{\left[\frac{S+D}{2}\right]} \times 100$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR-SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

% Difference (%D)
Used for serial dilution test in metals.

$$\%D = \left| \frac{X_1 - X_2}{X_1} \right| \times 100\%$$

where: %D = percent difference
X_1 = Initial concentration
X_2 = Duplicate concentration

- Record pertinent information onto the digestion log (Figure 2). The following information must be included: Date, start time, end time, analyst initials, method reference, sample IDs, sample weight or volume, MS/MSD/LCS spiking concentration and lot#, acid lot #, dilution factor, final volume and any pertinent remarks.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 & 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.

The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

12.0 WASTE DISPOSAL

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Samples.

- All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory waste water.

- As a "small generator" of metals, Merit Laboratories has been approved for this type of disposal from the local government.

Acid bottles.

- Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for metals a sample batch consists of 20 samples or less.

Method Blank (Laboratory Reagent Blank) (LRB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes carried through the complete sample prep and analytical procedure. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (MS) (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (MSD) (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

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TABLE 1 Quality Control Items, Frequency and Corrective Action

QA Items	Frequency	Acceptance Criteria	Corrective Action
Laboratory Reagent Blank (Method Blank)	One per sample batch	<RL/dilution	Remove contamination and re-digest sample set
Laboratory Control Sample	One per sample batch	85%-115%	Re-digest the sample set
Matrix Spike	One per every 20 samples	75%-125%	Analyze by Method of Standard Additions (MSA)
Matrix Spike Duplicate	One per ever 20 samples	75%-125% RPD <20%	Analyze by Method of Standard Additions (MSA)
Matrix Duplicate	One per every 20 samples	RPD <20%	Re-digest the sample set and QC.
Dilution	One per sample batch	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.

TABLE 2 Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Linear Dynamic Range (LDR) or High-level Check Standard	At initial set-up and checked every 6 months with a high standard at the upper limit of the range.	Within ±10% of true value.	Dilute samples within the calibration range, or re-establish/verify the LDR.	Flagging is not appropriate.	Data cannot be reported above the calibration range without an established/passing high-level check standard.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial Calibration (ICAL) for All Analytes	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r2 ≥ 0.99.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes, within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of the true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

			Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.		
Low-level Calibration Check Standard (LLCCV)	Daily.	All reported analytes within ± 20% of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid low-level calibration check standard (LLCCV). LLCCV should be less than or equal to the LOQ. If the concentration of the lowest calibration standard os less than or equal to the LOQ, the lowest standard may be re-quantified against the calibration curve as LLCCV. Otherwise, a separate standard must be analyzed as the LLCCV prior to the analysis of any samples.
Internal Standards (IS)	Every field sample, standard and QC sample.	IS intensity in the samples within 30-120% of intensity of the IS in the ICAL blank.	If recoveries are acceptable for QC samples, but not field samples, the field samples may be considered to suffer from a matrix effect. Reanalyze sample at 5- fold dilutions until criteria is met. For failed QC samples, correct problem, and rerun all associated failed field samples.	Flagging is not appropriate.	Samples suffering from matrix effect should be diluted until criteria are met, or an alternate IS should be selected.
Method Blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated	Results may not be reported without a valid method blank. Non-detects associated with positive blank infractions may be reported. Samples results > 10X the LOQ associated with negative blanks

				preparatory batch	may be reported. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV.	The absolute values of all analytes must be < ½ LOQ or 1/10th the amount measured in any sample.	ICB: Correct problem and repeat ICV/ICB analysis. If that fails, rerun ICAL. All samples following the last acceptable Calibration Blank must be reanalyzed. CCBs may not be re-analyzed without re-analysis of the associated samples and CCV(s).	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. Non-detects associated with positive blank infractions may be reported. Sample results > 10X the LOQ associated with negative blanks may be reported. For CCB, failures due to carryover may not require an ICAL.
Interference Check Solutions (ICS) (also called Spectral Interference Checks)	After ICAL and prior to sample analysis.	ICS-A: Absolute value of concentration for all nonspiked project analytes <1/2 LOQ (unless they are a verified trace impurity from one of the spiked analytes) ICS-AB: Within ± 20% of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the failed ICS.	All analytes must be within the LDR. ICS-AB is not needed if instrument can read negative responses.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits	Examine the project specific requirements. Contact the client as to additional	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to

		are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	measures to be taken.	are not met and explain in the case narrative.	determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Dilution Test	One per preparatory batch if MS or MSD fails.	Five-fold dilution must agree within ± 10% of the original measurement.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Only applicable for samples with concentrations > 50 X LOQ (prior to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post Digestion Spike (PDS) Addition	One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible).	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 6020 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	78	124
7440-36-0	Antimony	72	124
7440-38-2	Arsenic	82	118
7440-39-3	Barium	86	116
7440-41-7	Beryllium	80	120
7440-42-8	Boron	74	128
7440-43-9	Cadmium	84	116
7440-70-2	Calcium	86	118
7440-47-3	Chromium	83	119
7440-48-4	Cobalt	84	115
7440-50-8	Copper	84	119
7439-89-6	Iron	81	124
7439-92-1	Lead	84	118
7439-93-2	Lithium	75	120
7439-95-4	Magnesium	80	123
7439-96-5	Manganese	85	116
7439-97-6	Mercury	74	126
7439-98-7	Molybdenum	83	114
7440-02-0	Nickel	84	119
7440-09-7	Potassium	85	119
7782-49-2	Selenium	80	119
7440-22-4	Silver	83	118
7440-23-5	Sodium	79	125
7440-24-6	Strontium	75	129
7440-28-0	Thallium	83	118
7440-29-1	Thorium	81	116
7440-29-1	Tin	82	121
7440-32-6	Titanium	83	117
7440-61-1	Uranium	83	120

7440-62-2	Vanadium	82	116
7440-66-6	Zinc	82	119

Method 6020 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	84	117
7440-36-0	Antimony	85	117
7440-38-2	Arsenic	84	116
7440-39-3	Barium	86	114
7440-41-7	Beryllium	83	121
7440-42-8	Boron	73	130
7440-43-9	Cadmium	87	115
7440-70-2	Calcium	87	118
7440-47-3	Chromium	85	116
7440-48-4	Cobalt	86	115
7440-50-8	Copper	85	118
7439-89-6	Iron	87	118
7439-92-1	Lead	88	115
7439-93-2	Lithium	78	126
7439-95-4	Magnesium	83	118
7439-96-5	Manganese	87	115
7439-97-6	Mercury	70	124
7439-98-7	Molybdenum	83	115
7440-02-0	Nickel	85	117
7440-09-7	Potassium	87	115
7782-49-2	Selenium	80	120
7440-22-4	Silver	85	116
7440-23-5	Sodium	85	117
7440-24-6	Strontium	82	118
7440-28-0	Thallium	82	116
7440-29-1	Thorium	87	121

7440-29-1	Tin	86	115
7440-32-6	Titanium	83	115
7440-33-7	Tungsten	85	122
7440-61-1	Uranium	87	120
7440-62-2	Vanadium	86	115
7440-66-6	Zinc	83	119

FIGURE 1: STANDARD PREP LOG

Standard Preparation PE

Inorganic Stock Solution IV-28 (100 ppm) + CGSN1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 5.0 ppm	HNO_3	Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0002 ppm	0.20 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Standard Preparation HP

Inorganic Stock Solution IV-28(100 ppm) + CGSN1-1 (1000 ppm)

V. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

VI. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

VII. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

VIII. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 2.5 ppm	HNO_3	Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

ICP/MS MINERALS PREP LOG

Date	IS ID	Exp. Date	Analyst

Standards **ppm**	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	Final Volume
0.0	**0.0**		**2 mls**	**2 mls**	**100 mls**
0.50	**0.5**		**2 mls**	**2 mls**	**100 mls**
1.0	**1.0**		**2 mls**	**2 mls**	**100 mls**
2.0	**2.0**		**2 mls**	**2 mls**	**100 mls**
5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**
10.0	**10.0**		**2 mls**	**2 mls**	**100 mls**
ICV – 5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**

FIGURE 2: METALS DIGESTION LOG

Metals Digestion 3015A \ 3050B

DATE _____ PREP BATCH MTD-_____

TIME START _____ TIME FINISH _____ ANALYST _____

Pipet Calibration:

Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria	Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria
2	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value	3	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value
	2					2			
	3					3			

SAMPLE#	BTL ID	SAMPLE AMOUNT GRAMS (g)	FINAL VOLUME (ml)	REMARKS	% TOTAL SOLIDS	DILUTION FACTOR
LCS -	----	50	**50**		—	1
LRB-	----	50	**50**		—	1

NOTES: *1) Spike values (unless otherwise stated):*

LCS = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

1.1. Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution

Spiking Solution – Date Prepared: _____

2) Spike values for minerals (Ca-Mg-K-Na)

LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution

Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution

High Purity Stock Solution (HM)- Lot # _____

3) HNO_3 Lot # _____ *4) Centrifuge Tube Lot #* _____

5) Balance ID: _____ *Reviewed by* _____ *On* _____

STANDARD OPERATING PROCEDURE

MICROWAVE ASSISTED ACID DIGESTION OF LIQUID SAMPLES AND EXTRACTS US EPA METHOD 3015A

APPROVALS:

Barbara Ball

01/15/18

QA Officer Date

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01/15/18

Technical Director Date

Number	Description of Change	Date
001-007	Previous changes were not documented	
008	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
009	Emergency SOP Amendment Form updates	02/09/16
010	Updated to comply with DoD QSM 5.0 standards.	03/10/16
011	Updated to comply with DoD QSM 5.1 standards.	01/15/18
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1.0 SCOPE AND APPLICATION

This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced with in this SOP is SW-846 Method 3015A.

Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

Metal (Symbol)	CAS#:
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
*Boron (B)	7440-42-8
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
*Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
*Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
*Tin (Sn)	7440-31-5
*Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

* Not approved for DoD work

2.0 SUMMARY OF METHOD

A representative 0.5 to 25 g/ml aqueous sample is digested in 1 ml of concentrated nitric acid in a polypropylene digestion vessel heated using microwave heating and brought to a final volume of 50 ml. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis.

3.0 INTERFERENCES

Addition of nitric acid to samples that contain organics, such as TCLP extracts, could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided.

A smaller sample size can be used but the final water volume must be adjusted to approximately 10 ml prior to the heating stage.

4.0 APPARATUS AND MATERIALS

Microwave Digestion System CEM–Model MDS – 81D and MARSX-Model # 907600:

- The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to insure uniform microwave heating.

- The MARSX consists of a microwave drying system with an operator selectable power output of 0-1200 watts in, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon® coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

- Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

Analytical balances, 510g capacity, minimum accuracy ± 0.001g and 250g capacity, minimum accuracy ±0.0001g.

Filter funnel, glass or disposable polypropylene.

Glass-fiber filter paper, 0.45 μm.

Membrane filters, 0.45 μm.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Disposable polypropylene vessels, 50 ml, compatible with centrifuge.

Plastic containers to support minimum of 200 ml.

Disposable Pasteur pipettes.

Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 μl to 5,000 μl.

Centrifuge (IEC Centra GP8).

5.0 REAGENTS

Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM standard criteria.

Concentrated nitric acid, HNO_3, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank.

Standards added to digestion:

- Spiking Solutions
  - Spiking solutions are prepared according to the Standard Prep Log (Figure 1). The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used.
  - All standards are NIST traceable.
  - Multi-element standard solution **WS1** (Figure 1), contains 10 μg/ml (ppm) each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Sr, Sn, Ag, Tl, Ti, V, and Zn. The spiking solution is made by diluting the WS1, 2 to 1 (5 μg/ml). The 5 μg/ml spiking solution is added to the QC samples accordingly, 0.5 ml is added to MS/MSD samples and 0.5 ml is added to the laboratory control sample (LCS), using the Eppendorf automatic pipette.
  - Multi-element standard solution High Purity Mineral (**HM)** (Figure 1) contains 100 μg/ml each of Ca, K, Mg, and Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), by weighing the amounts (1.0 g, 0.50 g) on the scale.
- Internal Standards (After digestion):
  - Lithium 6, 1000 μg/ml stock solution.
  - Scandium, 1000 μg/ml stock solution.
  - Yttrium, 1000 μg/ml stock solution.
  - Rhodium, 1000 μg/ml stock solution.

- Rhenium, 1000 μg/ml stock solution.

- Internal Standard working solution (**IS-WS**): From the above stock solutions, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the bottle will be 2.5 μg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* standards, samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

  NOTE: The stock solutions are NIST traceable and provided with a certificate of analyses and MSDS sheets by the manufacturer.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Water samples are collected in HNO_3 pre-preserved plastic containers and are acidified to pH of <2. (Approximately 125 ml volume). Holding times for metals are 6 months from the date of sampling, with the exception of Mercury, which is not covered by this SOP.

7.0 PROCEDURE

1. The Microwave Accelerated Reaction Systems are equipped with a temperature feedback control system. Microwaves are calibrated once a year according to the manufacturer's operation manual.

2. All digestion vessels are disposable and are used only once, which allows for better sample control and prevents cross contamination.

   CAUTION: - Toxic nitrogen oxide fumes may evolve; therefore all work must be performed in a properly operating ventilation system.

   - *Loss of sample through splattering inside the microwave system must be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.*

3. Digestion using industrial Microwave.

   - A 0.5 to 25 ml/grams aliquot of a well shaken sample is transferred into the digestion vessel; sample volume is determined by sample matrix and sample history. The vessel is labeled with the sample number, which is also recorded on the digestion log (Figure 2).

- With every batch of 20 analytical samples measure a volume of reagent water equal to the sample volume as described at above into a vessel labeled LRB. This represents the Laboratory Reagent Blank (LRB), which is carried through the entire digestion procedure, the same as an analytical sample.

- With every batch of samples measure a volume of reagent water equal to the sample volume as described at above into a vessel labeled LCS. This represents the Laboratory Control Sample (LCS), which is carried through the entire digestion procedure, the same as an analytical sample.

- For every 10 samples measure, in a similar manner, an amount equal to the parent sample of the sample designated for Matrix Spike (MS) and Matrix Spike duplicate (MSD) or duplicate (Dup).

- For analysis of all metals except Ca, Mg, K and Na, add 0.5 ml of the QC Spiking Solution to the QC samples (LCS, MS/MSD). For Ca, Mg, K and Na, add 0.5 ml of the HM solution to the LCS, and 1.0 ml of the HM solution to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the digestion log (Figure 2).

- Add 1 $\pm$ 0.1 ml of concentrated nitric acid to each vessel, by using the bottle top dispensers in the fume hood.

CAUTION: Addition of nitric acid to the non-aqueous (solvents) samples needs to be performed slowly, dropwise if possible in order to control the potential reaction. When the reaction has subsided, swirl the vessel lightly, dilute the sample to approximately 10 mL, and go to the next step.

- Loosely cap the vessel and place into the carousel.
- Samples are slowly ramped in the microwave to 95 ± 5 degrees Celsius over the course of a few minutes and maintained at this temperature for 30 minutes.

- After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood.

- When the vessels have cooled to near room temperature, determine if the microwave vessels and caps are intact. If the sample vessel look compromised (i.e. cap is not on, sides of the vessel are wet), then the sample is considered compromised and the sample must be re-digested.

- Add 1 ml of the Internal Standard working solution, using an Eppendorf automatic pipettor, and dilute to the 50 ml mark with DI Water into a calibrated digestion vessel (per lot).

- If the digested sample contains particulate matter, which has the potential to clog the nebulizer, the sample needs to be centrifuged, allowed to settle, or filtered.

    - Settling: allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this; however this can frequently be accomplished in a few hours. If it does not, centrifuge or filter the sample.

    - Centrifugation: centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.

    - Filtering: the filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 μm filter paper and transfer the liquid to a new vessel. Glass fiber filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

4. Calculations:

Dilution factor (DF:

$$DF = \frac{Final\ Volume\ (50)}{Sample\ amount}$$

Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

% Difference (%D)
Used for serial dilution test in metals.

$$\%D = \left| \frac{X_1 - X_2}{X_1} \right| \times 100\%$$

where: %D = percent difference
X_1 = Initial concentration
X_2 = Duplicate concentration

- Record pertinent information onto the digestion log (Figure 2). The following information must be included: Date, start time, end time, analyst initials, method reference, sample IDs, sample weight or volume, MS/MSD/LCS spiking concentration and lot #, acid lot #, dilution factor, final volume and any pertinent remarks.

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 1 and 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. A dilution test is performed once per every 20 samples. The dilution test is performed by taking 10 mls of a parent sample after digestion and adding 0.8 mls acid and 0.8 mls internal standard and bringing to a final volume of 50 mls with DI water. The dilution test is used to identify matrix interference and is not applicable if the measured concentration is less than 100 times the MDL for each measured analyte.

The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

12.0 WASTE DISPOSAL

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Samples.

- All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory wastewater.

- As a "small generator" of metals, Merit Laboratories has been approved for this type of disposal from the local government.

Acid bottles.

- Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for metals a sample batch consists of 20 samples or less.

Method Blank (Laboratory Reagent Blank) (LRB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes carried through the complete sample prep and analytical procedure. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (MS) (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (MSD) (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Dilution Test: a digested sample is diluted five-fold and analyzed to determine if matrix interference is present.

14.0 REFERENCES

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TABLE 1 Quality Control Items, Frequency and Corrective Action

QA Items	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Laboratory Reagent Blank (Method Blank)	One per sample batch	<RL/dilution	Remove contamination and re-digest sample set
Laboratory Control Sample	One per sample batch	85%-115%	Re-digest the sample set
Matrix Spike	One per every 10 samples	75%-125%	Analyze by Method of Standard Additions (MSA)
Matrix Spike Duplicate	One per ever 10 samples	75%-125% RPD <20%	Analyze by Method of Standard Additions (MSA)
Matrix Duplicate	One per every 10 samples	RPD <20%	Re-digest the sample set and QC.
Dilution Test	One per sample batch	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.

TABLE 2 Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Linear Dynamic Range (LDR) or High-level Check Standard	At initial set-up and checked every 6 months with a high standard at the upper limit of the range.	Within ±10% of true value.	Dilute samples within the calibration range, or re-establish/verify the LDR.	Flagging is not appropriate.	Data cannot be reported above the calibration range without an established/passing high-level check standard.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial Calibration (ICAL) for All Analytes	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, $r2 \geq 0.99$.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes, within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of the true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

			Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.		
Low-level Calibration Check Standard (LLCCV)	Daily.	All reported analytes within ± 20% of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid low-level calibration check standard (LLCCV). LLCCV should be less than or equal to the LOQ. If the concentration of the lowest calibration standard os less than or equal to the LOQ, the lowest standard may be re-quantified against the calibration curve as LLCCV. Otherwise, a separate standard must be analyzed as the LLCCV prior to the analysis of any samples.
Internal Standards (IS)	Every field sample, standard and QC sample.	IS intensity in the samples within 30-120% of intensity of the IS in the ICAL blank.	If recoveries are acceptable for QC samples, but not field samples, the field samples may be considered to suffer from a matrix effect. Reanalyze sample at 5- fold dilutions until criteria is met. For failed QC samples, correct problem, and rerun all associated failed field samples.	Flagging is not appropriate.	Samples suffering from matrix effect should be diluted until criteria are met, or an alternate IS should be selected.
Method Blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated	Results may not be reported without a valid method blank. Non-detects associated with positive blank infractions may be reported. Samples results > 10X the LOQ associated with negative blanks

				preparatory batch	may be reported. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV.	The absolute values of all analytes must be < ½ LOQ or 1/10th the amount measured in any sample.	ICB: Correct problem and repeat ICV/ICB analysis. If that fails, rerun ICAL. All samples following the last acceptable Calibration Blank must be reanalyzed. CCBs may not be re-analyzed without re-analysis of the associated samples and CCV(s).	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. Non-detects associated with positive blank infractions may be reported. Sample results > 10X the LOQ associated with negative blanks may be reported. For CCB, failures due to carryover may not require an ICAL.
Interference Check Solutions (ICS) (also called Spectral Interference Checks)	After ICAL and prior to sample analysis.	ICS-A: Absolute value of concentration for all nonspiked project analytes <1/2 LOQ (unless they are a verified trace impurity from one of the spiked analytes) ICS-AB: Within ± 20% of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the failed ICS.	All analytes must be within the LDR. ICS-AB is not needed if instrument can read negative responses.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits	Examine the project specific requirements. Contact the client as to additional	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to

		are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	measures to be taken.	are not met and explain in the case narrative.	determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Dilution Test	One per preparatory batch if MS or MSD fails.	Five-fold dilution must agree within ± 10% of the original measurement.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Only applicable for samples with concentrations > 50 X LOQ (prior to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post Digestion Spike (PDS) Addition	One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible).	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 6020 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	78	124
7440-36-0	Antimony	72	124
7440-38-2	Arsenic	82	118
7440-39-3	Barium	86	116
7440-41-7	Beryllium	80	120
7440-42-8	Boron	74	128
7440-43-9	Cadmium	84	116
7440-70-2	Calcium	86	118
7440-47-3	Chromium	83	119
7440-48-4	Cobalt	84	115
7440-50-8	Copper	84	119
7439-89-6	Iron	81	124
7439-92-1	Lead	84	118
7439-93-2	Lithium	75	120
7439-95-4	Magnesium	80	123
7439-96-5	Manganese	85	116
7439-97-6	Mercury	74	126
7439-98-7	Molybdenum	83	114
7440-02-0	Nickel	84	119
7440-09-7	Potassium	85	119
7782-49-2	Selenium	80	119
7440-22-4	Silver	83	118
7440-23-5	Sodium	79	125
7440-24-6	Strontium	75	129
7440-28-0	Thallium	83	118
7440-29-1	Thorium	81	116
7440-29-1	Tin	82	121
7440-32-6	Titanium	83	117
7440-61-1	Uranium	83	120
7440-62-2	Vanadium	82	116
7440-66-6	Zinc	82	119

Method 6020 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	84	117
7440-36-0	Antimony	85	117
7440-38-2	Arsenic	84	116
7440-39-3	Barium	86	114
7440-41-7	Beryllium	83	121
7440-42-8	Boron	73	130
7440-43-9	Cadmium	87	115
7440-70-2	Calcium	87	118
7440-47-3	Chromium	85	116
7440-48-4	Cobalt	86	115
7440-50-8	Copper	85	118
7439-89-6	Iron	87	118
7439-92-1	Lead	88	115
7439-93-2	Lithium	78	126
7439-95-4	Magnesium	83	118
7439-96-5	Manganese	87	115
7439-97-6	Mercury	70	124
7439-98-7	Molybdenum	83	115
7440-02-0	Nickel	85	117
7440-09-7	Potassium	87	115
7782-49-2	Selenium	80	120
7440-22-4	Silver	85	116
7440-23-5	Sodium	85	117
7440-24-6	Strontium	82	118
7440-28-0	Thallium	82	116
7440-29-1	Thorium	87	121
7440-29-1	Tin	86	115
7440-32-6	Titanium	83	115
7440-33-7	Tungsten	85	122
7440-61-1	Uranium	87	120
7440-62-2	Vanadium	86	115
7440-66-6	Zinc	83	119

FIGURE 1: STANDARD PREP LOG

Standard Preparation PE

Inorganic Stock Solution IV-28 (100 ppm) + CGSN1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 5.0 ppm	HNO_3	Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0002 ppm	0.20 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Standard Preparation HP

Inorganic Stock Solution IV-28(100 ppm) + CGSN1-1 (1000 ppm)

V. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

VI. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

VII. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

VIII. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 2.5 ppm	HNO_3	Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

ICP/MS MINERALS PREP LOG

Date	IS ID	Exp. Date	Analyst

Standards **ppm**	**Volume of Working Stock**	**Source and Lot # of Working Stock (100ppm)**	**Internal Standard 5.0 ppm**	**HNO_3**	Final Volume
0.0	**0.0**		**2 mls**	**2 mls**	**100 mls**
0.50	**0.5**		**2 mls**	**2 mls**	**100 mls**
1.0	**1.0**		**2 mls**	**2 mls**	**100 mls**
2.0	**2.0**		**2 mls**	**2 mls**	**100 mls**
5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**
10.0	**10.0**		**2 mls**	**2 mls**	**100 mls**
ICV – 5.0	**5.0**		**2 mls**	**2 mls**	**100 mls**

FIGURE 2: METALS DIGESTION LOG

Metals Digestion 3015A \ 3050B

DATE _____ PREP BATCH MTD-_____

TIME START _____ TIME FINISH _____ ANALYST _____

Pipet Calibration:

Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria	Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria
2	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value	3	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value
	2					2			
	3					3			

SAMPLE#	BTL ID	SAMPLE AMOUNT GRAMS (g)	FINAL VOLUME (ml)	REMARKS	% TOTAL SOLIDS	DILUTION FACTOR
LCS -	----	50	**50**		—	1
LRB-	----	50	**50**		—	1

NOTES: *1) Spike values (unless otherwise stated):*

LCS = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

1.1. Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution

Spiking Solution – Date Prepared: _____

2) Spike values for minerals (Ca-Mg-K-Na)

LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution

Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution

High Purity Stock Solution (HM)- Lot # _____

3) HNO_3 Lot # _____ *4) Centrifuge Tube Lot #* _____

5) Balance ID: _____ *Reviewed by* _____ *On* _____

STANDARD OPERATING PROCEDURE

METALS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY METHODS 6020, 6020A, 200.8

APPROVALS:

Barbara Ball

01/15/18

QA Officer Date

01/15/18

Technical Director Date

Number	Description of Change	Date
001	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
002	Emergency SOP Amendment Form updates	02/09/16
003	Updated to comply with DoD QSM 5.0 standards.	03/10/16
004	Updated to comply with DoD QSM 5.1 standards.	01/15/18
005		
006		
007		
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable for the determination of sub-μg/L concentrations of a large number of elements in water samples and in waste extracts or digestions. When dissolved constituents are required, samples are filtered through 0.45 μm membrane filters and acid-preserved prior to analysis. No digestion is needed prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is performed for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are needed. Acid digestion is also needed prior to analysis to dissolve elements in water samples with turbidity <1 NTU. This SOP follows the guidelines of the EPA Methods 200.8, 6020, and 6020A. The metals that are determined by using this SOP are listed in Table 1 with associated reporting limits (RL) and quantitation limits (QL) and which methods can be used for each element.

If this SOP is followed to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method as well as method detection limit (MDL) and multi-point calibration. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality. Use of this SOP is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical and physical interferences in ICP-MS.

2.0 SUMMARY OF METHOD

Prior to analysis, samples which require total ("acid-leachable") values are digested using appropriate sample digestion procedures (Document #'s MET-003 and MET-001). This SOP describes the measurement of ions produced by radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios, and quantified with a channel electron multiplier. Potential interference from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundance. Interference corrections include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

3.0 INTERFERENCES

There are three fundamentally different sources of interference in ICP-MS: spectroscopic interferences, physical interferences, and memory interferences.

- **Spectroscopic Interferences** are interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass-to-charge (m/z ratio of the analyte elements). They can be isobaric elemental and isobaric molecular interferences (polyatomic, refractory oxide, and doubly charged ions).

  - Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the analyte element. These are managed by the selection of an alternate isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobaric interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca. In this case, the use of ^{43}Ca or ^{44}Ca is recommended. The appropriate elemental interference equations are incorporated in the methods (or parameter) used for calibration and data acquisition.

  - Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that affect ICP-MS determinations have been identified. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundance, the most precise coefficients for an instrument is determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics.

    - Example for As is as follows: Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic is calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06% of the $^{40}Ar^{35}Cl^+$ signal): Corrected arsenic signal (using natural isotopes abundance for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

      NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$ (e.g., $^{81}BrH^+$ from bromine wastes[6]).

- Example for Cd is as follows: corrected cadmium signal (using natural isotopes abundance for coefficient approximations) = (m/z 114 signal) - (0.027) (m/z 118 signal) - (1.63) (m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

  NOTE: Cadmium values are biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

  NOTE: Since there is a certain degree of uncertainty as to which equation is better to use, and in what cases, it is up to the analyst to determine how the interference is corrected, upon the evaluation of data. It is suggested that the <u>elemental</u> isobaric interference equations be <u>included</u> in all methods (parameters) from the beginning, but potential <u>polyatomic</u> species (masses) that could interfere be <u>only monitored</u> (except for $^{40}Ar^{35}Cl^+$ on As). When species monitored indicate that an isobaric molecular interference is present, the equations can be adjusted to correct for such interference and data be reprocessed to produce an interference free summary report. Generally, an interference is easy to spot when multiple isotopes of an element show different results. Since the interference is additive, the use of the isotope with the lowest result is suggested for data reporting, providing that all other QC criteria are met (See Table 6a & 6b for summary of QC requirements).

- Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Wing overlap interference can occur when a small ion peak is being measured adjacent to a large one. The potential for these interferences must be recognized, and the spectrometer resolution adjusted to minimize them. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require matrix separation, or analysis using another verified and documented isotope.

♦ **Physical Interferences** are associated with the physical processes, which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences can result in differences between instrument responses for the samples and calibration standards. Physical interferences can occur in the

transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects). To minimize some of these effects, acid composition and concentration must be matched for all standards, blanks, and samples. Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. Internal standardization is effectively used to compensate for many physical interference effects. Internal standards must ideally display similar analytical behavior to the elements being determined. Generally, an internal standard must be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, ^{185}Re, and ^{209}Bi.

- **Memory Interferences** result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition can occur is dependent on the sample and needs to be minimized through the use of a rinse blank between samples. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run must be recognized and suitable rinse times must be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition. High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If memory interference is suspected, the sample must be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.

4.0 APPARATUS AND MATERIALS

Inductively coupled plasma-mass spectrometers:

- **Perkin Elmer (PE) Elan 9000 ICP-MS:**
  - Windows XP Operating System
  - Elan 3.0 Software
  - Cetac Asx510 Autosampler
- **Hewlett-Packard (HP) 4500 ICP-MS**:
  - Windows 95 Operating system.
  - Chem Station Software.

- Cetac ASX150 Autosampler.

♦ **Agilent 7500Ce ICP MS:**

- Windows XP Operating system.
- Chem Station Software.
- Agilent ASX 500 Series autosampler .

Argon gas supply: liquid argon cylinders

Analytical balance, 510 g capacity, minimum accuracy ± 0.001 g.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.

Note: dispensers are calibrated quarterly according to SOP #010010.

Disposable Pasteur pipettes.

Polypropylene vessels, 50 mL.

Plastic cups to support minimum of 200 ml.

Plastic bottles.

5.0 REAGENTS & STANDARDS

Nitric Acid (HNO_3), concentrated, Trace Metal Grade. Acids used in the preparation of standards and for sample processing must be of high purity. Trace metal grade (also known as re-distilled) acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at 2% (v/v) or less in the solution to be analyzed is required for ICP-MS, in order to minimize damage to the interface.

Hydrochloric Acid (HCl), concentrated, Trace Metal Grade. Several polyatomic ion interferences result when HCl is used. However, its use is recommended to maintain stability in solutions containing high concentrations of antimony and silver. When used, corrections for the chloride polyatomic ion interference must be applied to all data.

Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

Internal Standard stock solutions:

♦ Lithium 6, 1000 µg/ml stock solution.

- Scandium, 1000 μg/ml stock solution.
- Yttrium, 1000 μg/ml stock solution.
- Rhodium, 1000 μg/ml stock solution.
- Rhenium, 1000 μg/ml stock solution.
- Internal Standard Working Solution (IS-WS): From the above stock solution, 2.5 ml of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight), which corresponds to 2.5 μg/ml. This represents the internal standard working solution from which 1 ml (for a 50 ml final volume) must be added to all calibration standards and blanks. This provides a 0.05 ppm of internal standard concentration in all calibration standards, similar to analytical samples.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for blank page of standard preparation log book page.

Multi-element standard stock solution from three of four different vendors:

- Inorganic Venture (IV), 100 mg/L each of Ag, Al, B, Ba, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of standards.
- High Purity Standards (HM), 100 μg/ml each of Ca, Mg, K, and Na. This solution is used for the preparation of the calibration standards and for the minerals standard.
- SPEX Industries (S), 100 μg/ml each of Al, Sb, As, Ba, Be, B, Cd, Ca Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of the initial calibration verification (ICV) standards.
- Phenova, concentration varies by lot number and element but contains all of the following Al, Sb, As, Ba, Be, B Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Zn, V, Th, and S.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for Standard Prep Log and Appendix 2 for ICV prep log.

Multi-element calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 2% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. The calibration standards are kept in plastic bottles and prepared every two weeks or more frequent if needed.

They must be verified using a quality control standard (ICV). Table 2 (metals) and Table 3 (minerals) are used as guidance, when preparing standards.

Blanks: Three types of blanks are required for the analysis. The calibration blank (std-0.00) is used in establishing the calibration curve. The Laboratory Reagent Blank (LRB) also known as method blank is used to monitor possible contamination resulting from the sample preparation procedure. The rinse blank (also called optional rinse or autosampler wash) is used to flush the system between all samples and standards.

- The calibration blank (std-0.00), the initial calibration blank (ICB), and the continuing calibration blank (CCB) consists of the same concentration(s) of the same acid(s) used to prepare the calibration standards, along with the appropriate concentration of internal standard. The preparation of these blanks can be found in the standards prep-log. The calibration blank is used in the calibration process, the ICB is used to check the instrument before analyzing samples, and the CCB is used to verify the instrument in the middle and end of analytical runs.

- The Laboratory Reagent Blank (LRB) also known as method blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

- The rinse blank consists of 2% HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between all standards, quality control samples, and analytical samples. Rinse blank is prepared by adding 20 ml of concentrated HNO_3 to 1000 ml of DI water in a large plastic container.

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interference such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

- Interference check stock solution A, containing 1000 μg/ml each of Al, Ca, Fe, Mg, Na, P, K, and S, 2000 μg/ml of C, 10000 μg/ml of Cl, and 20.0 μg/ml each of Mo and Ti. The ICS-A solution is prepared by weighing 10.0 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO_3, and dilution to 100 g on the scale with reagent water.

- Interference check stock solution AB, containing 2.0 μg/ml each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn. The ICS-AB solution is prepared by weighing 1.00 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO_3, and dilution to 100 g on the scale with reagent water.

- The final concentration of the elements in ICS-A and ICS-AB is listed in Table 4. These solutions are prepared fresh every 2 weeks or as needed.

The initial calibration verification solution (ICV) is used to verify the calibration before samples are analyzed. The ICV must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard (known as a second source) is defined as a standard from a source different from those used in the standards for instrument calibration.

Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Number 5, Section 7.0). This solution is also used to verify that the instrument has reached thermal stability (See See Number 4, Section 7.0).

- Tuning solution for HP 4500 ICP-MS: 10 μg/ml each of Li, Y, Ce, and Tl is used to tune the instrument according to the manufacturer instructions.

- Tuning solution for PE Elan 9000 and Agilent 7500Ce ICP-MS: 10μg/ml each of Li 7, Be 9, Mg 25, Co 59, In 115, Tl 205, and Pb 208.

Working standards and solutions are prepared every two weeks according to recipes in the standards prep log. The logbook is available in the metals lab. Concentrations of the LCS can be found on the laboratory bench sheet.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are collected in appropriate plastic or glass containers.

- Water samples are collected in HNO_3 pre-preserved plastic containers (approximately 125 ml volume), and are acidified to pH of <2.

- Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ±2 C° upon receipt.

Holding times for metals are 6 months from the date of sampling to analysis. For TCLP samples the holding time is 6 months from sampling to TCLP extraction then 6 months from TCLP extraction to analysis.

7.0 PROCEDURE

1. Solubilization and digestion procedures are presented in the Sample Preparation Document #'s (MET-003 and/or MET-001). A sample digestion log sheet is found in Figure 3.

2. Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.

3. Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

4. Operating conditions: The analyst must follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. The thermal stability must be verified by analyzing a tuning solution described in Section 5.0.

5. For all analysis tune instrument according to following parameters.

   - ♦ The tuning must include beryllium, magnesium, cobalt, indium, and lead. Conduct mass calibration and resolution checks in the mass regions of interest.

   - ♦ The mass calibration and resolution parameters are required criteria that must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value.

   - ♦ The resolution must be verified to be within 0.6-0.9 amu full width at 5 percent peak height (not applicable for HP4500 ICP-MS due to manufacturer presets).

   Note: A peak height of 5 percent is used instead of 10 percent because 5 percent is the tighter restriction and this SOP is written to meet the requirements of methods 200.8, 6020, and 6020A.

   - ♦ Perform tune after machine is warmed up and every 12 hours following.

   Note: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

6. The instrument is calibrated daily and re-calibrated as needed. Calibrate the instrument for the analytes of interest (recommended isotopes for the elements in Table 1 are provided in Table 5a and Table 5b), using the calibration blank and at least three non-zero calibration standards according to the instrument manufacturer's procedure. A multi-point calibration curve is analyzed and evaluated. For the calibration curve to be acceptable, a correlation coefficient of greater than or equal to 0.998 must be achieved. If the required correlation coefficient is not achieved then the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. If narrowing the linear range does not improve the correlation coefficient to 0.998, then replace the calibration standards and re-calibrate the instrument. The reporting limit (RL) must be greater than or equal to the lowest calibration point or the concentration of low level initial calibration verification (LLICV), whichever is lower.

The principle of calculation for the linear curve fit and the coefficient of determination (COD) is found in SW 846 method 8000C Sections 11.5.2.1 through 11.5.2.3. ICP-MS manufacturer software is preprogrammed for this calculation.

The multi point calibration is verified with a mid level ICV standard with control limits of 90%-110% and a low-level ICV with limits of 70%-130% (80%-120% for DoD projects). Table 2 and Table 3 (Section 5.0) provide information to what calibration standards are used. (More information on limits and corrective actions can be found in Section 8 and Table 6a & 6b). Flush the system with the rinse blank (Section 5.0) between each standard solution. The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

7. All masses that affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. Preferred isotopes are referenced in Tables 5a and 5b.

8. Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the initial calibration verification solution (ICV, Section 5.0) using a second source standard. When measurements exceed ± 10% of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. During the course of an analytical run, the instrument may require re-calibration to correct for instrument drift. A re-calibration must then be followed immediately by a new analysis of an ICV, LLICV, and initial calibration blank (ICB) before any further samples are analyzed. Corrective actions for specific situations are found in Section 8 and summarized in Table 6a & 6b.

9. A low-level initial calibration verification (LLICV) must be analyzed after every calibration to verify the linearity near the lower end of the calibration curve. The LLICV is made from the same source as the calibration standards at a concentration comparable to the reporting limits of elements being reported. When the LLICV measurements exceed ± 30% (± 20% for DoD projects) of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).

10. Flush the system with the rinse blank solution (Section 5.0) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (CCV), and the continuing calibration blank (CCB) at a frequency of at least once every 10 analytical samples (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).

11. Dilute and reanalyze samples that are more concentrated than the linear range (LR) (Section 8.0) for an analyte or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (Numbers 6 through 8, Section 7.0).

12. Interference Check Solutions (ICS) are run to verify the magnitude of elemental and molecular-ion isobaric interferences. This is performed every 12 hours. This is done by analyzing interference check solutions A and AB. (Concentration of elements in solution found in Table 4, other reagent information is in Section 5.0)

Corrective Action: The ICS needs to be within 70-135% (± 20%, of true value, for DoD projects). If the ICS fails, re-evaluate the equations used for the corrections, make the necessary adjustments, recalibrate the instrument and re-analyze the samples associated with the failed ICS. See Table 6a &6b for ICS summary and Section 8.0 for more information.

Note: Precipitation from solution AB can occur with some elements, specifically silver. Rinse the instrument 5 –10 minutes before analyzing any other samples to help improve performance.

13. Calculations: the quantitative values are reported in appropriate units, such as milligrams per liter (mg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples.

♦ The appropriate dilution factor (DF) on water samples resulted from sample preparation (see Document # MET-003) is entered in the data system for each sample at the time of programming the

sequence to be analyzed. If additional dilutions are performed, the appropriate corrections must be applied to the dilution factor, using the following equation

C *x* DF = SC
Where, C = digest concentration
DF = Dilution Factor
SC = Sample Concentration

The ICP/MS software carries out this calculation for the analyst.

- Generally, for solid samples, DF includes the correction necessary for the determination of a dry weight result. If this is not the case or if a dry weight result is requested at a later time, calculate results for solids on a dry-weight basis as follows:

  (1) A separate determination of percent solids must be performed.

  (2) A new DF is calculated, based on the original wet weight of the sample (from the preparation log) and the percent total solids. The sequence is updated with the new DF, data reprocessed, and a new quantitation report is generated by the data system.

  (3) Manual calculation of the dry weight concentration (DWC) by the formula:
  $$DWC(mg/kg) = \frac{CxV}{WxS}$$
  Where, C = Digest Concentration (mg/L).
  V = Final volume in liters after sample preparation.
  W = Weight in kg of wet sample.
  S = (% Total Solids)/100.

- Calculations performed by the data system include appropriate interference corrections, internal standard normalization, and the summation of signals (for example 206, 207 and 208 m/z for lead) to compensate for any differences in the abundances of these isotopes between samples and standards.

Note: The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

- Hardness by Calculation

  The preferred method for calculating Hardness Standard Method 2340B. Hardness is calculated from the Calcium and Magnesium results from this procedure using the following equation:

  CaCo3/L = 2.497 [Ca] + 4.118[Mg]
  Where:
  CaCO3 is the total hardness by calculation
  Ca is the total Calcium by 6020A in mg/L
  Mg is the total Magnesium by 6020A in mg/L

Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

% Difference (%D)
Used for serial dilution test in metals.

$$\%D = \left| \frac{X_1 - X_2}{X_1} \right| \times 100\%$$

where: %D = percent difference
X_1 = Initial concentration
X_2 = Duplicate concentration

8.0 QUALITY CONTROL

All quality control data must be maintained and be available for easy reference or inspection.

Demonstration of Performance.

- The demonstration of performance is used to demonstrate instrument performance and has two parts. The first is initial demonstration of performance this is done by performing method detection limit (MDL) studies, linear range studies, and precision and accuracy studies prior to the analysis of samples. The second is continual demonstration of performance is done by annual MDLs and linear range studies. MDL studies are performed by following SOP #060004 (Determination of Method Detection Limit). Analyst performance is demonstrated by analysis of proficiency test and blind samples multiple times per year.

- Linear calibration ranges: Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range must be established by determining the signal responses from a minimum of five different concentration standards. Care must be taken to avoid potential damage to the detector during this process. The linear calibration range, which is used for the analysis of samples, must be judged by the analyst from the resulting data. The upper LR is defined as the maximum concentration for which the measured concentration is within ±10% of the true value. Determined sample analyte concentrations that are greater than the upper LR limit must be diluted and reanalyzed. The LR must be verified whenever, in the judgment of the analyst, a change in analytical performance caused by

either a change in instrument hardware or operating conditions would dictate they be re-determined. See Section 7.6 for curve specific criteria.

To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If an interference source is present, and cannot be corrected, the sample elements impacted must be flagged. The ICS is used to verify the correction equations used by the instrument. Requirements are found in Section 8.0 and Table 4 and preparation information is in Section 5.0.

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard falls outside the control limits as compared with the first calibration standard (Calibration Blank or std-0.00), the following procedure is followed. Check for instrument drift, instrument drift is characterized by internal standards outside control limits for QC samples (Section 8.0), recalibrate instrument and reanalyze samples. If matrix interference is suspected, the sample must be diluted at least fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. (Summary of control limits and corrective actions can be found in Table 6a & 6b)

- The intensity levels of the internal standards for the ICV/ICB/LLICV, CCV/CCB, LCS/LRB must also be within the specified acceptance limits (refer to Section 8.0 for limits and Section 7.0, Numbers 6-12 for procedure information). If they are not within limits, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

Check the instrument calibration by analyzing appropriate quality control solutions as follows (Summarized in Table 6a & 6b):

- Initial Calibration must include a blank and minimum of three non-zero points. A correlation coefficient of 0.998 must be achieved. Section 7.0 for calibration procedure.

- Immediately after instrument calibration check instrument calibration by analyzing the ICV described in Section 5.0. ICV limits are 90%-110%. The ICB has to be less than the lower limit of quantitation for every target element. The lower limit of the calibration must be checked by analyzing the low-level initial calibration verification (LLICV) with acceptance limits of 70%-130% (± 20% for DoD projects). Summary of limits and corrective actions are found in Table 6a & 6b, the procedure for this is found in Section 7.0, Numbers 6 through 9.

- When running samples verify calibration at a frequency of every 10 analytical samples with the CCV standard with limits of 90-110% and the continuing calibration blank (CCB) with acceptance criteria of less than the lower limit of quantitation for every target element. These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. See Table 6a &6b for summary of acceptance criteria and corrective actions, the procedure for this information for this is found in Section 7.0, Number 10.

- Corrective action for out of compliance ICV, LLICV, and CCV, is to terminate the analysis, correct the problem, and recalibrate the instrument. Control limits and corrective actions are found in Section 8.0 and summarized in Table 6a & 6b.

Laboratory Reagent blank (LRB) also known as Method blank. Method blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate analytical process. The LRB has to be below the RL divided by the dilution factor for each target analyte. If the LRB does not contain target analytes at a level that interferes with the project specific requirements, then the LRB is acceptable. Control limits and corrective actions are summarized in Table 6a & 6b.

A Laboratory Control Sample (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS must be prepared and analyzed for each sample batch at a frequency of one LCS for a least every 20 samples or every 10 samples for drinking waters. The recovery limits for the LCS are 85-115% of the true value (stated in the preparation log). If the LCS is outside of the control limits the entire sample batch must be re-digested and re-analyzed. Control limits and corrective actions are summarized in Table 6a & 6b. (In method 200.8, the LCS is referred to as the Laboratory Fortified Blank, LFB).

Analyze one matrix spike (MS) sample for every 10 analytical water samples or every 20 analytical soil samples. For majority of the elements, the aqueous samples are spiked at levels similar to the LCS (0.05 ppm in the analysis solution). For solid samples, a concentration of 0.10 mg/kg is added pre-digestion. The acceptable limits for performance are summarized in Section 8.10 and Table 6a & 6b.

- Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery must be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} x100$$

where: R = percent recovery.
C_s = spiked sample concentration.
C = sample background concentration.
S = concentration equivalent of analyte added to fortify the sample.

Analyze one matrix duplicate (Dp) sample for every 10 water samples or every 20 soil samples. In some cases, a matrix spike duplicate (MSD) is used instead of the matrix duplicate, especially if the analytes in the sample are of low concentration. A control limit of 20% RPD must not be exceeded for analyte values greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user must be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed. Control limits and corrective actions are summarized in Table 6a & 6b.

The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{\left|D_1 - D_2\right|}{\frac{D_1 + D_2}{2}} x100$$

where: RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate).

The Quality Control requirements and limits vary slightly, based upon the method referenced in the analytical report (i.e. 6020A vs. 200.8). For both methods, the calibration is verified by the analysis of ICV/ICB and CCV/CCB. Recalibration is required when either one falls outside the limits. The performance of the method is evaluated by the analysis of the LCS/LRB pair for every batch of 20 samples, and MS/MSD/Dp for every 10 water samples and 20 soil samples. The acceptable limits for performance are summarized in Table 6a & 6b and the procedures can be found in Section 7.0, Numbers 6-12.

- Requirements for all methods:
  - When the recovery for ICV/CCV falls outside ±10% terminate the analysis and recalibrate the instrument. The samples from the last CCV that was within limits are to be re-analyzed, after recalibration of the instrument.
  - The MS is represented by a spiked sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular spike fails to meet QC criteria. An analyte spike added to a portion

of a prepared sample, or its dilution, must be recovered to within 75 to 125 percent of the known value. The spike addition must be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample is spiked and re-analyzed according to Figure 1. The same recovery limits apply to the spiked dilution.

- The MSD is represented by a spiked duplicate sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular duplicate spike fails to meet QC criteria. The evaluation of the MSD is similar to the evaluation of the duplicate analysis described in Section 8.0.

- When the intensity of any internal standard in the sample to falls outside 70-125% of the intensity of that internal standard in the initial calibration standard (Calibration Blank or std-0.00), follow the procedure described in Section 8.0. The intensity levels of the internal standards for the ICV/LLICV/ICB and CCV/CCB must agree within ± 20 percent of the intensity level of the initial calibration standard (Calibration Blank or std-0.00). If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

♦ Method 6020/6020A specific requirements:

- Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 x MDL), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected, and the results flagged. One dilution test must be included with every batch of twenty samples.

- Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. This is done by analyzing the interference check solutions ICS-A and ICS-AB. The recovery of the elements of interest in ICS-AB (listed in Table 4 at a concentration of 0.02 ppm) must be between 70-135% (± 20% for DoD projects) (see Section 7.0, Number 12 for procedure information and Table 6a & 6b for a summary).

- The LLICV is used to verify the linearity of the low end of the calibration curve. The LLICV must be analyzed after every new calibration with the measurements not exceeding ± 30% (± 20% for DoD projects) of the true value. If the LLICV is outside of these limits the run must

be stopped and the instrument recalibrated and the new calibration verified (see Section 7.0, Number 9 for procedure information and Table 6a & 6b for a summary).

The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method. In an EPA multi-laboratory study, laboratories applied the ICP-MS technique to both aqueous and solid samples. The results are listed at the end of methods 200.8, 6020 and 6020A.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

- Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

12.0 WASTE DISPOSAL

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Samples.

- All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory wastewater.

- As a "small generator" of metals, Merit Laboratories has been approved for this type of disposal from the local government.

Acid bottles.

- Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: also referred to as a Laboratory Reagent Blank. an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (spiked sample or fortified sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is

available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (spiked sample or fortified sample duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Internal Standard: a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. An acceptable MDL standard check must produce a signal at least three times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Calibration Standards: a series of known standard solutions used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. A minimum of 4 calibration points are used for calibration. Acceptance of the calibration requires a correlation coefficient of 0.997 or better. No samples shall be analyzed without acceptable calibration.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

Initial calibration blank (ICB): a reagent blank solution, which is analyzed immediately following the ICV. The ICB is analyzed to check for drifts in calibration or possible analyte carry-over.

Continuing Calibration Blank (CCB): a reagent blank solution, which is analyzed immediately following the CCV. The CCB is analyzed to check for drifts in calibration or possible analyte carry-over.

14.0 REFERENCES

Method 200.8, Revision 5.4, 1998.

SW-846, Method 6020A Revision 1, 2007.

SW-846, Method 8000C Revision 3, 2003.

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Table 1. List of elements analyzed.

Element	**Symbol**	**CAS#**	**Reporting Limits**		**Method Reference**			DoD Reportable	Quantitaion limit * ug/L	Laboratory performance based
			mg/L	**mg/kg**	**6020**	**200.8**	**6020A**			
Aluminum	Al	7429-90-5	0.05	0.5	X	X	X	X	0.5	
Antimony	Sb	7440-36-0	0.002	0.3	X	X	X	X	2.0	
Arsenic	As	7440-38-2	0.001	0.1	X	X	X	X	0.5	
Barium	Ba	7440-39-3	0.01	1.0	X	X	X	X	0.5	
Beryllium	Be	7440-39-3	0.001	0.50	X	X	X	X	0.5	
Boron	B	7440-42-8	0.01	1.0						X
Cadmium	Cd	7440-43-9	0.0005	0.2	X	X	X	X	0.5	
Calcium	Ca	7440-70-2	0.05	10.0	X		X	X	200	
Chromium	Cr	7440-47-3	0.005	2.0	X	X	X	X	0.5	
Cobalt	Co	7440-48-4	0.01	0.5	X	X	X	X	0.5	
Copper	Cu	7440-50-8	0.004	1.0	X	X	X	X	0.5	
Iron	Fe	7439-89-6	0.1	1.0	X		X	X	2.0	
Lead	Pb	7439-92-1	0.003	1.0	X	X	X	X	0.5	
Lithium	Li	7439-93-2	0.01	1.0						X
Magnesium	Mg	7439-95-4	1.0	4.0	X		X	X	200	
Manganese	Mn	7439-96-5	0.02	1.0	X	X	X	X	2.0	
Molybdenum	Mo	7439-98-7	0.005	0.50		X		X	2.0	
Nickel	Ni	7440-02-0	0.005	1.0	X	X	X	X	0.5	
Potassium	K	7440-09-7	1.0	5.0	X		X	X	200	
Selenium	Se	7782-49-2	0.005	0.2	X	X	X	X	0.5	
Silver	Ag	7440-22-4	0.0002	0.1	X	X	X	X	0.5	
Sodium	Na	7440-23-5	0.05	10.0	X		X	X	200	
Strontium	Sr	7440-24-6	0.005	0.50					1.0	X
Tin	Sn	7440-31-5	0.02	1.0						X
Titanium	Ti	7440-32-6	0.005	1.0					0.5	X
Thallium	Tl	7440-28-0	0.001	0.50	X	X	X	X	0.5	
Vanadium	V	7440-62-2	0.004	1.0	X	X	X	X	0.5	
Zinc	Zn	7440-66-6	0.01	1.0	X	X	X	X	2.0	
* Quantitation limit for individual samples is affected by sample dilutions										

Table 2.

Standard Preparation PE

Inorganic Stock Solution IV-28 (100 ppm) + CGSN1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 5.0 ppm	HNO_3	Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0002 ppm	0.20 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Standard Preparation HP

Inorganic Stock Solution IV-28(100 ppm) + CGSN1-1 (1000 ppm)

V. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO_3;
Bring to a final volume of 100 mls = 10 ppm

VI. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

VII. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

VIII. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 2.5 ppm	HNO_3	Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Table 3. Standard preparation for Ca, Mg, K, Na (minerals).

Standards ppm	Volume of Working Stock	Source and Lot # of Working Stock (100ppm)	Internal Standard 5.0 ppm	HNO_3	Final Volume
0.0	0.0	High Purity (HM) –	2 mls	2 mls	100 mls
0.20	0.2	High Purity (HM) –	2 ml	2 ml	100 ml
0.50	0.5	High Purity (HM) -	2 ml	2 ml	100 ml
1.0	1.0	High Purity (HM) -	2 ml	2 ml	100 ml
2.0	2.0	High Purity (HM) -	2 ml	2 ml	100 ml
5.0	5.0	High Purity (HM) -	2 ml	2 ml	100 ml
10.0	10.0	High Purity (HM) -	2 ml	2 ml	100 ml
ICV- 5.0	5.0	Spex –	2 ml	2 ml	100 ml

Table 4. ICS Components and Concentration.

Solution Component	ICS-A (ppm)	ICS-AB (ppm)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.020
Cd	0.0	0.020
Cr	0.0	0.020
Co	0.0	0.020
Cu	0.0	0.020
Mn	0.0	0.020
Ni	0.0	0.020
Ag	0.0	0.020
Zn	0.0	0.020

Table 5a. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
19	K	Sc, Rh		
23	Na	Sc, Rh		
24	Mg	Sc, Rh		
43	Ca	Sc, Rh		
44	Ca	Sc, Rh	$(-0.0271)(^{88}C)$	Sr^{++}

Notes:
- † Recommended for PE instrument.
- ‡ Recommended for HP instrument.
- C = Counts at specified mass.
- When the concentration of Na in the samples is high, the ionization of Sc is suppressed leading to positive bias of the results, therefore Rh must be used as the internal standard, even if more than 50 amu removed from the element of interest.

Table 5b. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
6	Li	**I.S.**	-(0.0813)(^{7}C)	
7	Li	^{6}Li, Sc		
9	Be	^{6}Li, Sc		
10	B	^{6}Li, Sc		
11	B	^{6}Li, Sc		
27	Al	^{6}Li, Sc		
45	Sc	**I.S.**		CO_2H^+
47	Ti	^{6}Li, Sc		
49	Ti	^{6}Li, Sc		
51	V	^{6}Li, Sc	-(3.127)(^{53}C)+(0.352)(^{52}C)	$^{35}ClO^+$, $^{34}SOH^+$
52†	Cr	Sc, Y, Rh		ArC^+, ArO^+, $^{35}ClHO^+$
53‡	Cr	Sc, Y, Rh		$^{37}ClHO^+$
54†	Fe	Sc, Y, Rh	-(0.0284)(^{52}C)	
55	Mn	Sc, Y, Rh		$ArNH^+$
56	Fe	Sc, Y, Rh		
57‡	Fe	Sc, Y, Rh		
58†	Ni	Sc, Y, Rh		
59	Co	Sc, Y, Rh		
60	Ni	Sc, Y, Rh		
62	Ni	Sc, Y, Rh		TiO
63†	Cu	Sc, Y, Rh		$^{31}PO_2^+$, $^{40}ArNa^+$, TiO
65‡	Cu	Sc, Y, Rh		TiO
66	Zn	Sc, Y, Rh		TiO
68	Zn	Sc, Y, Rh		
75	As	Y, Rh	-(3.132)(^{77}C)+(2.736)(^{83}C)	$^{40}Ar^{35}Cl^+$
76	$^{40}Ar^{36}Ar^+$	Y, Rh		$^{40}Ar^{37}Cl^+$
77	Se	Y, Rh		
78†	Se	Y, Rh	-(0.1869)(^{76}C)‡	$^{40}Ar^{38}Ar^+$
82‡	Se	Y, Rh		$^{81}BrH^+$
83	Kr	Y, Rh		
88	Sr	Y, Rh		
89	Y	**I.S.**		
90	Zr	Y, Rh		
95	Mo	Y, Rh		$^{79}BrO^+$
98	Mo	Y, Rh	-(0.146)(^{99}C)	$^{79}BrHO^+$
99	Ru	Y, Rh		
103	Rh	**I.S.**		
105	Pd	Rh		
106	Pd, Cd	Rh		ZrO,
107	Ag	Rh		ZrO
108	MoO	Rh		ZrO, MoO
109	Ag	Rh		ZrO, MoO
111	Cd	Rh		ZrO, MoO
112	Cd	Rh	-(0.040)(^{118}C)	ZrO, MoO
114	Cd	Rh	-(0.0269)(^{118}C)	MoO
118	Sn	Rh		
119	Sn	Rh		
120	Sn	Rh	-(0.0127)(^{125}C)	
121	Sb	Rh	-(0.124)(^{125}C)	$^{40}Ar^{81}Br^+$
123	Sb	Rh		
125	Te	Rh		
137	Ba	Rh		
138	Ba	Rh	-(8.91E-04)(^{139}C)-(2.82E-04)(^{140}C)	
139	La	Rh		
140	Ce	Rh		
185	Re	**I.S.**		
203	Tl	Re		
205	Tl	Re		
206	Pb	Re		
207	Pb	Re		
208	Pb	Re	+(1.0)(^{206}C)+(1.0)($^{2.07}$C)	

Notes:
- † Recommended for the PE instrument.
- ‡ Recommended for the HP instrument.

Table 6a. Summary of Quality Control Items, Frequency, and Corrective Action.*

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tuning	After warm-up Every 12 hours	Manufacturer specifications	Check operating parameters, clean cones, replace malfunctioning components if necessary. Reevaluate the tuning.
Calibration Curve	Once a day and as necessary	$R \geq 0.998$ The lowest non-zero calibration point must be at or below reporting limit	Remove allowed points keeping minimum of 3 non-zero points, replace calibration standards if needed and recalibrate instrument.
ICV	After every calibration	90-110%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, and recalibrate the instrument.
ICB	After every ICV	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank and/or increase the rinse time between analyses; reanalyze ICB; if within limits, continue the run; if still outside limits, determine the source of the problem, make the necessary corrections, and start from the beginning with a new calibration.
LLICV	After initial calibration	70-130% Not required for 200.8	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, prepare a fresh calibration blank, and recalibrate the instrument.
CCV	After Every 10 sample or less	90-110%	Recalibrate the instrument. Follow method specific requirements (6020, 6020A or 200.8) as to what data prior to the CCV can be used.
CCB	After Every 10 sample or less	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank; reanalyze CCB; if within limits, continue the run; if still outside limits, eliminate the source of the contamination, clean the sample introduction system if necessary, and recalibrate the instrument. Reanalyze all samples from the last good CCB.
LCS	Every batch of 20 samples or less	85-115%	Re-digest the entire sample batch and reanalyze.
LRB (MB)	Every batch of 20 samples or less	<RL/Dilution factor	Re-digest the entire sample batch and reanalyze.
Dp	Every 10 water samples or every 20 soil samples	0-20%	If all other QC acceptable continue the run; sample result must be flagged; otherwise recalibrate instrument and reanalyze samples.
MS	Every 10 water samples or every 20 soil samples, prior to digestion	75-125%	The sample is spiked and re-analyzed according to Figure 1. .
MSD†	Every 10 water samples or every 20 soil samples, prior to digestion	0-20%	Same as for duplicate.
Dil‡	Once with every batch of 20 samples or less	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.
ICS-A‡	Every 12 hours	<RL for water samples Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
ICS-AB‡	Every 12 hours	70-135% Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
IS Samples	With every sample	70-125%	Verify matrix interference by ruling out instrument drift by unacceptable IS recoveries in standards. Dilute 4+1 and reanalyze. Repeat until inside control limits.
IS QC Samples	With every QC Sample	80-120% for ICV/ICB and CCV/CCB	For CCV/CCB's recalibrate the instrument and reanalyze the affected samples.

NOTE:
- *This is a summery table for more information see Sections 8.4 to 8.10
- RL = Reporting Limit.
- Dil = Dilution Test.
- † MSD optional instead of duplicate sample.
- ‡ When Method 6020 & 6020A referenced in the analytical report.
- IS = Internal Standard

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Linear Dynamic Range (LDR) or High-level Check Standard	At initial set-up and checked every 6 months with a high standard at the upper limit of the range.	Within ±10% of true value.	Dilute samples within the calibration range, or re-establish/verify the LDR.	Flagging is not appropriate.	Data cannot be reported above the calibration range without an established/passing high-level check standard.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial Calibration (ICAL) for All Analytes	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r2 ≥ 0.99.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes, within ± 10% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of the true value.	Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Low-level Calibration Check Standard (Low Level ICV)	Daily.	All reported analytes within ± 20% of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the LOQ.
Internal Standards (IS)	Every field sample, standard and QC sample.	IS intensity in the samples within 30-120% of intensity of the IS in the ICAL blank.	If recoveries are acceptable for QC samples, but not field samples, the field samples may be considered to suffer from a matrix effect. Reanalyze sample at 5- fold dilutions until criteria is met. For failed QC samples, correct problem, and rerun all associated failed field samples.	Flagging is not appropriate.	Samples suffering from matrix effect should be diluted until criteria are met, or an alternate IS should be selected.
Method Blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Before beginning a sample run, after every 10 field samples, and at end of the analysis sequence.	No analytes detected > LOD.	Correct problem and repeat ICAL. All samples following the last acceptable calibration blank must be reanalyzed.	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. For CCB, failures due to carryover may not require an ICAL.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Interference Check Solutions (ICS) (also called Spectral Interference Checks)	After ICAL and prior to sample analysis.	ICS-A: Absolute value of concentration for all nonspiked project analytes < LOD (unless they are a verified trace impurity from one of the spiked analytes); ICS-AB: Within ± 20% of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the failed ICS.	All analytes must be within the LDR. ICS-AB is not needed if instrument can read negative responses.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20%	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		(between MS and MSD or sample and MD).			
Dilution Test	One per preparatory batch if MS or MSD fails.	Five-fold dilution must agree within ± 10% of the original measurement.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Only applicable for samples with concentrations > 50 X LOQ (prior to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post Digestion Spike (PDS) Addition	One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible).	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 6020 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	78	124
7440-36-0	Antimony	72	124
7440-38-2	Arsenic	82	118
7440-39-3	Barium	86	116
7440-41-7	Beryllium	80	120
7440-42-8	Boron	74	128
7440-43-9	Cadmium	84	116
7440-70-2	Calcium	86	118
7440-47-3	Chromium	83	119
7440-48-4	Cobalt	84	115
7440-50-8	Copper	84	119
7439-89-6	Iron	81	124
7439-92-1	Lead	84	118
7439-93-2	Lithium	75	120
7439-95-4	Magnesium	80	123
7439-96-5	Manganese	85	116
7439-97-6	Mercury	74	126
7439-98-7	Molybdenum	83	114
7440-02-0	Nickel	84	119
7440-09-7	Potassium	85	119
7782-49-2	Selenium	80	119
7440-22-4	Silver	83	118
7440-23-5	Sodium	79	125
7440-24-6	Strontium	75	129
7440-28-0	Thallium	83	118
7440-29-1	Thorium	81	116
7440-29-1	Tin	82	121
7440-32-6	Titanium	83	117

7440-61-1	Uranium	83	120
7440-62-2	Vanadium	82	116
7440-66-6	Zinc	82	119

Method 6020 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	84	117
7440-36-0	Antimony	85	117
7440-38-2	Arsenic	84	116
7440-39-3	Barium	86	114
7440-41-7	Beryllium	83	121
7440-42-8	Boron	73	130
7440-43-9	Cadmium	87	115
7440-70-2	Calcium	87	118
7440-47-3	Chromium	85	116
7440-48-4	Cobalt	86	115
7440-50-8	Copper	85	118
7439-89-6	Iron	87	118
7439-92-1	Lead	88	115
7439-93-2	Lithium	78	126
7439-95-4	Magnesium	83	118
7439-96-5	Manganese	87	115
7439-97-6	Mercury	70	124
7439-98-7	Molybdenum	83	115
7440-02-0	Nickel	85	117
7440-09-7	Potassium	87	115
7782-49-2	Selenium	80	120
7440-22-4	Silver	85	116
7440-23-5	Sodium	85	117
7440-24-6	Strontium	82	118
7440-28-0	Thallium	82	116

7440-29-1	Thorium	87	121
7440-29-1	Tin	86	115
7440-32-6	Titanium	83	115
7440-33-7	Tungsten	85	122
7440-61-1	Uranium	87	120
7440-62-2	Vanadium	86	115
7440-66-6	Zinc	83	119

FIGURE 1.
ICP/MS STANDARDS PREP LOG

DATE	Standards	IS id	Exp. Date	Analyst

Source:_____

Lot #: _____

Exp. Date: _____

FIGURE 2
ICP/MS INITIAL CALIBRATION VERIFICATION (ICV) PREP LOG

DATE	ICV ID	IS id	EXP. DATE	Analyst

Source ID **Lot#** **Expiration Date**

S = SPEX _____ _____

H = High Purity _____ _____

E = ERA _____ _____

FIGURE 2: METALS DIGESTION LOG

Metals Digestion 3015A \ 3050B

DATE _____ PREP BATCH MTD-_____

TIME START _____ TIME FINISH _____ ANALYST _____

Pipet Calibration:

Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria	Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria
2	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value	3	1			Bias: Mean ± 2% of nominal value Precision: RSD ≤1% of nominal value
	2					2			
	3					3			

SAMPLE#	BTL ID	SAMPLE AMOUNT GRAMS (g)	FINAL VOLUME (ml)	REMARKS	% TOTAL SOLIDS	DILUTION FACTOR
LCS -	----	50	**50**		—	1
LRB-	----	50	**50**		—	1

NOTES: *1) Spike values (unless otherwise stated):*

LCS = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

14.1. Samples: Water = 0.05 ppm = 50 mls / 0.50 mls of 5ppm Spiking Solution

Soil = 0.10 ppm = 50 mls / 1.0 mls of 5ppm Spiking Solution

Spiking Solution – Date Prepared: _____

2) Spike values for minerals (Ca-Mg-K-Na)

LCS = 1.0 ppm = 50 mls / 0.50 mls HM Stock Solution

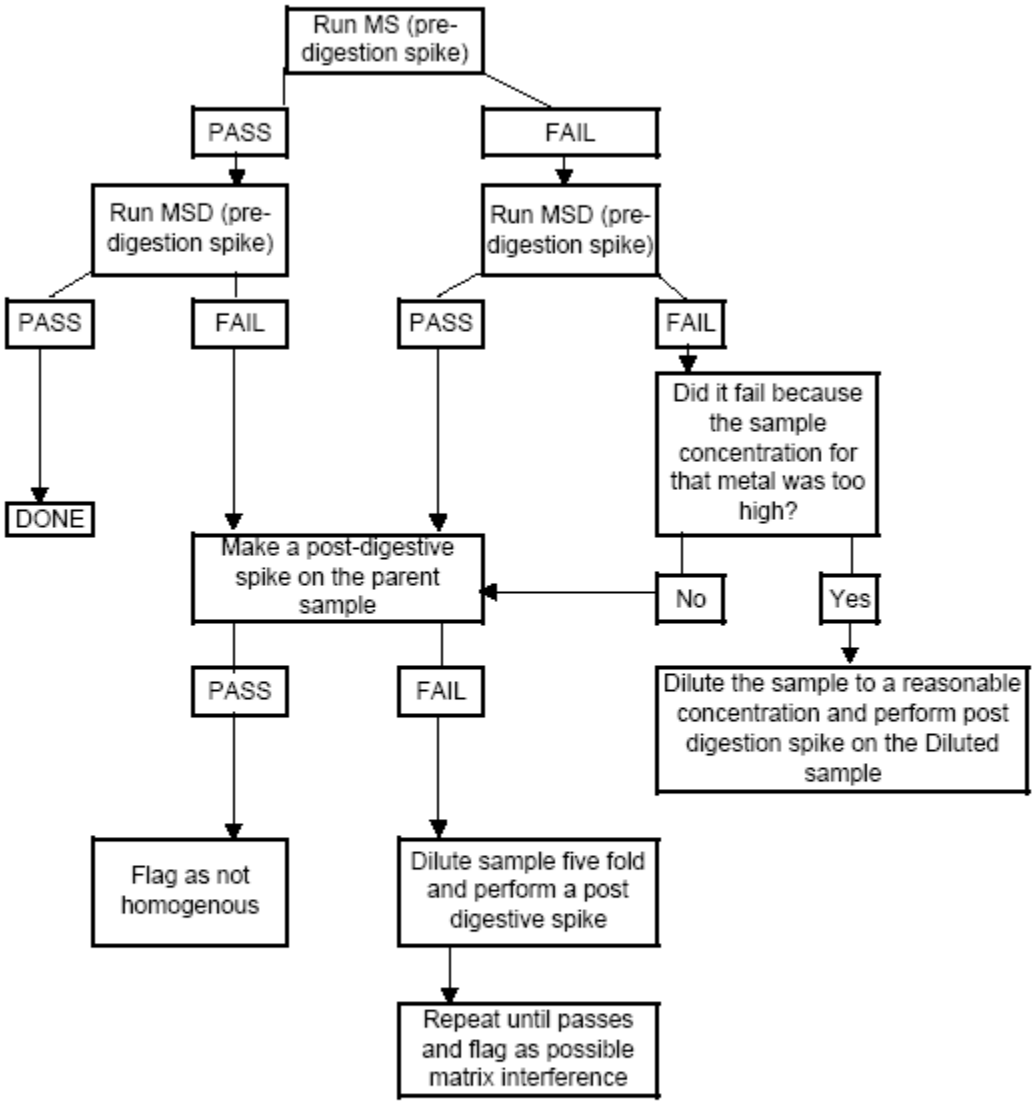
Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HM Stock Solution

High Purity Stock Solution (HM)- Lot # _____

3) HNO_3 Lot # _____ *4) Centrifuge Tube Lot #* _____

5) Balance ID: _____ *Reviewed by* _____ *On* _____

FIGURE 4 MS/MSD CORRECTIVE ACTION FLOW CHART



STANDARD OPERATING PROCEDURE

MERCURY IN WATERS, SOLIDS, AND WASTES (COLD-VAPOR TECHNIQUE) USEPA METHOD 245.1 AND SW-846 METHODS 7470A/7471B

APPROVALS:

Barbara Ball

01/12/18

QA Officer Date

Maya Mushahwar

01/12/18

Technical Director Date

Number	Description of Change	Date
001-008	Previous changes were not documented	
009	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
010	Updated to include Emergency SOP Amendment fixes.	04/18/12
011	Updated for EPA Method 7471B	09/13/13
012	Updated to comply with DoD QSM 5.0 standards.	04/01/16
013	Updated to comply with DoD QSM 5.1 standards.	01/12/18
014		
015		
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

This cold-vapor atomic absorption (CVAA) procedure is used for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters, soils, solid and sludge-type wastes. This SOP is not applicable for OHIO VAP samples.

2.0 SUMMARY OF METHOD

The cold-vapor atomic absorption technique is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured as a function of mercury concentration. Method references include SW846 7470A and 7471B, and 245.1. Typical detection limit for aqueous samples is 0.2 μg/L. This range may be extended above or below the normal range by increasing or decreasing sample size or by optimizing instrument sensitivity. With the operating conditions and parameters stated in this SOP, a detection limit for aqueous samples as low as 0.01 μg/L, with a practical quantitation limit of 0.1 μg/L can be obtained without difficulty. Solid reporting limits range from 0.005 mg/kg to 0.10 mg/kg.

3.0 INTERFERENCES

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide does not interfere with the recovery of added inorganic mercury from reagent water.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

Seawaters, brines, and industrial effluents high in chlorides require additional potassium permanganate (as much as 25 ml) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

Certain volatile organic materials that absorb at this wavelength may also cause interference. The indication that an organic interference is present is usually suggested by peak broadening with increase in the retention approximately 0.4-0.5 minutes more than the retention time of the calibration standards.

For qualitative purposes, ICP/MS verification is possible to confirm the presence of mercury.

4.0 APPARATUS AND MATERIALS

Quick Trace Mercury Analyzer M-7500 consisting of the following components:

- Computer-controlled 4-channel high-performance peristaltic pump (12-roller pump head).
- Computerized thermally ozone-free Hg lamp with a thermally controlled Hg lamp housing (for a stabilized Hg vapor lamp).
- Stable high performance Gas-Liquid Separator (GLS). Non-foaming/non-bubbling "thin liquid film" GLS design, which allows trouble-free direct analysis of blood, urine, and fish tissue digests as well as standard water and waste analysis.
- Integrated ASX-510 Auto Sampler for accommodation of calibration standards and up to 360 samples.

Digestion block.

Polypropylene digestion vessels.

VWR Brand Digital Pipettor dispensing variable volumes from 100 to 1000 µl.

Pipette Dispenser Bottles with adjustable volume 0 - 5 ml in 0.2 ml increments.

Graduated cylinder 100 ml, 1000 ml or equivalent.

Disposable Pasteur pipettes.

Disposable Serological pipettes, 0-10 ml in 0.1 ml increments, 0-5 ml in 0.1 ml increments, and 0-1 ml in 0.01 ml increments.

Disposable plastic cups.

Analytical balance, 300 g capacity, minimum accuracy ± 0.001 g.

Filter funnel, glass or disposable polypropylene.

Glass-fiber filter paper, 0.45 µm.

Teflon bottles for calibration standards.

Centrifuge.

Tongue Depressors.

Membrane Filters.

Filter flask.

Computer.

5.0 REAGENTS

Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

Sulfuric acid (H_2SO_4), concentrated: Trace metal grade, expiration date taken from manufacturer guidelines.

Hydrochloric Acid (HCl), concentrated: Trace metal grade, expiration date taken from manufacturer guidelines.

Nitric acid, 10% (v/v): Measure 900 g reagent water on the scale and add to it 100 ml of concentrated nitric acid in the hood. Prepare as needed, shelf life of 1 year from date prepared. End of day rinse.

Nitric acid (HNO_3), concentrated: Trace metal grade, expiration date taken from manufacturer guidelines.

Stannous chloride: 10% stannous chloride in 7% HCl. Prepare as needed, can be stored for 3 days.

Sodium chloride-Hydroxylamine hydrochloride solution, 12%w/v: Dissolve 120 g of sodium chloride and 120 g of Hydroxylamine hydrochloride in 1000 g reagent water. Prepare as needed, shelf life of 1 year from date prepared.

Potassium permanganate ($KMnO_4$), 5% solution (w/v): Dissolve 50 g of potassium permanganate in 1000 g of reagent water. Prepare as needed, shelf life of 1 year from date prepared.

Potassium persulfate ($K_2S_2O_8$), 5% solution (w/v): Dissolve 50 g of potassium persulfate in 1000 ml of reagent water. Prepare as needed, shelf life of 1 year from date prepared.

Stock mercury solutions: 10 ppm mercury solutions from SPEX CertiPrep (**SPEX**) and High Purity Standards (**HPS**).

The HPS stock solution is used for preparing calibration standards; the SPEX stock solution is used for preparing the initial calibration verification (ICV) standard.

- Mercury working standard: Dilute the stock mercury solution to obtain a working standard containing 100 μg/L mercury (1 g of the stock solution to 100 g reagent water, on the scale). The working solutions must be prepared fresh before making standards. Acidity of the working standard must be maintained at 7% HCl (v/v). This acid (7 ml) must be added immediately after measuring the standard aliquot, and before dilution to final volume (100 g). [According to instrument documentation calibration standards contain 7% HCl].

Instrument rinse solution: 1% HNO_3 and 1% HCl solution.

Note: All reagents purchased for Mercury analyses are of high purity (ACS Reagent Grade or better). Verification is done by the laboratory through the analysis of the reagent blank (LRB).

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are collected in appropriate containers. For water samples, the samples are collected in HNO_3 pre-preserved plastic container, ensuring acidification to pH of < 2. Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples should be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigerate samples at 4^0C. Holding time for mercury must not exceed 28 days, from time of collection to time of analysis.

7.0 PROCEDURE

Turn on the Hot Block and allow it to heat to 95^0 C while the samples are being prepared.

1. Sample Preparation:

- ♦ Liquids
  - o Using a disposable serological pipette, transfer 25 ml/g sample or a smaller amount, if the sample is expected to foam or if it is not aqueous to a polypropylene vessel. The amount of sample used is recorded in the digestion log. Vessels are labeled with sample ID.
  - o Repeat this procedure for a batch of 20 samples or less.
  - o Each batch needs to include a matrix (spike) duplicate and a matrix spike for every 10 samples, and a Laboratory Control Sample (LCS) and a Laboratory Reagent Blank (LRB) for every 20 samples.
  - o To each of the samples, MS-MSD, LCS, standards, and blanks add (under a hood) 1.25 mL conc. H_2SO_4 and 0.66 mL conc. HNO_3 and let set.
  - o Dilute to 25 ml (g) with deionized water if needed.
  - o The LCS is prepared by adding 0.5 ml of the 100 ppb HPS working standard to 25 ml/g DI water (measured using a disposable serological pipette).

- Prepare MS/MSD by adding 0.5 ml of the 100 ppb HPS working standard solution to the QC samples (measured using a disposable serological pipette).
- Add 3.75 ml Potassium permanganate ($KMnO_4$) solution to all vessels.
- Wait 15 min. The purple permanganate color must remain for at least 15 minutes. If the purple color is gone, add additional $KMnO_4$ in 1 mL aliquots until the purple color remains for at least 15 minutes. Record any extra permanganate added in the sample digestion log (figure 1). The same amount of extra $KMnO_4$ will have to be added to all other samples and standards. (Corrections to the dilution factor will be performed as per 7.1.1.15)
- To all samples, standards, and blanks add 2.0 mL potassium persulfate ($K_2S_2O_8$) solution.
- Place the loosely capped samples in the block digester.
- Heat samples at $95^0C \pm 3^0C$ for 2 hours. Record start and end block digester times on the digestion bench sheet.
- Following digestion, remove the samples and place under a hood to cool.
- When the samples are cool, add 1.5 mL Sodium chloride-hydroxylamine hydrochloride solution to all samples, standards, and blanks. Tightly cap and mix by inverting until samples are clear. Samples are now ready for analysis.
- Calculate the dilution factor (DF) by the formula:

$$DF = \frac{FinalVolume(25)}{Sampleamount} \times \frac{100}{\%Totalsolids} \times CF$$

If needed, calculate the correction factor (CF) due to additional $KmnO_4$ (x):

$$CF = \frac{35.16 + x}{35.16}$$

This is recorded in the sample digestion log (Figure 1) and is used in the determination of the mercury result by the CVAA analyzer.

♦ Solids

- Homogenize sample by chopping and mixing sample with a tongue depressor or spatula. Remove any foreign object such as sticks, leaves, or rocks. Weigh

approximately 0.5 g homogenized sample and place into polypropylene vessel. Label vessel with sample ID.

- The amount of sample used is recorded in the preparation log. Repeat this procedure for a batch of 20 samples or less.
- Each batch needs to include a matrix (spike) duplicate, a matrix spike, a Laboratory Control Sample (LCS), and a LRB for every 20 samples.
- LRB and LCS: Weigh out approximately 0.5 grams sand. Record Lot # of sand on digestion log.
- To each of the samples, MS-MSD, LCS, standards, and blanks add (under a hood) 1.25 mL conc. H_2SO_4 and 0.66 mL conc. HNO_3 and let set.
- Dilute to 25 ml (g) with deionized water.
- LCS and MS/MSD: Add 0.5 ml of the 100 ppb HPS working standard solution to the QC sample.
- Add 3.75 mL of potassium permanganate solution to each sample and let stand at least 15 min.
- Add additional portions of potassium permanganate solution, if needed, until the purple color persists for at least 15 min (see 7.1.1.9). Ensure that equal amounts of potassium permanganate are added to standards and blanks.
- Heat for 2 hours min at 95 ± 3 ^{o}C. Record start and end digestion block times on digestion bench sheet.
- Cool and add 1.5 mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate.
- Calculate the dilution factor (*DF*) by the formula:

$$DF = \frac{FinalVolume(25)}{Sampleamount} \times \frac{100}{\%Totalsolids} \times CF$$

If needed, calculate the correction factor (CF) due to additional $KmnO_4$ (x):

$$CF = \frac{35.16 + x}{35.16}$$

This is recorded in the sample digestion log (Figure 1) and is used in the determination of the mercury result by the CVAA analyzer.

2. Calibration Procedure:

- Prepare 7 point calibration curve: From the HPS working standard solution weigh out aliquots of 0.0 ml, 0.1 ml, 0.2 ml, 0.5 ml, 1.0 ml, 2.0 ml, 6.0 ml and 10 ml in 8 Teflon bottles (125 ml) add 7 ml HCl and bring to 100 ml then add 5 ml H_2SO_4, 2.5 ml HNO_3, 15 ml $KMnO_4$, 8 ml $K_2S_2O_8$, and 6 ml Sodium chloride-Hydroxylamine Hydrochloride. This will provide a calibration curve of 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 6.0, 10.0 μg/L. The minimum acceptable correlation coefficient is provided in Tables 1 and 2.

- Prepare in a similar manner an Initial Calibration Verification (ICV) standard made from a different source than the calibration standards(from the SPEX stock solution) at a concentration of 5.0 μg/L, to verify the calibration. In addition, for verifying the calibration solution, an optional LCS standard can be used from a different vendor. The second source standard comes with performance acceptance limits, and is prepared according to the instructions provided by the manufacturer and dilute to middle of calibration, followed by the steps described in Section 7.0.

- Continuing Calibration Verification (CCV) standard is also prepared as in 7.0 from the HPS working standard, to a concentration of 2.0 μg/L.

- The standard solutions described above must be kept in sealed Teflon bottles, and are to be prepared every 2 weeks or fresh daily for all DoD projects. Usually, the CCV standard is prepared more often because it is used more frequent than the other solutions. The LCS is used to evaluate the performance of the method and is to be prepared with every batch, from the same mercury working standard.

3. Sample Analysis:

- Turn on the Mercury Analyzer and allow it to warm up for a minimum of 1 hour.

- Transfer the appropriate standards and samples to the labeled vials, and load the auto-sampler starting with the calibration standards, calibration verification samples, and the batch of samples to be analyzed (QC samples included).

- Start the Quick Trace program.
  - Click on the instrument button then the analyzer button.

- Set the pump to 50% and the gas to 100 ml/minute.

♦ Check to make sure the reagent has a smooth segmented flow. Once this has be established set the pump speed to 100% and the gas flow to 300 ml/minute.

- Disconnect the GLS exhaust tubing and crimp the waste tubing just before the mixing tee.

- This will wet the GLS center post, after this is done reset the pump speed to 50% and the gas flow to 100 ml/minute.

- Wait for the water to drain out of the GLS and then attach the GLS exhaust tubing.

♦ Place the reagent capillary in the reagent bottle and appropriate tubing into the rinse solution.

♦ Type in the number of samples that you are running. Then go into method editor and click "read sample" to zero mercury analyzer and pick a standard

♦ Verify the baseline and peak are correct for the standard.

♦ Exit method editor and press start to analyze samples

4. Data Reporting: The instrument reports final mercury concentrations as μg/L for aqueous samples, and mg/Kg dry weight (when appropriate) for solid samples.

5. Shutting down instrument: Rinse 10% Nitric Acid through the instrument for 10 minutes then DI water for 1 minute, drain out, and shut off.

6. Calculations:

Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

All quality control data must be maintained and available for easy reference or inspection.

Initial Demonstration of Performance.

- The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic range) and laboratory performance (determination of method detection limit) prior to analyses conducted by this method.

- Linear calibration ranges - The upper limit of the linear calibration range must be established for mercury by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Linear calibration ranges must be determined initially, and whenever a significant change in instrument response is observed.

- A Method Detection Limit (MDL) study is performed annually or whenever a significant change in background or instrument response is expected (e.g. detector change) by following the procedure from SOP #QA-009.

Assessing Laboratory Performance.

- The laboratory must analyze at least one LRB with each batch of 20 samples of samples or less. LRB data is used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. If a mercury value in a LRB exceeds 2.2 x MDL or the reporting limit (1/2 the reporting limit for DoD projects), whichever is greater, laboratory or reagent contamination is suspected. Any determined source of contamination should be eliminated and the batch re-digested and re-analyzed.

- The laboratory must analyze at least one LCS with each batch of 20 samples or less. Calculate accuracy as percent recovery. If recovery of mercury falls outside control limits (See Table 1 and Table 2), the method is judged out of control. The source of the problem should be identified and resolved and new aliquots of the samples re-digested and reanalyzed.

- Instrument performance:

- The calibration curve correlation coefficient must be ≥ 0.997. If this is not achieved prepared fresh standards and re-analyze.

- Check instrument calibration by analyzing the initial calibration verification solution (ICV), made from a source different than the calibration standards (Section 5.0), and the initial calibration blank (ICB). Corrective action listed in Tables 1 and 2.

- Verify calibration at a frequency of every 10 analytical samples with the CCV standard and the continuing calibration blank (CCB). These solutions must also be analyzed at the beginning of the analysis and after the last sample.

Assessing Analyte Recovery and Data Quality.

- The laboratory must analyze a matrix spike (MS) with every 10 aqueous samples or 20 soil samples. Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery can be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} x100$$

where: R = percent recovery.
C_s = spiked sample concentration.
C = sample background concentration.
S = concentration equivalent of analyte added to fortify the sample.

The acceptance limits for MS samples are provided in Tables 1 and 2. If the recovery falls outside the designated range, and the laboratory performance is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the recovery problem encountered with the spiked sample is judged to be matrix related, not system related. The data user must be informed that the result for the unspiked sample is suspect due to matrix interference. Recovery is not required if the concentration of the mercury added is less than 25% of the concentration of mercury in the original sample.

- Analyze one matrix duplicate (Dp) sample for every 10 aqueous samples or 20 soil samples. A matrix spike duplicate (MSD) can be used instead of the matrix duplicate, especially if the analyte in the sample is of low concentration. A control limit of 20% RPD should not be exceeded for measured mercury concentration greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user must be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be re-digested and reanalyzed.

Quality control items employed and evaluated are provided in Table 1 (Table 2 for DoD projects). In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.

The analyst will follow SOP QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include changing drain line and or waste lines.

11.0 SAFETY

Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures. Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

- Concentrated sulfuric acid is toxic and damaging to skin and mucus membranes. If eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.

- The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

- Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for mercury analysis, a sample batch consists of 20 samples or less.

Laboratory Reagent Blank (LRB) (also known as Method Blank): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The LRB is carried through the complete sample preparation and analytical procedure. The LRB is used to document contamination resulting from the analytical process.

Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. An acceptable MDL standard check must produce a signal at least 3 times the instrument's noise level. Also, a MDL check injection must be

made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Calibration Standards: a series of known standard solutions used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. A minimum of 5 calibration points are used for Mercury calibration. Acceptance of the calibration requires a correlation coefficient of 0.997 or better. No samples shall be analyzed without acceptable calibration.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

Initial calibration blank (ICB): a reagent blank solution, which is analyzed immediately following the ICV. The ICB is analyzed to check for drifts in calibration or possible analyte carry-over.

Continuing Calibration Blank (CCB): a reagent blank solution, which is analyzed immediately following the CCV. The CCB is analyzed to check for drifts in calibration or possible analyte carry-over.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

Quick Trace Mercury Analyzer M-7500 Instrument Manual.

USEPA, *Methods for the Determination of Metals in Environmental Samples*. EPA/600/R94/111, Method 245.1.

USEPA, SW-846, Revision 3, Method 7470A.

USEPA, SW-846, Revision 2, Method 7471B.

Table 1: Quality Control Items, Frequency and Corrective Action

QA Items	**Frequency**	**Acceptance Criteria**	**Corrective Action**
Initial Calibration Verification (ICV)	Following Calibration	90-110%	Terminate analysis, correct problem, and recalibrate instrument
Initial Calibration Blank (ICB)	Following Calibration	< Reporting Limit of aqueous samples	Correct problem, re-analyze ICV and ICB
Continuing Calibration Verification (CCV)	Before and after each batch of 10 analytical samples (not including QC samples)	90-110%	Terminate analysis, correct problem, and recalibrate instrument. Re-analyze all samples following last acceptable calibration
Continuing Calibration Blank (CCB)	Before and after each batch of 10 analytical samples (not including QC samples)	< Reporting Limit of aqueous samples	Correct problem, re-analyze all samples following last acceptable calibration blank
Laboratory Control Sample (LCS)	One per batch or 20 samples or less	85-115%	Identify and resolve problem. Re-digest and re-analyze sample set
Laboratory Reagent Blank (Method Blank) (LRB)	One per batch or 20 samples or less	< Reporting Limit	Identify and eliminate source of contamination. Re-digest and re-analyze sample set
Matrix Duplicate (Dp)	One per 20 soil samples or 10 liquid samples, maybe replaced by MSD	DUP RPD < 20%	Evaluate to determine if due to matrix interference.
Matrix Spike (MS)	One per 20 soil samples or 10 liquid samples	80-120%	Evaluate to determine if due to matrix interference.
Matrix Spike Duplicate (MSD)	One per 20 soil samples or 10 liquid samples	DUP RPD <20%	Evaluate to determine if due to matrix interference.

Table 2: Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial calibration (ICAL) for all analytes	Daily ICAL prior to sample analysis.	$R^2 \geq 0.99$.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	FLAA and GFAA: minimum three standards and a calibration blank. CVAA/Mercury: minimum 5 standards and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within ± 10% of the true value.	Correct problem. Rerun ICV. If that fails, rerun ICAL.	Flagging is appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Low-level Calibration Check Standard (LLCCV)	Daily.	All reported analytes within ± 20% of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid Low-Level Calibration Check Standard (LLCCV). LLCCV should be less than or equal to the LOQ. If the concentration of the lowest calibration standard is less than or equal to the LOQ, the lowest standard may be re-quantified against the calibration curve as a LLCCV. Otherwise, a separate standard must be analyzed as the LLCCV prior to the analysis of any samples.
Continuing calibration verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within ± 10% of the true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all affected samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	the specific analyte(s) in all samples since the last acceptable CCV.	
Method blank (MB)	One per preparatory batch.	The absolute values of all analytes must be < ½ LOQ or <1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate where the samples cannot be reprepped or reanalyzed. Non-detects associated with positive blank infractions may be reported. Samples results > 10X the LOQ associated with negative blanks may be reported.
Initial and Continuing Calibration blank (ICB/CCB)	Immediately after the ICV and immediately after every CCV.	The absolute values of all analytes must be < ½ LOQ or <1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater.	ICB: Correct problem and repeat ICV/ICB analysis. If that fails, rerun ICAL. All samples following the last acceptable Calibration Blank must be reanalyzed. CCBs may not be re-analyzed without re-analysis of the associated samples and CCV(s).	Flagging is not appropriate..	Results may not be reported without a valid calibration blanks. Non-detects associated with positive blank infractions may be reported. Sample results >10X the LOQ associated with the negative blanks may be reported. For CCB, failures due to carryover may not require an ICAL.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch	Correct problem, then reprep and reanalyze the LCS and all samples in the	If reanalysis cannot be performed, data must be qualified and explained in the	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	associated preparatory batch for failed analytes, if sufficient sample material is available.	case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified..	Examine the project-specific requirements. Contact the client as to additional measures to be taken	For specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to the source of difference (i.e., matrix effect or analytical error).
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For specific analyte(s) in the parent sample, J-apply flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: % Recovery and RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Dilution Test (Flame AA and	One per preparatory batch if	Five-fold dilution must agree within ± 10% of	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J-flag if	Only applicable for samples with concentrations > 50 X LOQ (prior

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
GFAA only)	MS or MSD fails.	the original measurement.		acceptance criteria are not met and explain in the case narrative.	to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post-Digestion Spike (PDS) Addition (flame AA and GFAA only)	One per preparatory batch if MS or MSD fails.	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 7470 - 7471 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7439-97-6	Mercury	80	124

DoD Appendix C LCS Limits
Method 7470 - 7471 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7439-97-6	Mercury	82	119

Figure 1

Mercury Digestion

Method # 245.1, 7471B, 7470A (OHIO VAP)

TIME START**: _____** Beginning End DATE _____

TIME FINISH_____ TEMP: block #1_____º C block #1_____º C ANALYST_____

PREP BATCH: HGD-_____ block #2_____º C block #2_____º C REVIEWED BY_____

BALANCE ID:_____ block #3_____º C block #3_____º C REVIEW DATE_____

SAMPLE#	BTL ID	SAMPLE AMOUNT GRAMS (g)	%TOT. SOLIDS	DRY SAMPLE WT.	DILUTION FACTOR	FINAL VOLUME	REMARKS
LCS-	------		--------	---------		25g	
LRB	------		--------	---------		25g	

NOTES: 1) Spike values (unless otherwise stated):

2.0 ppb for LCS: 0.50 ml of HPS solution (Lot# Exp)

2.0 ppb for liquid samples: 0.50 ml of HPS solution (Lot# Exp.)

0.002 ppm for solid samples: 0.50 ml of HPS solution (Lot# Exp.)

Centrifuge Tube Lot #

HNO_3 Lot #

Pipet Calibration:

Test #	Pipet Volume Setting mL	Vial wt. = Tare wt., g	Wt. of water from pipet, g	Notes
1				
2				
3				

Figure 2

Date	Analyst	Standard ID and PPB conc. (bold)	Source	mls of 100 ppb working solution/ final volume	Expiration Date	Remarks
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		020-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		Wibby	Wibby			
		5.00- S (ICV)	SPEX			
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		0.20-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		Wibby	Wibby			
		5.00-S (ICV)	SPEX			
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		0.20-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		Wibby	Wibby			
		5.00-S (ICV)	SPEX			
		HP working stock	HPS			
		0.00-H	HPS			
		0.10-H	HPS			
		0.20-H	HPS			
		0.50-H	HPS			
		1.00-H	HPS			
		2.00-H	HPS			
		6.00-H	HPS			
		10.0-H	HPS			
		CCV	HPS			
		Wibby	Wibby			
		5.00-(ICV)	SPEX			

Source ID	**Lot#**	**Expiration Date**
Spex	_____	_____
High Purity (HPS)	_____	_____
Wibby	_____	_____

STANDARD OPERATING PROCEDURE

POLYCHLORINATED BIPHENYLS (PCBS) BY GC METHOD 8082A

APPROVALS:

Barbara Ball

01/16/18

QA Officer — Date

Maya Mushaly

01/16/18

Technical Director — Date

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Number	Description of Change	Date
001-010	Previous changes were not documented	
011	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
012	Updated to include 8082A Method references	7/19/11
013	Updated to comply with DoD QSM 5.0 standards.	03/03/16
014	Updated to comply with DoD QSM 5.1 standards.	01/16/18
015		
016		
017		
018		
019		
020		
021		

1.0 SCOPE AND APPLICATION

This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD). The target compounds listed below may be determined by a dual-column analysis system.

Parameter	*CAS #:*
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards. Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment.

This method also includes different clean-up procedures used to assist in removing some of the more common found interferences.

This method describes a dual-column GC set up for the determination of total PCB Aroclor concentrations. A hardware configuration of two analytical columns joined to a single injection port is utilized.

The Method Detection Limits (MDLs) for Aroclors are determined annually on all instruments analyzing PCBs. Estimated method detection limits are available on Merit's network and VLIMs.

This method is restricted to use by, or under the supervision of trained analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method as well as a working knowledge of Chrom Perfect and the PCB calculator software.

2.0 SUMMARY OF METHOD

A measured volume or weight of sample (approximately 1 L for liquids, 20 g for soil, and 0.3 g for oil samples) is extracted using the appropriate matrix-specific sample extraction technique[1].

Note: Unusually contaminated samples may be extracted with lower sample amounts. The reporting limits are corrected accordingly. Sample specific notes are added and samples flagged.

Aqueous samples are extracted at neutral pH with methylene chloride using Merit's SOP #: EXL-003 (PCB Extraction Liquid).

Solid samples are extracted with hexane using Merit's SOP#: EXL-004 (PCB Extraction Solid).

Extracts for PCB analysis are subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for PCBs. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, the analysis of pesticides is not covered by this SOP.

After the acid clean-up, a sulfur clean-up is performed. The activated copper reacts with the sulfur interference to form a precipitate (ex. $2RSH + Cu^{++} \rightarrow Cu(SR)^2 + 2H^+$, where R is the organic radical and SH is the mercaptan radical).

After the clean-up procedures, the extract is analyzed by injecting a 1-2 uL aliquot into a gas chromatograph with narrow-bore fused silica capillary column and electron capture detector (GC/ECD).

The chromatographic data is used to determine the seven Aroclors in Section 1.0.

3.0 INTERFERENCES

Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are provided, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.

- Contaminated solvents, reagents, or sample processing hardware.
- Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
- Compounds extracted from the sample matrix to which the detector will respond.

[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Liquid Liquid Separatory Funnel Extraction, and, Method 3550C, Ultrasonic Extraction.

Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

- Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters are minimized by avoiding contact with any plastic materials and checking all solvents and reagents for interferences.

- Exhaustive cleanup of solvents, reagents, and glassware may be required to eliminate background phthalate ester contamination. These materials can be removed through the use of procedure described in Number 2, Section 7.0 (sulfuric acid/permanganate cleanup), which is required for all PCB analysis.

- Cross-contamination of clean glassware is avoided by scrupulously cleaning and then baking glassware in a 550ºC oven for 4 – 12 hours.

    - Clean all glassware as soon as possible after use by rinsing with the last solvent used. This is followed by detergent washing with hot water, and rinses with tap water and DI water. Drain the glassware, and let dry for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.

    - Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur is removed using procedure described in Section 7.0).

4.0 APPARATUS AND MATERIALS

Gas chromatograph - An analytical system complete with a gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and a data system.

GC columns - The dual-column arrangement used by this method involves a single injection that is split between two columns mounted in a single gas chromatograph. Each column is connected to a separate ECD detector.

- Narrow-bore columns are installed in split/splitless (Grob-type) injectors.
- 30m x 0.25mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, 0.25um film thickness).

- 30m x 0.25mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, 0.25um film thickness)

- Column pair is mounted in a press-fit Y-shaped glass 3-way fused-silica connector (Supelco)

Column rinsing kit - Bonded-phase column rinse kit.

Glass vials for sample storage, cleaning, and standard preparation.

Hamilton Syringes (1ul to 1000 ul).

Sample Vials: 1.8 ml screw cap with PTFE liner and 4.0 ml calibrated screw cap.

Maintenance Logbook.

Disposable Pipettes.

Beakers.

5.0 REAGENTS

Reagent grade or pesticide grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

Note: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4 ± 2ºC in polytetrafluoroethylene (PTFE)-sealed amber containers, or in a dark area. When a lot of standards is prepared, the aliquots of that lot are stored in individual small vials. All stock standard solutions are replaced every 12 months or sooner depending if the QC indicates a problem. All working standard solutions are replaced after six months or sooner if routine QC indicates a problem.

Sample extracts are prepared by liquid - liquid extraction (SOP#: EXL-003 for waster samples or ultrasonic extraction (SOP#: EXL-004) for solid and oil samples. Both procedures undergo a solvent exchange step prior to analysis. The following solvents are necessary for dilution of sample extracts. All solvent lots must be pesticide quality or equivalent.

- n-Hexane, $C_6H_{14.}$
- Methanol, CH_3OH.
- Acetone, $CH_3COCH_{3.}$
- Ethyl Ether (6%)

Deionized (DI) Water.

Stock standard solutions (1000 mg/L). Commercially prepared stock standard solutions are used. All standards that are purchased must be certified by the manufacturer or by an independent source.

Calibration standards for Aroclors.

- A standard containing a mixture of Aroclor 1016 and Aroclor 1260 includes many of the peaks represented in the other five Aroclor mixtures. A multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations demonstrates the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors.

- The 1016/1260 mixture is used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, if they are present in a sample. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with hexane. The curve concentrations bracket the linear range of the detector. (0.1 to 1.0 ppm, see Table 6).

- Method 8082A states that: "Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor…The concentrations should correspond to the mid-point of the linear range of the detector." During a sample batch, if an Aroclor is identified in a sample, a standard of that Aroclor is analyzed. If the standard concentration falls within the control limits for that Aroclor, the sample is quantitated using the 5-point curve for that Aroclor.

Copper balls, pre-cleaned. A method blank must be analyzed demonstrating that there is no interference.

Copper powder.

Sodium Sulfate Na_2SO_4, pre-cleaned with Methylene Chloride, a method blank must be analyzed demonstrating that there are no interferences.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are sampled using 1L Amber glass jars or 4 –8 oz. glass jars for solids. Oil and wipe samples must only be collected in glass jars.

Aqueous samples are extracted within 7 days from sample collection. Solid samples must be extracted within 14 days of sample collection.

Extracts are stored under refrigeration at $4 \pm 2^{o}C$ and are analyzed within 40 days of extraction.

7.0 PROCEDURE

1. Samples are extracted using the SOP#'s EXL-003 and EXL-004.

   - Water samples are extracted at a neutral pH with methylene chloride using a separatory funnel.
   - Solid samples are extracted with ultrasonic extraction.
   - Spiked samples are used to verify the applicability of the selected extraction technique for each new sample type (*i.e.* water, soil, oil, *etc.*). These samples are spiked with Aroclor 1016/1260 mixture at 0.500 mg/l concentration.

2. Extract clean-ups.

   - **Sulfuric Acid Clean-up**[2]: this method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method is used to reduce elevated baselines in overly complex chromatograms that prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate. (MANDATORY FOR ANALYSIS AND QC SAMPLES)

     - Place up to 2 ml of concentrated sulfuric acid into the final hexane extract 4 ml vial. Make sure this is done only in the hood area. Safety glasses must be worn at all times.
     - Place the cap on the vial and shake the extract with the acid causing a visible vortex. The acid will dissolve and carbonize the interferences commonly found in PCB samples.
     - Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.
     - Allow the phase to separate for at least one minute. Examine the hexane (hexane) layer, it must not be highly colored, nor have a visible emulsion or cloudiness. If a clean phase separation is achieved, proceed to Number 2.
     - If the acid is "carbonized" or turns a dark brown color remove the sulfuric acid layer from the vial and dispose of it properly. Add another portion of the sulfuric acid and repeat bullets three and four under Number 2.

[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665: Sulfuric Acid

- Transfer the hexane to a clean 4 ml vial. Take care not to include any of the acid layer in this clean vial, as it can cause damage to the instrumentation. Once the hexane layer is removed, perform a second extraction of the acid layer.

- Add an additional 1 ml of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitated transfer of the PCBs, when needed. If still dirty, go to the alumina cleanup.

♦ **Sulfur Clean-up**[3]: This clean-up is performed at the GC laboratory station. Elemental sulfur is encountered in many liquid and sediment samples (commonly found in industrial wastes). The solubility of sulfur in various solvents is very similar to the organochlorine compounds of interest. Therefore, the sulfur interference follows along with the target compounds through the normal extraction and Florisil cleanup techniques. Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors. (MANDATORY FOR ANALYSIS AND QC SAMPLES)

- Add approximately 1g of high grade, activated copper shots or copper powder to the final hexane sample extract. The activated copper is prepared by rinsing the copper with diluted nitric acid, rinsed with acetone and dried before use.

- Vortex for 1 minute. Allow the copper to settle to the bottom. If a high precipitate occurs, the sample can be centrifuged. If the copper seems to be saturated, more can be added.

- If copper powder is used, follow Sulfur Clean-up and Alumina Clean-up and then carefully transfer the "cleaned" extract using a disposable pipette into another vial to prevent the "powder" from plugging up the auto syringe.

♦ **Alumina Clean-up** is an adsorption technique used when the chromatogram base line is still elevated after the two clean-up procedures listed above were performed. Alumina clean-up[4] is used to separate the high molecular weight petroleum wastes from PCBs using liquid chromatography.

Alumina Column Clean-up: the column is packed with the required amount of adsorbent, topped with a water adsorbent (Na_2SO_4), and then loaded with the sample to be analyzed.

[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.
[4] Reference for Alumina clean-up is SW-846, Revision 3, December 1996 Method 3611B: Alumina Column Clean-up & Separation of Petroleum Products.

Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The elute is then concentrated (if necessary).

- Place a clean glass wool plug in the bottom of a 50 ml disposable chromatographic column.
- On top of this plug, add 2 cm of anhydrous Na_2SO_4 and tap it down.
- Pour about 10 g of activated (130°C for 12 hours) Alumina (150 mesh) into the column.
- Tap it down and place 2 cm of anhydrous (130°C for 12 hours) Na_2SO_4 on top of the Alumina.
- Rinse the column with 40 ml hexane.

Note *The column must not be allowed to become dry throughout the rest of the analysis. The disposable column will stop flowing naturally when the solvent level is at the top of the Na_2SO_4.*

- Using a long pasture pipette, place the sample extract on the column followed by rinse of the sample vial and the column with 2 ml hexane.
- Wash the column with 20 ml hexane and place the eluted hexane in a beaker labeled "Dirty Used Hexane". This washes the aliphatic interferences out of the sample.
- Elute 80 ml 6% ethyl ether in hexane through the column and collect it for the analysis of PCBs.
- Concentrate the eluted hexane to 0.5 ml inside the Zymark Evaporation Station.
- Transfer it quantitatively to a graduated 4 ml vial rinsing the evaporating tube with 0.5 ml hexane, bringing the volume of cleaned sample in the vial to 1 ml.
- Add 2 ml Sulfuric Acid (H_2SO_4) (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds*.
- Record alumina cleanup on bench sheet.

- **Dioxin cleanup:** This cleanup is similar to alumina but with a finer mesh column. The columns are pre-made and located in second drawer under the glassware ovens in the organic prep lab.
    - Set up is the same as alumina, except the columns are pre-made and placed in the slots in back.
    - Place clean beakers under the columns. All solvent extracted in this process will be kept. Label beakers with sample ID #.
    - Flush column with 120 ml hexane, this can take 4 columns worth of solvent. The column portion is thicker and media is finer so it requires more solvent to saturate.
    - Add sample to column, place columns over evaporation tubes, and flush column with collected hexane.
    - Evaporate samples in the evaporation tubes, to make room for additional hexane.
    - Once evaporated, place tubes back under their respective columns and add 120 ml of Hexane.
    - Evaporate to 0.5 ml, transfer and adjust to final of 1 ml of sample and analyze.
    - Add 2 ml Sulfuric Acid (H_2SO_4) (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds*.
    - Record dioxin cleanup on bench sheet and write "dx" on sample label.

3. GC conditions.

- **Dual-column analysis:** The dual-column/dual-detector has two 30m x 0.25mm ID fused-silica open-tubular columns of different polarities, and thus has different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors. For types of columns see Table 1.
- GC temperature programs and flow rates are listed in Table 1.

4. Calibration.

- Prepare calibration standards as described in the standard preparation logbook for PCBs/Pesticides (See Table 6). Both initial calibration and calibration verification standards are prepared using two different vendors to insure the quality and correctness of the standards.

Note: Prior to calibration, GC operating conditions must be established which optimize both peak resolution and sensitivity. The total run time must be long enough permit the elution of the second surrogate standard (DCBP). Once established, the same operating conditions must be used for both calibrations and sample analyses.

Note: Because of the sensitivity of the electron capture detector, the injection port and column must always be cleaned prior to performing the initial calibration.

- PCBs are quantitatively determined as Aroclors. The initial calibration consists of the following protocols:
  - A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Therefore, this mixture of 1016/1260 is used to demonstrate the linearity of the detector (RPD value of the curve) and that a sample does *not* contain peaks that represent any one of the Aroclors. This standard is also used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, if they are present in a sample. Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260.
  - Standards of the other five Aroclors are necessary for pattern recognition. SW 846 states: "These standards are also used to determine a single-point calibration factor for each Aroclor… The Aroclor 1016/1260 mixture is used to determine correct detector response." Positive identification of Aroclors other than 1016 or 1260, require the appropriate Aroclor standard to be run and samples re-analyzed.
  - In situations where only a few Aroclors are of interest for a specific project, the analyst can use a five-point initial calibration of each of the Aroclors of interest (*e.g*., five standards of Aroclor 1254 if this Aroclor is of concern) and not use the 1016/1260 mixture.
- An auto sampler is used to inject 1-2uL volumes of each calibration standard. Depending on the volume of sample injected (*i.e.* 1 or 2 uL), the initial calibration, the QC samples, and samples must be analyzed with the same injection volume.
- Record the peak area for each characteristic Aroclor peak to be used for quantitation using the Chrom Perfect Software.
- A minimum of three peaks is chosen for each Aroclor, and preferably 5 peaks (See Table 2 for Quantification Peaks). The peaks are characteristic of the Aroclor in question. If possible,

choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of three to five peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

- Tables 2a and 2b list recommended diagnostic peaks in each Aroclor, along with their retention times on two GC columns suitable for dual-column analysis.

- Calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

- Calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. The PCB calculator initial calibration report is generated which involves the calculation of the mean calibration factor, the standard deviation, and the relative standard deviation (RSD) for each Aroclor. The RSD for a given calibration range must be $\leq$ 20% in order to employ the calibration method described in the seventh main bullet under Number 6. [5]

- A better representation of the calibration data may be obtained by narrowing the calibration range (by lowering the upper level standard) or by using a least-squares regression in accordance with SW-846, Method 8000. A linear regression may be used with a 5-point calibration curve, and the coefficient of determination (C.O.D.) must be > 0.99. Additional standards must be analyzed in order to utilize a non-linear calibration (*see* Method 8000). All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior.

5. Retention Time Windows.

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. The width of the retention time window is established by analyzing successive calibration standards of the same Aroclor mixture. The standard deviation (σ) of these repeated measurements is used to determine this window. The window is defined as the mean retention time $\pm$ 3σ. The results of this analysis are contained in

[5] Reference for RSD values is SW-846, Revision 3, December 1996 Method 8000B Determinative Chromatographic Separations

Table 3. Given that the maximum window for an individual PCB is approximately 0.08 min., a nominal identification window of 0.1 minutes is utilized for all PCBs.

6. Gas chromatographic analysis of sample extracts.

- The same GC operating conditions used for the initial calibration are used for sample analyses and calibration verification.

- An analytical sequence of laboratory samples and QC samples is templated using the following:

  - Calibration verification mixture (1016/1260)
  - Laboratory control sample
  - Blank
  - Reagent Blank
  - Up to 20 samples
  - Duplicate sample
  - Matrix spike and/or matrix spike duplicate sample
  - Batch-terminating standard.

- Verify the calibration each 12-hour shift by injecting a calibration verification standard prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples. The calibration verification standard is a mixture of Aroclor 1016 and Aroclor 1260 from a different source then the initial calibration standards.

- The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 20 % when compared to the mean calibration factor from the initial calibration curve:

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

- Corrective action: if this criterion is exceeded for any calibration factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements based

on the last initial calibration, then a new initial calibration must be performed. Please refer to Table 8 Quality Control Items, Frequency and Corrective Action.

- Inject a 1-2 uL (third main bullet under Number 6) aliquot of the concentrated sample extract.
- Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Number 9.
- Quantitative results are determined for each identified Aroclor, using the procedures described in Number 10. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.
- Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.
- A batch of 20 sample injections (including QC samples, see above) may continue as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. A smaller batch than 20 samples can be analyzed in order to minimize the number of samples that must be re-injected if the standards fail the QC limits. The sequence ends when the set of samples has been injected or when quantitative QC criteria are exceeded.
- If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample or additional clean-ups are warranted.
- Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7. Qualitative Identification (The equations governing the quantification, recovery and precision are referenced in the glossary section of the QA/QC manual).

- The identification of PCBs as Aroclors using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with

the retention times and windows established through the analysis of standards of the target analytes (*see* Tables 2a, 2b, and 3).

- Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification is confirmed using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern. The second column is calibrated and utilized for purposes of qualitative identification only.

- Tentative identification of an Aroclor pattern is based upon an approximate match of the relative characteristic peak heights between the sample and reference standard. Use the individual Aroclor standards (not the 1016/1260 mix) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 are evident in the mixed calibration standards (See Figure 1).

- Positive identifications require a second column confirmation. Both QC samples and calibrations are verified with the second (confirmation) column.

- Project-specific requirements must be followed when reporting data. If project-specific requirements have not been specified, method requirements must be followed. If the method does not include reporting requirements, then report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

8. Quantitation of PCBs

- The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

- The characteristic quantitative peaks for each Aroclor are listed in Tables 2a and 2b and illustrated in Figure 1. The amount of Aroclor is calculated using the 5-point calibration curve for each of the 3 to 5 characteristic peaks chosen. The concentration is determined using the average concentration for each of the characteristic peaks.

- In the event that the data system is unable to properly integrate the peaks of interest (typically due to peak co-elution or matrix interference), a manual integration procedure is performed. The applicability, procedure, and documentation of the manual integration are addressed in the SOP Manual Integration of Chromatographic Data # ORL-003.

- Compound identifications are supported by at least one additional qualitative technique (i.e., second column confirmation).
    - For Ohio VAP samples and DoD Projects, both columns must meet the calibration and QC criteria.
- The second column quantitation can be applied upon request to any project. In this case, all QC requirements listed above are applied to each set of chromatographic data. PCB concentrations from each column are reported.

Note: Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems.

9. Chromatographic System Maintenance as Corrective Action.

- When system performance does not meet the established QC requirements, corrective action is required, and can include one or more of the following.
    - Splitter connections for dual columns which are connected using a press-fit a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent back-flush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.
- Metal injector body.
    - Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.
    - Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

- Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

♦ Column rinsing.

- The column is rinsed with hexane.

10. Calculations

Relative Percent Difference: $$RPD = \frac{(S - D)}{\left[\frac{S + D}{2}\right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $$\frac{SSR - SR}{SA} \times 100$$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

Quality control procedures necessary to evaluate the GC system operation include evaluation of retention time windows, calibration verification and chromatographic analysis of samples are listed in Table 8a and 8b. In addition the tables indicate the frequency of the QC item along with the course of corrective action.

The QC Reference Sample is a sample that is analyzed prior to any analysis to demonstrate the initial proficiency of the analyst or the instrument. In cases when a new instrument is introduced or a new analyst, this sample when analyzed within the control limits of ±20% demonstrates the initial proficiency of the method. The QC reference sample must be spiked with in the linear calibration range. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260.

Method Detection Limit (MDL). The MDL is performed annually based on the procedure in SOP # QA-009. MDL are available on Merit's network and in VLIMs.

Accuracy & Precision - Accuracy & Precision are determined for sample matrices of interest by computing the mean recovery and relative standard deviation of the LCS analysis. The upper and lower control limits for matrix spike recovery are determined as the mean ± 3σ. The results for the water and solid matrices are given in Table 4.

The Continuing Calibration Verification (CCV) concentrate must contain PCBs as Aroclors at mid-point of the curve. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the CCV.

- The frequency of analysis of the CCV analysis is equivalent to a minimum of 1 per 12 hours not to exceed 20 samples between CCVs. A closing calibration verification is required at the end of the run.

- If the averaged recovery of compounds found in the CCV is less than 80% or greater than 120% of the true value, the laboratory performance is judged to be out of control, and the problem must be corrected. Please refer to Table 8 Quality Control Items, Frequency and Corrective Action.

- Include a calibration standard after each group of 20 samples. The response factors for the calibration must be within 20 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory must halt the analysis and take corrective action. Please refer to Table 8a and 8b Quality Control Items, Frequency and Corrective Action.

Sample Quality Control for Preparation and Analysis – A batch includes the analysis of QC samples including a method blank, a matrix spike, matrix spike duplicate and/or a duplicate (per client request), and a laboratory control sample (LCS). Surrogates are added to each field and QC sample.

- Documenting the effect of the matrix must include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories must use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors must be used for spiking. If samples are expected to contain target analytes, then laboratories can use one matrix spike and a duplicate analysis of an unspiked field sample.

- If a sample is qualitatively identified as having an Aroclor which was *not* analyzed as part of the QC samples, the sample is subsequently re-analyzed along with a calibration check standard of the appropriate type.

- A Laboratory Control Sample (LCS) is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results

of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

Surrogate recoveries - Surrogate recovery data is analyzed from individual samples in order to determine matrix-specific control limits. The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). TCX will be evaluated on a client/project specific basis. The surrogate standard is prepared by the GC analyst at a concentration of 0.03mg/l. and utilized by the extraction analyst. Table 5 contains surrogate recovery data and laboratory-established control limits, and is inclusive of the effect of copper and sulfuric acid clean-up procedures. The surrogate standards are calibrated using a 5-point curve.

The MS/MSD and LCS spikes contain a mixture of Aroclor 1016/1260. This spike must be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.5mg/l.

The analyst will follow SOP# QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in this document.

The MDLs and PQLs can be found on Merit's network and in VLIMs.

Table 5 presents the lower and upper acceptance criteria for all surrogates.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings must be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual must be followed. Maintenance includes: clipping/replacing the column, replacing the heat detector, solvent backflushing, cleaning injector port, and replacing the calibration standard. Refer to Number 9 in Section 7.0 for specific procedures.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has an eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour

when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances. Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested) and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

Matrix Spike (MS): an aliquot of sample spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): intra-laboratory split samples spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Method Reporting Limit (MRL): the method reporting limit is a threshold value below which the laboratory reports a result as non-detect. The highest value reported for the method reporting limit is dependent upon project-specific action or decision levels. Method reporting limits are adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. Depending on project specifics, MDLs will be in the form of a MDL check standard or the MDL is subject to extraction procedures. An acceptable MDL standard check must produce a signal at least three times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Surrogate (SURR): an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The surrogates are; 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl.

Initial Calibration (ICAL): an analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of Aroclors 1016/1260. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte. Alternative ICALs for Aroclors can be substituted for the 1016/1260 ICAL if specified by project or program.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

USEPA, SW-846, Revision 3; Method 3510C.

USEPA, SW-846, Revision 2; Method 3550B.

USEPA, SW-846, Revision 1; Method 3665A.

USEPA, SW-846, Revision 2; Method 3611B.

USEPA, SW-846, Revision 2; Method 3660B.

USEPA, SW-846, Revision 2; Method 8000B.

USEPA, SW-846, Revision 1; Method 8082A.

Varian/Brueker User Manual 450 GC.

Table 1. GC Operating Conditions For PCBs As Aroclors (Dual Column)

Property	*Setting*
Column #1	DB-5, 30m x 0.25mm ID, 0.25µm film thickness
Column #2	DB-608, 20 m x 0.25 mm ID, 0.25 µm film thickness
Carrier gas flow (He)	6ml/min
Makeup gas flow (N_2)	20ml/min
Temperature program	T_o = 180ºC, hold 1.0min 180ºC to 250ºC, ramp at 6.0ºC/min T_f = 250ºC, hold 2.34min
Injector temperature	250ºC
Detector temperature	320ºC
Injection volume	1-2 µl, no air plug
Solvent	Hexane
Injector	On-column
Detector	Dual ECD
Range attenuation	10/8
Splitter	Supelco press-fit Y-shaped inlet splitter

Table 2a. Summary of Characteristic PCB Peak Retention Times (DB-5 Column) used for quantitation

Peak	*1016*	*1221*	*1232*	*1242*	*1248*	*1254*	*1260*
1	3.20	2.53	2.68	3.04	3.46	4.34	5.10
2	3.45	2.61	3.46	3.21	4.07	4.56	5.33
3	3.54	2.67	3.55	3.46	4.32	4.88	5.57
4	3.61		3.61	3.55	4.35	5.12	6.17
5	4.06		4.07	4.07	4.50	5.57	6.42

Table 2b. Summary of Characteristic PCB Peak Retention Times (DB-608 Column)

Peak	*1016*	*1221*	*1232*	*1242*	*1248*	*1254*	*1260*
1	3.11	2.89	3.11	3.53	3.88	4.90	5.62
2	3.52	3.04	3.52	3.89	4.51	4.96	5.70
3	3.88	3.10	3.88	4.04	4.77	5.45	6.14
4	4.04		4.04	4.77	4.82	5.56	6.60
5	4.17		4.82	4.82	5.45	6.10	7.02

Table 3. Retention Time Extraction Windows

Aroclor	*Main Peak Retention Time*			*σ (min)*	*Window (min)*
PCB-1016	3.459	3.455	3.45	0.004509	±0.013527
PCB-1260	5.567	5.572	5.564	0.004041	±0.012123

Table 4. Matrix Spike Accuracy and Precision Data

Aroclor	*Matrix*	*Spike*	*n*	*%Rec.*	*%RSD*	*LCL(%)*	*UCL(%)*	*LCL(%) DOD*	*UCL(%)DOD*
PCB-1016/1260	Water	0.5 µg/l	457	91.4	10.8	59.1	123.7	46/45	129/134
PCB-1016/1260	Soil	25.0 µg/kg	567	88.2	11.8	52.9	123.4	47/53	134/140

Key:
n: number of runs
% Rec: % Recovery
% RSD: % Relative Standard Deviation
LCL: Lower Control Limits
UCL: Upper Control Limits

Table 5. Surrogate Standard Recovery Ranges

Compound	*Matrix*	*Spike*	*n*	*%Rec.*	*%RSD*	*LCL(%)*	*UCL(%)*	*LCL(%) DOD*	*UCL (%) DOD*
TCX (Tetrachloro-m-xylene)	Water	0.01 µg/l	845	85.7	16.8	34.1	137.1	44	130
	Soil	0.50 µg/kg	445	82.6	16.8	33.0	135.3		
DCBP (Decachlorobiphenyl)	Water	0.01 µg/l	810	81.9	18.8	30.0	138.6		
	Soil	0.50 µg/kg	393	81.8	18.8	30.0	137.0		

Key:
n: number of runs
% Rec: % Recovery
% RSD: % Relative Standard Difference
LCL: Lower Control Limits
UCL: Upper Control Limits

Table 6. Calibration Concentration Mixtures

Aroclor		*C_1 (ppm)*	*C_2 (ppm)*	*C_3 (ppm)*	*C_4(ppm)*	*C_5(ppm)*
PCB-1016		0.1	0.3	0.5	0.8	1.0
PCB-1221		0.1	0.3	0.5	0.8	1.0
PCB-1232		0.1	0.3	0.5	0.8	1.0
PCB-1242		0.1	0.3	0.5	0.8	1.0
PCB-1248		0.1	0.3	0.5	0.8	1.0
PCB-1254		0.1	0.3	0.5	0.8	1.0
PCB-1260		0.1	0.3	0.5	0.8	1.0
PCB-1016/1260[†]	0.05	0.1	0.3	0.5	0.8	1.0

[†]: The concentration for the 1016/1260 mixture is the concentration of each Aroclor.

Table 7. Standard Preparation for Calibration Mixtures

Mixture Volume: 1000 ul
Mixture Concentration: 100 mg/l
Mixture Name: ***PCB 1016/1260***

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016	1000	100	100.00
PCB 1260	1000	100	100.00
Solvent - Hexane			800.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.5** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.5	5.00
TCX/DCBP	1.0	0.006	6.00
Solvent - Hexane			989.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.1** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.1	1.00
TCX/DCBP	1.0	0.002	2.00
Solvent - Hexane			997.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.8** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.8	8.00
TCX/DCBP	1.0	0.008	8.00
Solvent - Hexane			984.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.3** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	0.3	3.00
TCX/DCBP	1.0	0.004	4.00
Solvent - Hexane			993.00

Mixture Volume: 1000 ul
Mixture Concentration: **1.0** mg/l

Compound/Mix	*C(stock) mg/l*	*C(final) mg/l*	*V(stock) ul*
PCB 1016/1260	100	1	10.00
TCX/DCBP	1.0	0.010	10.00
Solvent - Hexane			980.00

Table 8. Quality Control Items, Frequency and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (IC)	Prior to all analytical runs	Method-based	Examine the entire analytical system; perform some or all of the following: clip/replace column, replace heat detector, change injection septum, replace calibration standards, re-calibrate.
Continuing Calibration (CCV)	20 Samples / 12 hours	80 – 120%	Examine the entire analytical system; perform some or all of the following: clip/replace column, replace heat detector, change injection septum, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Table 4	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	≤20% RPD	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	< Reporting Limit	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated extraction glassware should result in a thorough re-cleaning of the affected glassware. If the method blank contamination for a batch is above the reporting limit, the blank should be re-extracted and re-analyzed. If additional sample exists, the samples associated with a failed, re-extracted blank should also be re-extracted and re-analyzed.
Surrogate Standard	All samples	Table 5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Breakdown check(Endrin/DDT Method 8081 only)	Before sample analysis and at the beginning of each 12-hour shift.	Degradation of DDT and Endrin must each be ≤15%.	Correct problem, then repeat breakdown checks.	Flagging is not appropriate.	No samples shall be run until degradation of DDT and Endrin is each ≤15%.
Initial Calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	ICAL must meet one of the three options below: Option 1: RSD for each analyte ≤ 20%; Option 2: linear least squares regression for each analyte: $r^2 \geq 0.99$; Option 3: non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. Quantitation for multicomponent analytes such as chlordane, toxaphene, and Aroclors must be performed using a 5-point calibration. Results may not be quantitated using a single point. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and surrogate.
Retention Time (RT) window width	At method set-up and after major maintenance (e.g., column change).	RT width is ± 3 times standard deviation for each analyte RT from the 72-hour study or 0.03 minutes, whichever is greater.	NA.	NA.	Calculated for each analyte and surrogate. Only applicable if internal standard calibration is not used.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within established RT windows. All reported analytes within ± 20% of true value.	Correct problem, rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	Before sample analysis, after every 10 field samples, and at the end of the analysis sequence with the exception of CCVs for	All reported analytes and surrogates within established RT windows. All reported analytes and surrogates within ± 20% of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without	If reanalysis cannot be performed, data must be qualified and explained in the case narrative.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

	Pesticides multi-component analytes (i.e. Toxaphene, Chlordane and Aroclors other than 1016 and 1260), which are only required before sample analysis.		reanalysis. If either fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	
Internal Standards (IS)	If employed, every field sample, standard, and QC sample.	Retention time within ± 0.06 RRT UNITS from retention time of the midpoint standard in the ICAL; Internal standard signal (area or height) within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the Case Narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging is not appropriate for failed standards.	NA.
Method Blank (MB)	One per preparatory batch.	No analytes detected > 1/2 LOQ or > $1/10^{th}$ the amount measured in any sample or $1/10^{th}$ the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

				associated preparatory batch.	
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD $\leq$ 30% (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate Spike	All field and QC samples.	QC acceptance criteria specified by the project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed.	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

			sample material is available. If obvious chromatographic interference is present, reanalysis may not be necessary, but the client must be notified prior to reporting data, and the failures must be discussed in the Case Narrative.		
Confirmation of positive results (second column)	All results > the DL must be confirmed (except for single column methods such a TPH by Method 8015 where confirmation is not an option or a requirement).	Calibration and QC criteria for second column are the same as for initial or primary column analysis. Results between primary and secondary column RPD ≤ 40%.	NA.	Apply J-flag if RPD > 40%. Discuss in the case narrative.	Use project-specific reporting requirements if available; otherwise, use method requirements if available; otherwise report the result from the primary column.

DoD Appendix C LCS Limits
Method 8082 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
12674-11-2	Aroclor 1016	47	134
11097-69-1	Aroclor 1254	67	135
11096-82-5	Aroclor 1260	53	140
877-09-8	Tetrachloro-m-xylene	44	130

Method 8082 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
12674-11-2	Aroclor 1016	46	129
11097-69-1	Aroclor 1254	34	127
11096-82-5	Aroclor 1260	45	134

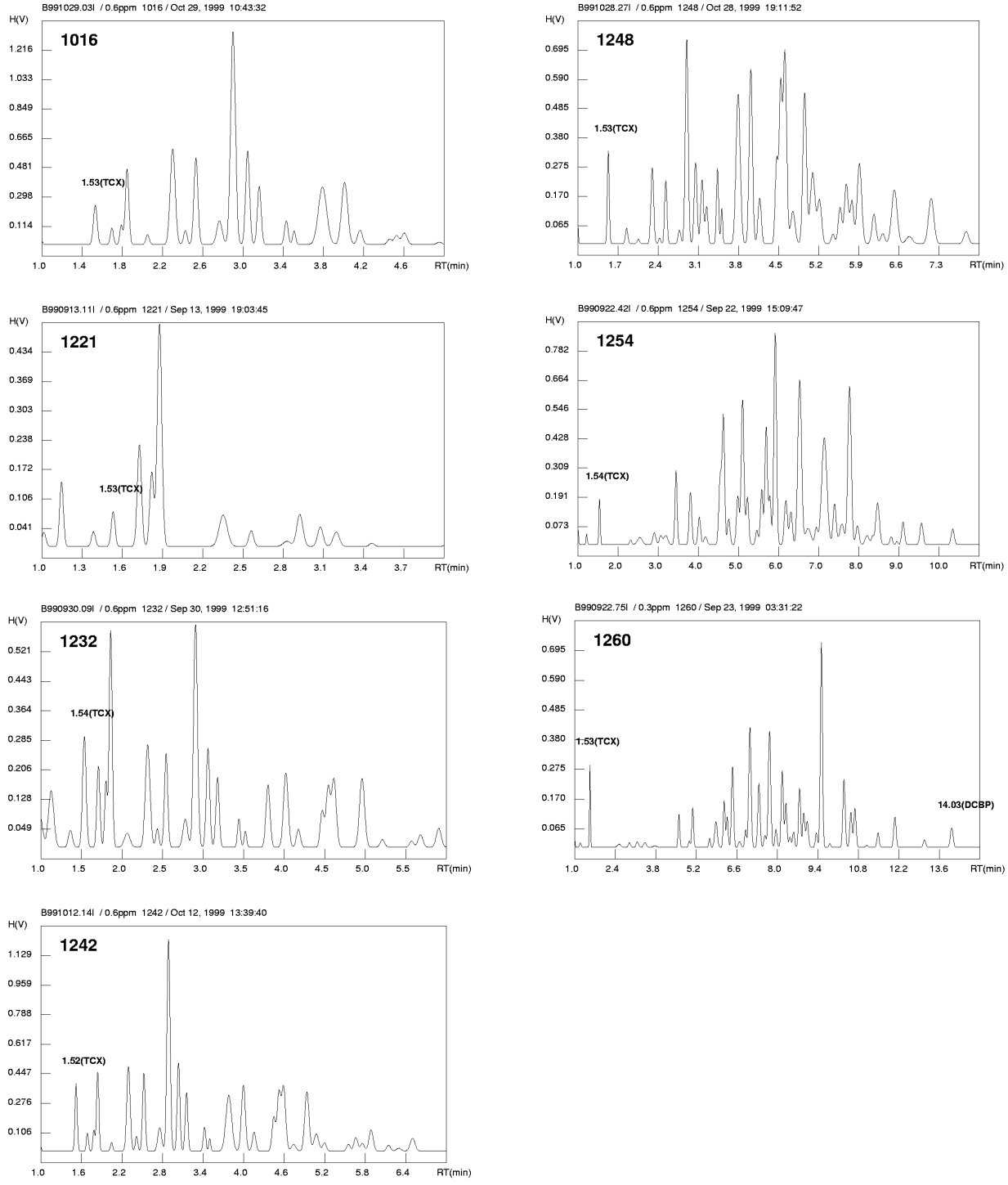


Figure 1. Example Aroclor chromatographic patterns from midpoint calibration standards for PCB 1016, 1221, 1232, 1242, 1248, 1254, and 1260 (column DB-5).

STANDARD OPERATING PROCEDURE

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
METHOD SW-846 8270D

APPROVALS:

Barbara Ball 01/16/18

QA Officer Date

Maya Mushaly 01/16/18

Technical Director Date

Number	Description of Change	Date
001-010	Previous revisions not documented	
011	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
012	Updated to method 8270D	9/4/13
013	Emergency SOP Amendment Form updates	2/9/16
014	Updated to comply with DoD QSM 5.0 standards.	04/01/16
015	Updated to comply with DoD QSM 5.1 standards.	01/16/18
016		
017		
018		
019		
020		

1.0 SCOPE AND APPLICATION

1.1 This SOP can be used to quantitate most basic, neutral and acidic organic compounds (BNAs) that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons (PNAs), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. This SOP is applicable to groundwater, surface water, aqueous sludges, water oily solvents, wastes, soil and sediment samples. See Tables 1a and 1b for a list of compounds (along with their characteristic ions) that have been evaluated.

1.2 In most cases, this method is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, *etc*., because of limited sensitivity for those analytes. When these analytes have been identified by another technique, this method is appropriate for confirmation of the presence of these analytes when concentration in the extract permits.

1.3 The following compounds may require special treatment when being determined by this method:

- Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.
- Under the alkaline conditions of the extraction step from aqueous matrices, α-BHC, β-BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
- N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline,

4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the gas chromatograph (GC) system is contaminated with high boiling material.

- Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.
- In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.4 The practical quantitation limits (PQL) for determining an individual compound is approximately 330 μg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 μg/L for ground water samples. PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

- *Method Detection Limits (MDL) and Practical Quantitation Limits (PQL) are available in Merit's LIMs system.*

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF THE METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Methods 3500, 3510, 3550).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a GC with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point (or more) calibration curve.

2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. This is virtually never a problem for direct injection GC/MS analysis, provided that the sample syringe is rinsed with solvent between sample injections. If carryover is suspected, questionable samples should be re-injected after the system has been demonstrated to be free of contamination.

4.0 APPARATUS AND MATERIALS

Gas chromatograph/mass spectrometer system

4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 Column - 30 m × 0.25 mm ID × 0.5 μm film thickness silicone-coated fused-silica capillary column (Hewlett Packard HP-5ms SV or equivalent).

4.1.3 Mass spectrometer capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 4 when 1 μL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP)

4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

4.2 Syringes - 1 to 1000 μL Hamilton syringes are used in the preparation of standards, spiking solutions, and standards.

4.3 Balance - Analytical, capable of weighing 0.0001 g.

4.4 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

4.5 Maintenance logbooks

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

5.3 Stock standard solutions

5.3.1 Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.

5.3.2 Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a stock solution of 1000 to 10000 mg/L).

5.3.3 Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.

5.3.4 Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards used are 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12} (see Table 2a). Internal standards are spiked into the sample extracts and calibration standards at a uniform concentration of 40 ng/μL (≡ 40 mg/L).

5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP), pentachlorophenol, and benzidine is used to evaluate GC/MS tuning criteria, injection port inertness, and GC column performance.

5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. If possible, the lowest calibration standard corresponds to a sample concentration at or below the standard reporting limit. The remaining standards should correspond to the working range of the GC/MS system (10-100 ng/μL for BNAs, and 2-100 ng/μL for PNAs). Each standard should contain each analyte for detection by this method. The preparation instructions for the creation of calibrations standards from stock solutions commonly used in BNA and PNA analysis can be found in the SVOC.QC-Reference Document.

5.7 Surrogate standards - The surrogates used are Phenol-d_6, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitrobenzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14}. See Method 3500 for instructions on preparing the surrogate solutions. For BNA analysis, all six surrogate standards are used. For PNA analysis, only Nitrobenzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14} are used.

5.7.1 Surrogate spiking mixes are created at 100 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract as 100ng/μL.

5.7.2 Surrogate Standard Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard is used as the laboratory control standard (LCS).

5.8.1 Matrix spiking mixes for single component analytes are generally created at 50 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract is 50ng/μL.

5.8.2 Matrix Spike Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of matrix spike standards. It is recommended that this check be done whenever a new matrix spiking solution is prepared.

5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE HANDLING AND PRESERVATION

Unanalyzed samples are refrigerated at 4 ± 2 degrees Celsius and protected from light in amber sealed containers.

Aqueous samples are shall be extracted within 7 days from sample collection and analyzed within 40 days from extraction.

Soil samples shall be extracted within 14 days from sample collection and analyzed within 40 days thereafter.

7.0 PROCEDURE

Sample preparation

7.1.1 Soil and water are prepared via an extraction procedure (*cf*. SW-846 Methods 3500, 3510, 3550; SOP# EXL-005 and EXL- 006) prior to GC/MS analysis.

7.1.2 In cases where the sample is an oil or solvent, the sample is simply diluted with methylene chloride and analyzed at a concentration appropriate for the level of analytes/interferences in the sample. In this situation, the sample is reported on a weight basis and analyzed in a batch of soil samples.

7.2 GC/MS operating conditions - see Table 3 for routine operating conditions for both BNA and PNA analysis.

7.3 Initial calibration

7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP prior to the analysis of calibration standards and samples.

7.3.1.1 In the absence of any other manipulations, evaluate the mass spectrum of the highest intensity level from the total ion chromatogram for the DFTPP peak. This is the default approach used.

7.3.1.2 If the above evaluation is adversely affected by ion peak asymmetry or background contamination, average the three highest intensity scans for the DFTPP peak. Perform a background subtraction with a spectrum within 20 scans of the DFTPP peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.

7.3.1.3 The DFTPP mass intensity criteria in Table 4 are used as tuning acceptance criteria.

7.3.1.4 All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.

7.3.1.5 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol should be present at their normal responses, and the peak tailing factor should be less than 2.

7.3.1.6 The injection port is replaced prior to any calibration sequence or 12-hour BNA analytical sequence. If chromatography is still poor, it may also be necessary to clip off the first 6-12 in. of the capillary column. Clipping the column may necessitate recalibration, as retention times and responses can shift considerably.

7.3.2 Analyze 1-2 μL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Tables 1a and 1b). A set of at least five calibration standards is necessary. The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Depending on the current state of the GC/MS system, a 2 μL injection may be required to achieve appropriate responses for the lower levels of the least sensitive compounds. When possible, however, a 1 μL can be used to yield a better dynamic range for the high sensitivity compounds.

7.3.3 Calculate response factors (*RF*s) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.

7.3.4 Minimum Response Factor compounds

7.3.4.1 A system performance check must be performed to ensure that minimum *RF*s are met before the calibration curve is used. It is also recommended that a minimum response factor for the most common target analytes as

noted in Table 2c, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration level is important in demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed, some compounds will fail to meet this criteria. In particular, late eluting compounds, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene and Benzo(g,h,i)perylene are likely to fail this criteria but have been demonstrated to perform adequately overall.

7.3.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. Replacing the calibration standards, and/or clipping/replacing the column will likely solve this problem.

7.3.5 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. The retention time extraction windows are set in the Chemstation software.

7.3.6 Linearity of target analytes - If the %RSD of any target analyte is 20% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation

7.3.6.1 Refer to SW-846 Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Note that quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. (All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior). In any event, the coefficient of determination (COD) for any regression fit should be ≥0.99. In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters. If more than 10% of the compounds included with the initial

calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Compounds that fail the 20% and (0.99) criteria should not be reported unless estimated values are acceptable to project goals.

7.3.6.2 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc*.

7.3.6.3 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and the quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve. The recalculated concentration of the low calibration point should be within 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives. For analytes which do not meet the minimum quantitation calibration re-fitting criteria reporting those analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.

7.3.6.4 The initial calibration function should be verified immediately after performing the standard analyses using a second source standard at a concentration near the midpoint of the calibration range. The acceptance limits are 70-130% or project specific. Analytes that fail this criteria are considered estimated values.

7.3.6.5 The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e*. average RF or

regression coefficients), and the appropriate calibration quality metric (*i.e*. %RSD or COD).

7.3.6.6 Refer to Table 5b for DoD project requirements.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the DFTPP.

7.4.2 The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration (50 ng/μL) for the calibration range of the GC/MS. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the targetcompounds. In addition the internal standards should be within 30s of those in the midpoint calibration standard and the internal standard responses should be 50-200% of those in the midpoint calibration standard.

7.4.3 A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants.

7.4.4 Minimum Response Factor compounds

7.4.4.1 A calibration verification standard must be analyzed during every 12-hour analytical shift. Each of the most common targetcompounds in the calibration verification standard should meet the minimum response factor noted in Table 2c. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins (see previous).

7.4.5 Calibration check compounds

7.4.5.1 After the minimum response factor check is met all target compounds of interest must be evaluated using a 20% variability criterion. If the percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when a failed compound is present, the concentration is an estimated value. Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = \left|C - C_{spike}\right| \Big/ C_{spike}$

7.4.5.2 Problems similar to those listed under initial calibration could affect the calibration verification. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

7.4.5.3 Refer to Table 5b for DoD project requirements.

7.5 GC/MS analysis of samples

7.5.1 Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Allow the sample extract to warm to room temperature. 3 μL of the internal standard solution is added to a 300 μL aliquot of sample in a crimp-top vial for subsequent autosampler analysis. If the sample extract is to be diluted prior to analysis, a smaller sample volume is used (even though the net volume of nominally 300 μL remains the same). SVOC Dilution Reference Document has a list of commonly used dilutions as well as the required amount of sample, solvent, and internal standard for each dilution.

7.5.3 Inject a 1-2 μL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration.

7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system by more than 10%, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.

7.5.5 The extracted ion current potential (EICP) area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Tables 5a and 5b). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.

7.6 Qualitative analysis

7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Tables 1a and 1b. Compounds are identified when the following criteria are met.

7.6.1.1 Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time.

7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.1.7 In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of continued uncertainty, the analyst should preferentially make a conservative judgement and accept an identified hit, allowing the potential for a false positive.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1 [C_s/C_i] + k_2 [C_s/C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th}-order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv$ <RF>, while k_0, $k_2 \equiv 0$.

7.7.3 The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the TIC areas for the nearest internal standard and target compound. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.4 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-cresol).

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 5a and 5b. In addition, the tables indicate the frequency of each QC item along with appropriate courses of corrective action. Control limits for surrogates and matrix spikes are listed in Table 6. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Laboratory specific performance data is provided on in Merit's LIMs system. Each sample batch contains a method blank, laboratory control sample and matrix spike samples. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention shall be paid (but not limited) to:

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike (LCS): Milli-Q water (for water) or Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias, to verify the analytical system performance, and to document method accuracy for each matrix.

Laboratory Control Spike Duplicate (LCSD): A duplicate Milli-Q water (for water) or Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike duplicate is used to document the precision and bias of a method. This QC type is only performed when sufficient amount of sample is unavailable for performing a matrix spike and matrix spike duplicate.

Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. It is used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with identical concentration of target analytes. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Method Reporting Limit (MRL): The method reporting limit is a threshold value below which the laboratory reports a result as a non-detect. The highest value reported for the method reporting limit is dependant upon project-specific action or decision levels. Method reporting limits are adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

Method Detection Limit (MDL): The method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. Depending on project, specific MDL checks are either in the form of an

MDL check standard or the MDL is subject to extraction procedures. An acceptable MDL standard check must produce signals for the qualifier ions. An MDL standard injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Surrogate (SURR): Organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The acid surrogates are at twice the concentration of the Base/Neutral surrogates. The acid surrogate compounds are: 2-Fluorophenol, Phenol $d_{5,}$ and 2,4,6-Tribromophenol. The base/neutral surrogates are: Nitrobenzene $d_{5,}$ 2-Fluorobiphenyl, and p-Terphenyl $d_{14.}$ o-Terphenyl d_{14} is also added when the samples are analyzed for PAHs in selected ion monitoring (SIM) mode.

Initial Calibration (ICAL): An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of an analyte. This relationship is depicted graphically and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): A standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis. A CCV must be made during each 12 hour shift.

DFTPP: Decafluorotriphenylphosphine. This compound is used in tuning the GC/MS. To acquire the mass spectrum of DFTPP, three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction to eliminate column bleed or instrument background noise is accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The DFTPP standard must also contain Pentachlorophenol, Benzidine, and DDT to assess GC column performance and injection port inertness. Benzidine and Pentachlorophenol must have tailing factors less than 2. Breakdown of DDT to DDD and DDE must be less than 20%

Internal standard (ISTD): Internal Standard involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample extract prior to injection. The ratio of the peak area of the target compound in the sample extract to the peak area of the internal standard in the sample extract is compared to a similar ratio derived for each calibration standard. The internal standards are; 1,4-Dichlorobenzene $d_{4,}$ Naphthalene $d_{8,}$ Acenaphthene $d_{10,}$ Phenanthrene $d_{10,}$ Chrysene d_{12} and Perylene $d_{12.}$ In addition, Benzo[a]anthracene d_{12} is added when the samples are analyzed for PAHs in selected ion monitoring (SIM) mode.

System Performance Check Compounds (SPCC): SPCCs are system performance compounds that are a part of the Continuing Calibration Verification standard (CCV). The SPCCs must meet a minimum response factor of 0.050. The SPCC criteria also apply to the average response factor of the initial calibration curve.

Calibration Check Compounds (CCC): CCCs are calibration check compounds that are a part of the Continuing Calibration Verification standard (CCV). The CCC percent difference must be less than or equal to 20%.

Instrument Blanks: Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it can be followed by the analysis of an instrument blank (methylene chloride + Internal Standards) to check for cross-contamination.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, Based on ISO/IEC 17025:2005€ and The NELAC Institute (TNI) Standards, Volume 1, (September 2009), Version 5.1, 2017.

U.S. EPA 40 CFR Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule*, October 26, 1984.

EPA SW-846, *Test Methods for Evaluation Solid Waste*, 3rd Edition, Update I dated 7/92, Update II dated 9/94, Update IIA dated 8/93, Update IIB dated 1/95, Update III dated 12/96, Update IV dated 1/08.

International Standards Organization (ISO), 2005. *General Requirements for the Competence of Testing and Calibration Laboratories.* ISO 17025.

National Environmental Laboratory Accreditation Conference (NELAC), 2003. *Standards, Chapters 1–6*, EPA/600/R-04/003.

Table 1a. Summary of Retention Times† and Characteristic Ions for Base/Neutral/Acid Semi-Volatile Organics

#	**Compound**	t_R	$t_R/t_{R,I}$	$t_R-t_{R,I}$	1^0	2^0	3^0	4^0
		(min)	**(-)**	***(min)***	***m/z***	***m/z***	***m/z***	***m/z***
1)	1,4-DICHLOROBENZENE-D4	6.92	1.000	0.00	152	150	115	
2)	N-Nitrosodimethylamine	3.79	0.548	-3.13	74	42	43	
3)	2-Picoline	4.61	0.666	-2.31	93	92	66	
4)	Methyl methanesulfonate	5.16	0.746	-1.76	80	79	95	
5)	2-Fluorophenol	5.31	0.767	-1.61	112	92	64	
6)	Ethyl methanesulfonate	5.99	0.866	-0.93	79	109	97	
7)	Phenol-d5	6.45	0.932	-0.47	99	71	42	
8)	Phenol **	6.47	0.935	-0.45	94	66	65	
9)	Aniline	6.53	0.944	-0.39	93	65	66	
10)	2-Chlorophenol **	6.68	0.965	-0.24	128	130	92	
11)	Bis(2-chloroethyl)ether	6.59	0.952	-0.33	93	63	95	
12)	1,3-Dichlorobenzene	6.94	1.003	0.02	146	148	111	
13)	1,4-Dichlorobenzene **	6.94	1.003	0.02	146	148	111	
14)	1,2-Dichlorobenzene	7.18	1.038	0.26	146	148	111	
15)	Bis(2-chloroisopropyl)ether	7.3	1.055	0.38	45	121	77	
16)	Benzyl Alcohol	7.09	1.025	0.17	108	107	79	77
17)	Acetophenone	7.46	1.078	0.54	105	77	120	
18)	o-Cresol	7.24	1.046	0.32	108	107	79	
19)	p,m-Cresol	7.42	1.072	0.50	107	108	79	
20)	Hexachloroethane	7.59	1.097	0.67	117	119	201	
21)	N-Nitrosodi-n-propylamine*	7.48	1.081	0.56	70	43	42	41
22)	NAPHTHALENE-D8	8.59	1.000	0.00	136	68	108	
23)	Nitrobenzene-d5	7.66	0.892	-0.93	82	128	98	
24)	Nitrobenzene	7.69	0.895	-0.90	123	123	65	
25)	N-Nitrosopiperidine	7.89	0.919	-0.70	114	55	56	
26)	Isophorone	7.98	0.929	-0.61	82	95	138	
27)	2-Nitrophenol	8.11	0.944	-0.48	139	109	65	
28)	2,4-Dimethylphenol	8.12	0.945	-0.47	107	122	121	
29)	Bis(2-chloroethoxy)methane	8.25	0.960	-0.34	93	63	95	
30)	2,4-Dichlorophenol	8.4	0.978	-0.19	162	164	98	

#	Compound	t_R (*min*)	$t_R/t_{R,I}$ (-)	$t_R-t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
31)	1,2,4-Trichlorobenzene **	8.52	0.992	-0.07	180	182	145	
32)	Naphthalene	8.61	1.002	0.02	128	127	129	
33)	4-Chloroaniline	8.69	1.012	0.10	127	129	65	
34)	2,6-Dichlorophenol	8.71	1.014	0.12	162	164	127	
35)	Hexachlorobutadiene	8.83	1.028	0.24	225	223	227	
36)	N-Nitroso-di-n-butylamine	9.13	1.063	0.54	84	116	158	
37)	4-Chloro-3-methylphenol **	9.28	1.080	0.69	107	142	77	
38)	2-Methylnaphthalene	9.5	1.106	0.91	141	142	115	
40)	1,2,4,5-Tetrachlorobenzene	9.77	1.137	1.18	216	214	218	
41)	Hexachlorocyclopentadiene	9.79	1.140	1.20	237	235	239	
42)	2,4,6-Trichlorophenol	9.94	1.157	1.35	196	198	200	
43)	2,4,5-Trichlorophenol	9.94	1.157	1.35	196	198	132	
44)	2-Fluorobiphenyl	9.98	1.162	1.39	172	171	173	
45)	2-Chloronaphthalene	10.13	1.179	1.54	162	127	164	
46)	1-Chloronaphthalene	10.18	1.185	1.59	162	164	127	
47)	2-Nitroaniline	10.29	1.198	1.70	138	65	92	
48)	Acenaphthylene	10.67	1.242	2.08	152	151	150	
49)	Dimethyl Phthalate	10.54	1.227	1.95	163	164	77	
50)	2,6-Dinitrotoluene	10.64	1.239	2.05	165	121	148	
51)	3-Nitroaniline	10.82	1.260	2.23	138	92	65	
52)	Acenaphthene **	10.91	1.270	2.32	154	153	152	
53)	2,4-Dinitrophenol	10.95	1.275	2.36	184	63	107	
54)	Dibenzofuran	11.12	1.295	2.53	168	169	139	
55)	4-Nitrophenol **	10.99	1.279	2.40	65	139	81	109
56)	2,4-Dinitrotoluene **	11.15	1.298	2.56	165	89	63	
57)	2,3,4,6-Tetrachlorophenol	11.32	1.318	2.73	232	230	234	131
58)	Fluorene	11.56	1.346	2.97	166	165	167	
59)	Diethyl phthalate	11.43	1.331	2.84	149	150	177	
60)	4-Chlorophenyl phenyl ether	11.53	1.342	2.94	204	141	206	
61)	4-Nitroaniline	11.61	1.352	3.02	138	65	92	
62)	2,4,6-Tribromophenol	11.89	1.384	3.30	330	332	141	
63)	PHENANTHRENE-D10	12.8	1.000	0.00	188	80	94	

#	Compound	t_R (*min*)	$t_R/t_{R,I}$ (-)	$t_R-t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
64)	4,6-Dinitro-2-methylphenol	11.67	0.912	-1.13	198	121	105	
65)	N-Nitrosodiphenylamine	11.69	0.913	-1.11	169	168	167	
66)	1,2-Diphenylhydrazine	11.74	0.917	-1.06	182	105	77	
67)	Azobenzene	11.74	0.917	-1.06	182	105	77	
68)	4-Bromophenyl phenyl ether	12.16	0.950	-0.64	248	250	77	
69)	1,3,5-Trinitrobenzene	12.08	0.944	-0.72	213	74	75	
70)	Phenacetin	12.11	0.946	-0.69	108	109	179	137
71)	Hexachlorobenzene	12.37	0.966	-0.43	249	282	286	
72)	4-Aminobiphenyl	12.51	0.977	-0.29	169	168	170	
73)	Pentachlorophenol **	12.6	0.984	-0.20	266	264	268	
75)	Pronamide	12.6	0.984	-0.20	173	174	145	
76)	Pentachloronitrobenzene	12.72	0.994	-0.08	237	249	295	
77)	Phenanthrene	12.83	1.002	0.03	178	176	179	
78)	Anthracene	12.83	1.002	0.03	178	176	179	
79)	di-N-butyl phthalate	13.62	1.064	0.82	149	150	104	
80)	Fluoranthene	14.65	1.145	1.85	202	200	203	
81)	Terphenyl-d14	15.28	1.194	2.48	244	122	212	
82)	CHRYSENE-D12	17.34	1.000	0.00	240	236	120	
83)	Benzidine	14.83	0.855	-2.51	184	185	92	
84)	Pyrene **	15.03	0.867	-2.31	202	200	203	
85)	p-Dimethylaminoazobenzene	15.57	0.898	-1.77	225	120	77	
86)	Butyl benzyl phthalate	16.23	0.936	-1.11	149	91	206	
88)	Benzo(a)anthracene	17.29	0.997	-0.05	228	226	229	
89)	3,3'-Dichlorobenzidine	17.25	0.995	-0.09	252	254	126	
90)	Chrysene	17.38	1.002	0.04	228	226	229	
92)	PERYLENE-D12	20.3	1.000	0.00	264	260	265	
91)	Bis(2-ethylhexyl)phthalate	17.42	0.858	-2.88	149	167	279	
93)	Di-n-octyl phthalate	18.66	0.919	-1.64	149	43	167	
95)	Benzo(b)fluoranthene	19.47	0.959	-0.83	252	253	126	
96)	7,12-Dimethylbenz(a)anthracene	19.5	0.961	-0.80	256	241	239	
97)	Benzo(k)fluoranthene	19.47	0.959	-0.83	252	253	126	
98)	Benzo(a)pyrene	20.16	0.993	-0.14	252	253	126	

#	**Compound**	t_R	$t_R/t_{R,I}$	t_R-$t_{R,I}$	1^0	2^0	3^0	4^0
		(min)	**(-)**	**(*min*)**	***m/z***	***m/z***	***m/z***	***m/z***
99)	3-Methylcholanthrene	21.04	1.036	0.74	268	252	253	269
100)	Dibenz(a,j)acridine	22.54	1.110	2.24	279	280	139	278
101)	Indeno(1,2,3-cd)pyrene	23.1	1.138	2.80	276	138	277	
102)	Dibenzo(a,h)anthracene	23.14	1.140	2.84	278	139	279	
103)	Benzo(ghi)perylene	23.92	1.178	3.62	276	138	277	

†: Absolute retention times (t_R) listed are from calibration BU061002.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e*. new, clipped, *etc*.), but the differential retention times (t_R - $t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

Table 1b. Summary of Retention Times† and Characteristic Ions for Polynuclear Aromatic Semi-Volatile Organics

#	**Compound**	t_R	$t_R/t_{R,I}$	t_R-$t_{R,I}$	1^0	2^0	3^0	4^0
		(min)	**(-)**	**(*min*)**	***m/z***	***m/z***	***m/z***	***m/z***
1)	1,4-DICHLOROBENZENE-D4	3.96	1.000	0.00	152	152		
2)	NAPHTHALENE-D8	5.21	1.000	0.00	136	68	108	
3)	Nitrobenzene-d5	4.52	0.868	-0.69	82	54	128	
4)	Naphthalene	5.23	1.004	0.02	128	127	129	
5)	2-Methylnaphthalene	5.88	1.129	0.67	141	141	115	
6)	ACENAPHTHALENE-D10	6.94	1.000	0.00	164	162	160	
7)	2-Fluorobiphenyl	6.23	0.898	-0.71	172	171	173	
8)	Acenaphthylene	6.78	0.977	-0.16	152	151	150	
9)	Acenaphthene **	6.97	1.004	0.03	154	153	76	
10)	Fluorene	7.49	1.079	0.55	166	165	167	
11)	PHENANTHRENE-D10	8.52	1.000	0.00	188	80	94	
12)	Phenanthrene	8.54	1.002	0.02	178	176	179	
13)	Anthracene	8.6	1.009	0.08	178	176	179	
14)	Fluoranthene	10.09	1.184	1.57	202	200	203	
15)	Terphenyl-D14	10.62	1.246	2.10	244	122	212	
16)	CHRYSENE-D12	12.5	1.000	0.00	240	236	120	
17)	Pyrene **	10.44	0.835	-2.06	202	101	200	
18)	Benzo(a)anthracene	12.46	0.997	-0.04	228	226	229	
19)	Chrysene	12.54	1.003	0.04	228	226	229	
20)	PERYLENE-D12	15.22	1.000	0.00	264	260	132	
21)	Benzo(b)fluoranthene	14.51	0.953	-0.71	252	253	126	
22)	Benzo(k)fluoranthene	14.56	0.957	-0.66	252	253	125	
23)	Benzo(a)pyrene	15.12	0.993	-0.10	252	253	126	
24)	Indeno(1,2,3-cd)pyrene	17.38	1.142	2.16	276	138	277	
25)	Dibenzo(ah)anthracene	17.39	1.143	2.17	278	139	279	
26)	Benzo(ghi)perylene	17.99	1.182	2.77	276	138	277	

†: Absolute retention times (t_R) listed are from calibration PF060829.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e*. new, clipped, *etc*.), but the differential retention times (t_R - $t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

Table 2a. Summary of Applicable Performance Compounds - Base/Neutral/Acid Analysis

#†	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	1,4-DICHLOROBENZENE-D4			✔		
6	2-Fluorophenol				✔	
8	Phenol-d5				✔	
9	Phenol **	✔				✔
11	2-Chlorophenol **					✔
14	1,4-Dichlorobenzene **	✔				✔
22	N-Nitrosodi-n-propylamine**		✔			✔
23	NAPHTHALENE-D8			✔		
24	Nitrobenzene-d5				✔	
28	2-Nitrophenol	✔				
31	2,4-Dichlorophenol	✔				
32	1,2,4-Trichlorobenzene **					✔
37	Hexachlorobutadiene	✔				
39	4-Chloro-3-methylphenol **	✔				✔
41	ACENAPHTHALENE-D10			✔		
43	Hexachlorocyclopentadiene		✔			
44	2,4,6-Trichlorophenol	✔				
46	2-Fluorobiphenyl				✔	
50	Acenaphthylene	✔				
54	Acenaphthene **					✔
55	2,4-Dinitrophenol		✔			
57	4-Nitrophenol **		✔			✔
58	2,4-Dinitrotoluene **					✔
66	2,4,6-Tribromophenol				✔	
67	PHENANTHRENE-D10			✔		
69	N-Nitrosodiphenylamine	✔				
77	Pentachlorophenol **	✔				✔
83	Fluoranthene	✔				
84	Terphenyl-d14				✔	
85	CHRYSENE-D12			✔		
87	Pyrene **					✔
95	Di-n-octyl phthalate	✔				
96	PERYLENE-D12			✔		
100	Benzo(a)pyrene	✔				

†: Compound identification numbers listed are from calibration BX010711.M.

Key

CCC: Calibration Check Compound

SPCC: System Performance Check Compound

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

MS: Matrix Spiking Compound

Table 2b. Summary of Applicable Performance Compounds - Polynuclear Aromatic Analysis

#†	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	1,4-DICHLOROBENZENE-D4			✔		
2	NAPHTHALENE-D8			✔		
3	Nitrobenzene-d5				✔	
4	Naphthalene	✔	✔			✔
6	ACENAPHTHALENE-D10			✔		
7	2-Fluorobiphenyl				✔	
8	Acenaphthylene		✔			
9	Acenaphthene **	✔				✔
11	PHENANTHRENE-D10			✔		
12	Phenanthrene		✔			
14	Fluoranthene	✔				✔
15	CHRYSENE-D12			✔		
16	Pyrene **	✔				✔
17	Terphenyl-d14				✔	
20	PERYLENE-D12			✔		
21	Benzo(b)fluoranthene		✔			
23	Benzo(a)pyrene	✔				✔

†: Compound identification numbers listed are from calibration PN010526.M.

Key

CCC: Calibration Check Compound

SPCC: System Performance Check Compound

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

MS: Matrix Spiking Compound

Table 2c. Recommended Minimum Relative Response Factor Criteria For Initial And Continuing Calibration Verification.

Semivolatile Compounds	Minimum Response Factor (RF)[a]
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010

Semivolatile Compounds	Minimum Response Factor (RF)[a]
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

[a] The Project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed.

Table 3. GC/MS Operating Conditions - Base/Neutral/Acid (BNA) and Polynuclear Aromatic (PNA) Semi-Volatile Organics Analysis†

Operating Parameter	**BNA Analysis**	**PNA Analysis**
Chromatographic Column	HP-5MS SV, *L* = 30 *m*, *ID* = 0.25 *mm*	HP-5MS SV, *L* = 30 *m*, *ID* = 0.25 *mm*
Carrier Gas	Helium (He) at 2 *ml*/*min*	Helium (He) at 2 *ml*/*min*
Temperature Program	*Variable-Instrument dependent*	*Variable-Instrument dependent*
Injector Temperature	250°C	250°C
Detector Temperature	280°C	280°C
Injection Volume	1-2μ*l*	1μ*l*
Mass Scanning Range	35 *m*/*z* - 500 *m*/*z*	35 *m*/*z* - 500 *m*/*z*
Mass Scanning Rate	1.8 *Hz*	1.4 *Hz*

Note: the above is subject to change based on GC and/or sample conditions.

Table 4. DFTPP Tune Evaluation Criteria

Target *m/z*	**Relative *m/z***	**LCL (%)**	**UCL (%)**
51	198	30.0	80.0
68	69	0.0	2.0
69	198	0.0	NA
70	69	0.0	2.0
127	198	25.0	75.0
197	198	0.0	1.0
198	198	100.0	100.0
199	198	5.0	9.0
275	198	10.0	30.0
365	198	1.0	NA
441	443	0.0	100.0
442	198	40.0	110.0
443	442	15.0	24.0

Table 5a. Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
DFTPP	12-hour	Table 4	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	SPCC RF <0.050 CCC $\leq$ 20%	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Table 6	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	<RL	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated extraction glassware should result in a thorough re-cleaning of the affected glassware. If the method blank contamination for a batch is atypical (*i.e*. non phthalate esters), the blank should be re-extracted and re-analyzed. If additional sample exists, the

QC Item	Frequency	Acceptance Criteria	Corrective Action
			samples associated with a failed, re-extracted blank should also be re-extracted and re-analyzed.
Internal Standard	All samples	Section 7.5.5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate. Internal standards recoveries below 50% require re-analysis
Surrogate Standard	All samples	Table 6	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated. Two out three surrogates are to be within limits, as long as the third surrogate is above 10%.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 5b. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Tune Check	Prior to ICAL and prior To each 12-hour period of sample analysis	Specific ion abundance criteria of BFB or DFTPP from method.	Retune instrument and verify.	Flagging criteria is not appropriate.	No samples shall be analyzed without a valid tune.
Performance Check (Method 8270 only)	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation ≤ 20% for DDT. Benzidine and pentachlorophenol shall be present at their normal responses and shall not exceed a tailing factor of 2.	Correct problem, then repeat performance checks.	Flagging is not appropriate.	No sample shall be analyzed until performance check is within criteria. The DDT breakdown and Benzidine/Pentachlorophenol tailing factors are considered overall system checks to evaluate injector port inertness and column performance and are required regardless of the reported analyte list.
Initial calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	Each analyte must meet one of the three options below: Option 1. RSD for each analyte ≤ 15%;. Option 2: linear least squares regression $r^2 \geq 0.99$; Option 3:non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging criteria is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. No samples shall be analyzed until ICAL has passed. If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements must also be met.
Retention time window position establishment	Once per ICAL and at the beginning of the	Position shall be set using the midpoint standard of the ICAL curve	NA.	NA.	Calculated for each analyte and surrogate.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
and surrogate	analytical sequence.	when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.			
Evaluation of relative retention times (RRT)	With each sample.	RRT of each reported analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	After maintenance is performed which may affect retention times, RRTs may be updated based on the daily CCV. RRTs shall be compared with the most recently updated RRTs.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within ± 20% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within ± 20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.		
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	NA
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
				analyte(s) in all samples in the associated preparatory batch.	
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be	For the specific analyte(s) in the parent sample, apply J-flag if	MSD: Must contain all surrogates and all analytes to be reported. The data shall be evaluated to determine the source of difference.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	taken.	acceptance criteria are not met and explain in the case narrative.	For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed..	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative..	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

DoD Appendix C LCS Limits
Method 8270 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
92-52-4	1,1-Biphenyl	40	117
95-94-3	1,2,4,5-Tetrachlorobenzene	37	119
120-82-1	1,2,4-Trichlorobenzene	34	118
95-50-1	1,2-Dichlorobenzene	33	117
528-29-0	1,2-Dinitrobenzene [1,2-DNB]	44	115
122-66-7	1,2-Diphenylhydrazine [Azobenzene]	41	125
99-35-4	1,3,5-Trinitrobenzene [1,3,5-TNB]	57	121
541-73-1	1,3-Dichlorobenzene	30	115
99-65-0	1,3-Dinitrobenzene [1,3-DNB]	43	127
106-46-7	1,4-Dichlorobenzene	31	115
100-25-4	1,4-Dinitrobenzene	37	132
130-15-4	1,4-Naphthoquinone	55	108
90-13-1	1-Chloronaphthalene	48	115
90-12-0	1-Methylnaphthalene	40	119
58-90-2	2,3,4,6-Tetrachlorophenol	44	125
935-95-5	2,3,5,6-Tetrachlorophenol	40	112
608-27-5	2,3-Dichloroaniline	44	121
95-95-4	2,4,5-Trichlorophenol	41	124
118-79-6	2,4,6-Tribromophenol	39	132
88-06-2	2,4,6-Trichlorophenol	39	126
120-83-2	2,4-Dichlorophenol	40	122
105-67-9	2,4-Dimethylphenol	30	127
121-14-2	2,4-Dinitrotoluene	48	126
87-65-0	2,6-Dichlorophenol	41	117
606-20-2	2,6-Dinitrotoluene	46	124
53-96-3	2-Acetylaminofluorene	54	134
91-58-7	2-Chloronaphthalene	41	114
95-57-8	2-Chlorophenol	34	121
321-60-8	2-Fluorobiphenyl	44	115
367-12-4	2-Fluorophenol	35	115

91-57-6	2-Methylnaphthalene	38	122
95-48-7	2-Methylphenol (o-Cresol)	32	122
88-74-4	2-Nitroaniline	44	127
119-75-5	2-Nitrodiphenylamine	53	123
88-75-5	2-Nitrophenol	36	123
109-06-8	2-Picoline [2-Methylpyridine]	27	103
91-94-1	3,3'-Dichlorobenzidine	22	121
56-49-5	3-Methylcholanthrene	56	134
99-09-2	3-Nitroaniline	33	119
65794-96-9	3/4-Methylphenol [m/p-Cresol]	34	119
534-52-1	4,6-Dinitro-2-methylphenol	29	132
101-55-3	4-Bromophenyl phenyl ether	46	124
59-50-7	4-Chloro-3-methylphenol	45	122
106-47-8	4-Chloroaniline [p-Chloroaniline]	17	106
7005-72-3	4-Chlorophenyl phenyl ether	45	121
106-44-5	4-Methylphenol [p-Cresol]	42	126
100-02-7	4-Nitrophenol	30	132
99-55-8	5-Nitro-o-toluidine [2-Amino-4-nitrotoluene]	23	117
57-97-6	7,12-Dimethylbenz(a)-anthracene	50	142
83-32-9	Acenaphthene	40	123
208-96-8	Acenaphthylene	32	132
98-86-2	Acetophenone	33	115
120-12-7	Anthracene	47	123
1912-24-9	Atrazine	47	127
103-33-3	Azobenzene	39	125
56-55-3	Benz(a)anthracene	49	126
50-32-8	Benzo(a)pyrene	45	129
205-99-2	Benzo(b)fluoranthene	45	132
191-24-2	Benzo(g,h,i)perylene	43	134
207-08-9	Benzo(k)fluoranthene	47	132
100-51-6	Benzyl alcohol	29	122
111-91-1	bis(2-Chloroethoxy)methane	36	121
111-44-4	Bis(2-chloroethyl) ether	31	120

39638-32-9	bis(2-Chloroisopropyl) ether	33	131
117-81-7	Bis(2-ethylhexyl) phthalate	51	133
103-23-1	bis(2-Ethylhexyl)adipate	61	121
85-68-7	Butyl benzyl phthalate	48	132
105-60-2	Caprolactam	46	117
86-74-8	Carbazole	50	123
510-15-6	Chlorobenzilate	49	150
218-01-9	Chrysene	50	124
84-74-2	Di-n-butyl phthalate	51	128
117-84-0	Di-n-octyl phthalate	45	140
2303-16-4	Diallate [cis or trans]	56	132
53-70-3	Dibenzo(a,h)anthracene	45	134
132-64-9	Dibenzofuran	44	120
84-66-2	Diethyl phthalate	50	124
60-51-5	Dimethoate	28	108
131-11-3	Dimethyl phthalate	48	124
60-11-7	Dimethylaminoazobenzene	64	134
88-85-7	Dinoseb	16	119
101-84-8	Diphenyl ether	78	114
122-39-4	Diphenylamine	48	111
62-50-0	Ethyl methanesulfonate	34	136
206-44-0	Fluoranthene	50	127
86-73-7	Fluorene	43	125
118-74-1	Hexachlorobenzene	45	122
87-68-3	Hexachlorobutadiene	32	123
67-72-1	Hexachloroethane	28	117
1888-71-7	Hexachloropropene	32	132
95-13-6	Indene	59	112
193-39-5	Indeno(1,2,3-cd)pyrene	45	133
465-73-6	Isodrin	56	132
78-59-1	Isophorone	30	122
120-58-1	Isosafrole	43	136
66-27-3	Methyl methanesulfonate	38	117
100-75-4	N-Nitorosopiperidine	60	119

924-16-3	N-Nitrosodi-n-butylamine	59	124
621-64-7	N-Nitrosodi-n-propylamine	36	120
55-18-5	N-nitrosodiethylamine	41	124
62-75-9	N-Nitrododimethylamine	23	120
86-30-6	N-Nitrosodipehenylamine	38	127
10595-95-6	n-Nitrosomethylethylamine	34	123
59-89-2	n-Nitrosomorpholine	50	133
930-55-2	n-Nitrosopyrrolidine	45	126
91-20-3	Naphthalene	35	123
98-95-3	Nitrobenzene	34	122
4165-60-0	Nitrobenzene-d5	37	122
56-57-5	Nitroquinoline-1-oxide	18	165
126-68-1	O,O,O-Triethyl phosphorothioate	59	124
593-45-3	Octadecane	44	131
608-93-5	Pentachlorobenzene	54	125
76-01-7	Pentachloroethane	39	102
87-86-5	Pentachlorophenol	25	133
82-68-8	Pentachloronitrobenzene	38	134
62-44-2	Phenacetin	57	133
85-01-8	Phenanthrene	50	121
108-95-2	Phenol	34	121
4165-62-2	Phenol-d5	33	122
23950-58-5	Pronamide	56	130
129-00-0	Pyrene	47	127
91-22-5	Quinoline	54	126
94-59-7	Safrole	47	129
1718-51-0	Terphenyl-d14	54	127
3689-24-5	Tetraethyl dithiopyrophosphate [Sulfotep]	52	137
297-97-2	Thionazine	62	127

DoD Appendix C LCS Limits
Method 8270 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
92-52-4	1,1-Biphenyl	49	115
95-94-3	1,2,4,5-Tetrachlorobenzene	35	121
120-82-1	1,2,4-Trichlorobenzene	29	116
95-50-1	1,2-Dichlorobenzene	32	111
528-29-0	1,2-Dinitrobenzene [1,2-DNB]	59	109
122-66-7	1,2-Diphenylhydrazine [Azobenzene]	49	122
99-35-4	1,3,5-Trinitrobenzene [1,3,5-TNB]	41	137
541-73-1	1,3-Dichlorobenzene	28	110
99-65-0	1,3-Dinitrobenzene [1,3-DNB]	49	128
106-46-7	1,4-Dichlorobenzene	29	112
90-13-1	1-Chloronaphthalene	58	111
90-12-0	1-Methylnaphthalene	41	119
134-32-7	1-Naphthylamine	24	124
58-90-2	2,3,4,6-Tetrachlorophenol	50	128
935-95-5	2,3,5,6-Tetrachlorophenol	50	121
608-27-5	2,3-Dichloroaniline	70	129
95-95-4	2,4,5-Trichlorophenol	53	123
118-79-6	2,4,6-Tribromophenol	43	140
88-06-2	2,4,6-Trichlorophenol	50	125
120-83-2	2,4-Dichlorophenol	47	121
105-67-9	2,4-Dimethylphenol	31	124
51-28-5	2,4-Dinitrophenol	23	143
121-14-2	2,4-Dinitrotoluene	57	128
87-65-0	2,6-Dichlorophenol	50	118
606-20-2	2,6-Dinitrotoluene	57	124
53-96-3	2-Acetylaminofluorene	60	138
91-58-7	2-Chloronaphthalene	40	116
95-57-8	2-Chlorophenol	38	117
93951-73-6	2-Chlorophenol-d4	54	106

321-60-8	2-Fluorobiphenyl	44	119
367-12-4	2-Fluorophenol	19	119
91-57-6	2-Methylnaphthalene	40	121
95-48-7	2-Methylphenol (o-Cresol)	30	117
88-74-4	2-Nitroaniline	55	127
119-75-5	2-Nitrodiphenylamine	64	131
88-75-5	2-Nitrophenol	47	123
109-06-8	2-Picoline [2-Methylpyridine]	34	109
91-94-1	3,3'-Dichlorobenzidine	27	129
56-49-5	3-Methylcholanthrene	56	133
99-09-2	3-Nitroaniline	41	128
65794-96-9	3/4-Methylphenol [m/p-Cresol]	29	110
534-52-1	4,6-Dinitro-2-methylphenol	44	137
101-55-3	4-Bromophenyl phenyl ether	55	124
59-50-7	4-Chloro-3-methylphenol	52	119
106-47-8	4-Chloroaniline [p-Chloroaniline]	33	117
7005-72-3	4-Chlorophenyl phenyl ether	53	121
106-44-5	4-Methylphenol [p-Cresol]	25	120
99-55-8	5-Nitro-o-toluidine [2-Amino-4-nitrotoluene]	38	126
57-97-6	7,12-Dimethylbenz(a)-anthracene	61	133
83-32-9	Acenaphthene	47	122
208-96-8	Acenaphthylene	41	130
98-86-2	Acetophenone	46	118
120-12-7	Anthracene	57	123
140-57-8	Aramite	34	132
1912-24-9	Atrazine	44	142
103-33-3	Azobenzene	61	116
56-55-3	Benz(a)anthracene	58	125
50-32-8	Benzo(a)pyrene	54	128
205-99-2	Benzo(b)fluoranthene	53	131
191-24-2	Benzo(g,h,i)perylene	50	134
207-08-9	Benzo(k)fluoranthene	57	129
100-51-6	Benzyl alcohol	31	112

111-91-1	bis(2-Chloroethoxy)methane	48	120
111-44-4	Bis(2-chloroethyl) ether	43	118
39638-32-9	bis(2-Chloroisopropyl) ether	37	130
117-81-7	Bis(2-ethylhexyl) phthalate	55	135
85-68-7	Butyl benzyl phthalate	53	134
86-74-8	Carbazole	60	122
510-15-6	Chlorobenzilate	58	150
218-01-9	Chrysene	59	123
124-18-5	Decane	29	105
84-74-2	Di-n-butyl phthalate	59	127
117-84-0	Di-n-octyl phthalate	51	140
2303-16-4	Diallate [cis or trans]	67	124
226-36-8	Dibenz(a,h)acridine	75	134
53-70-3	Dibenzo(a,h)anthracene	51	134
132-64-9	Dibenzofuran	53	118
84-66-2	Diethyl phthalate	56	125
131-11-3	Dimethyl phthalate	45	127
60-11-7	Dimethylaminoazobenzene	62	132
88-85-7	Dinoseb	61	126
101-84-8	Diphenyl ether	68	115
122-39-4	Diphenylamine	55	111
298-04-4	Disulfoton	55	130
62-50-0	Ethyl methanesulfonate	62	118
206-44-0	Fluoranthene	57	128
86-73-7	Fluorene	52	124
118-74-1	Hexachlorobenzene	53	125
87-68-3	Hexachlorobutadiene	22	124
67-72-1	Hexachloroethane	21	115
95-13-6	Indene	53	135
193-39-5	Indeno(1,2,3-cd)pyrene	52	134
465-73-6	Isodrin	68	128
78-59-1	Isophorone	42	124
120-58-1	Isosafrole	56	126
66-27-3	Methyl methanesulfonate	33	107

298-00-0	Methyl parathion	45	159
100-75-4	N-Nitorosopiperidine	56	121
924-16-3	N-Nitrosodi-n-butylamine	60	121
621-64-7	N-Nitrosodi-n-propylamine	49	119
55-18-5	N-nitrosodiethylamine	43	121
86-30-6	N-Nitrosodipehenylamine	51	123
10595-95-6	n-Nitrosomethylethylamine	41	117
59-89-2	n-Nitrosomorpholine	55	117
930-55-2	n-Nitrosopyrrolidine	48	113
91-20-3	Naphthalene	40	121
98-95-3	Nitrobenzene	45	121
4165-60-0	Nitrobenzene-d5	44	120
126-68-1	O,O,O-Triethyl phosphorothioate	66	119
95-53-4	o-Toluidine	30	110
593-45-3	Octadecane	50	128
56-38-2	Parathion	66	140
608-93-5	Pentachlorobenzene	59	123
76-01-7	Pentachloroethane	30	92
87-86-5	Pentachlorophenol	35	138
82-68-8	Pentachloronitrobenzene	54	135
62-44-2	Phenacetin	71	124
85-01-8	Phenanthrene	59	120
298-02-2	Phorate	38	139
23950-58-5	Pronamide	65	129
129-00-0	Pyrene	57	126
91-22-5	Quinoline	69	132
94-59-7	Safrole	61	119
1718-51-0	Terphenyl-d14	50	134
3689-24-5	Tetraethyl dithiopyrophosphate [Sulfotep]	61	133
297-97-2	Thionazine	72	132

Table 6. Summary of Control Limits: Surrogate and Matrix Spiking Compounds Percent Recovery[†]

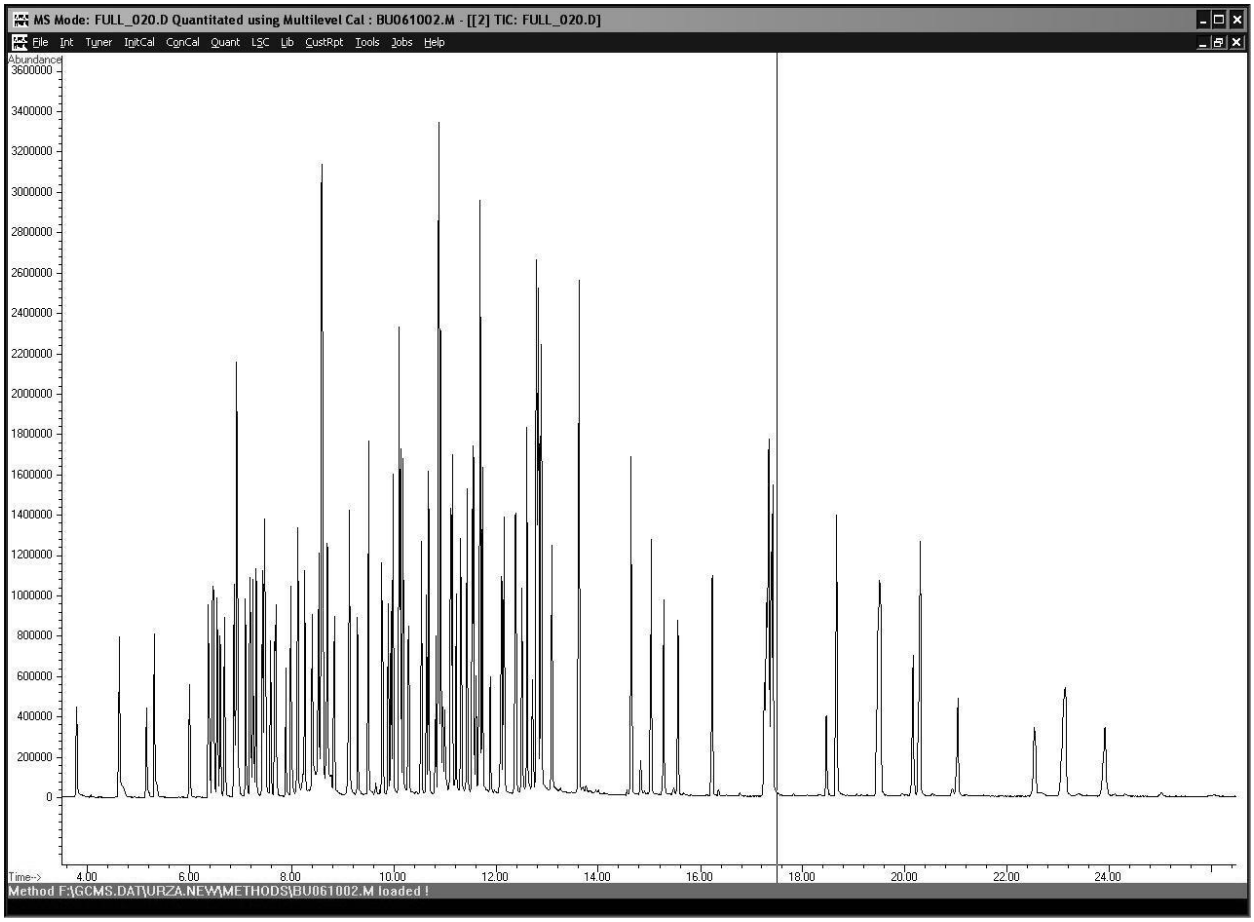
#[‡]	COMPOUND	Water Matrix		Solid Matrix	
		LCL (%)	UCL (%)	LCL (%)	UCL (%)
6	2-Fluorophenol	10.0	110.0	13.2	121.0
8	Phenol-d5	10.0	110.0	16.9	113.0
24	Nitrobenzene-d5	10.0	114.0	18.5	120.0
46	2-Fluorobiphenyl	10.0	116.0	10.0	115.0
66	2,4,6-Tribromophenol	10.0	123.0	13.0	122.0
84	Terphenyl-d14	10.0	141.0	10.3	137.0
9	Phenol **	10.0	110.0	16.3	118.6
11	2-Chlorophenol **	14.0	123.0	18.3	116.5
14	1,4-Dichlorobenzene **	16.8	110.0	13.2	110.0
22	N-Nitrosodi-n-propylamine**	31.3	119.6	24.7	126.0
32	1,2,4-Trichlorobenzene **	20.5	110.0	15.6	110.0
39	4-Chloro-3-methylphenol **	20.8	120.7	18.1	120.8
54	Acenaphthene **	26.4	118.0	19.0	137.0
57	4-Nitrophenol **	10.0	110.0	10.0	114.0
58	2,4-Dinitrotoluene **	24.0	110.0	14.7	112.6
77	Pentachlorophenol **	10.0	110.0	10.0	110.0
87	Pyrene **	23.0	127.5	16.2	142.0
n/a	Diesel Range Organics	30.0	130.0	30.0	130.0

[†]: Results based on recovery data from 2001.

[‡]: Compound identification numbers listed are from calibration BX010711.M.

All target compounds must be included in the spike for DoD projects. DoD acceptance criteria is provided in the DoD QSM.

Figure 1. Example Total Ion Chromatogram for a Midpoint BNA Calibration Standard†



†: Data file FULL_020.D from calibration BU061002.M (20 ng/μL). GC/MS acquisition parameters are given by Table 3 for BNA Analysis.

STANDARD OPERATING PROCEDURE

PURGE AND TRAP FOR AQUEOUS AND HIGH AND LOW CONCENTRATION SOIL SAMPLES
METHOD 5030C/5035A

APPROVALS:

Barbara Ball

01/16/18

QA Officer — Date

Technical Director — Date

Number	Description of Change	Date
001-005	Previous changes were not documented	
006	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
007	Updated SOP for Method 5035A high and low level soil prep	6/14/12
008	Updated SOP for Method 5030C	9/03/13
009	Updated to comply with DoD QSM 5.0 standards.	04/01/16
010	Updated to comply with DoD QSM 5.1 standards.	01/16/18
011		
012		
013		
014		
015		
016		

1.0 SCOPE AND APPLICATION

This SOP describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of low and high concentration soil and waste sample extracts prepared in Method 5035A. The method is applicable to Gas Chromotography/Mass Spectrometry (GC/MS) Method 8260B. Method 5030C can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process. This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method. This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF METHOD

Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. High Concentration Extracts from Method 5035A: An aliquot of the extract prepared in Method 5035A is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS. Low Concentration Soils: An aliquot of the soil is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and–trap GC or GC/MS. Air samples in Tedlar Bags: A volume of air is extracted from the Tedlar Bag using a gas tight syringe and is introduced to a vial of reagent water. An inert gas is bubbled through a portion of the aqueous sample at ambient temperature. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

3.0 INTERFERENCES

Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealant, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it must be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

The laboratory where volatiles analysis is performed must be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas must be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing must be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, and 500-µL.

Gas tight 5ml syringes.

Vials – 40-mL, for GC autosampler (Archon).

Magnetic stir bars.

Scale capable of displaying weight to the nearest hundredth of a gram.

Purge-and-trap device. The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber.

- The Vocarb3000 trap by Supelco is used. It is preconditioned at 270°C for 60 minutes upon installment as suggested by supplier.

Gas Chromatograph.

Mass Spectrometer.

pH paper.

5.0 REAGENTS

Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

Purge and Trap grade methanol.

Sodium Bisulfate.

See SOP ORL-007 for specifications on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aqueous Samples

- Samples must be stored in capped bottles, with minimum headspace, at (4 ± 2)°C in an area free of solvent fumes.

- All samples must be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values. The pH of the samples is checked with pH strips after the sample has been prepared for the autosampler. If the pH is greater than 2 as determined by the pH strip the fact is noted. If the sample with pH > 2 is not analyzed within seven days of the collection date then it is noted on the report that the sample was not properly preserved. The pH is recorded on the volatile sample prep log (Figure 1).

Soil Samples

- High concentration soil samples collected and preserved in the field.
    - The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment.
    - Add 10 mL of methanol to each vial. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the

tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label.

- (10 ± 0.5)g of sample are weighed out and added to the vial in the field.
- Upon arrival to the lab, samples are stored at (4 ±2)°C.

♦ High concentration soil samples collected without a preservative.

- When high concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.
  - The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way must be preserved in methanol within 48 hours of the sampling time. This preservation is documented in the High Level Extraction Sheet (Figure 3).
- Weigh out (10 ±0.5)g of soil sample into a 40-mL vial and add 10-mL of Methanol.
- Sonicate for twenty minutes.
- Sample extracts are transferred to 4 ml vials and stored at (4 ± 2)°C.
- Frozen samples are not acceptable for all OHIO VAP samples.

♦ Low concentration soil samples collected and preserved in the field.

- The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be preserved in the field with sodium bisulfate and reagent water and analyzed by the aqueous purge-and-trap equipment described in this SOP. Note: The sampling and preservation techniques required for low concentration analysis vary widely by state and regulating agency. The end-use of the data must be considered before selecting a sampling and preservation technique and may include procedures not in this SOP.
- Add 5 mL of reagent water and a magnetic stir bar to each vial as well as 0.2g of sodium bisulfate for every 1g of sample to be collected. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label, and Low Level Extraction Log (Figure 2).

- (1-5 ± 0.5)g of sample are weighed out and added to the vial in the field.
- Upon arrival to the lab, samples are stored at (4 ±2)°C.

♦ Low concentration soil samples collected without a preservative.

- When low concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler or an empty 40 ml vial is employed.
  - The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way must be preserved with sodium bisulfate within 48 hours of the sampling time. This preservation is documented in the Low Level Extraction Log (Figure 2).
- Weigh out (1-5 ±0.5)g of soil sample into a 40-mL vial and add 5ml of reagent water and 0.2g of sodium bisulfate for every 1g of sample. Alternatively, weigh out (1-5 ±0.5)g of soil sample into a 40-mL vial and freeze (-7°C) for up to 14 days.
- The preserved samples are stored at (4 ± 2)°C.
- Bulk sample collection using USEPA Method 5030C can be used for approved sites/QAPPs.

7.0 PROCEDURE

1. The purge-and-trap technique for aqueous samples is found in Number 2 and method for analysis of solvent extracts from the High Concentration Method in Method 5035A is found in Number 3. The gas chromatographic determinative steps are found in SOP ORL-007. The method is also applicable to the analysis of gasoline, using SOP ORL-010.

2. This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

♦ Initial calibration. Calibrate system in accordance with Method 8260B.

♦ If necessary or for project specific purposes, screen samples prior to purge-and-trap analysis to provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system. Screen the sample by GC/MS.

♦ Sample introduction and purging.

- Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in method SOP ORL-007 and SOP ORL-010.

- A daily check standard containing surrogates, internal standards and 20ug/l bromoform must be analyzed prior to the analysis of the daily check standard. If levels of chloromethane or bromomethane exceed 0.5ug/l, then the trap may be too contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced and the system recalibrated. This can be achieved in the same run as the BFB.

- GC or GC/MS calibration verification criteria must be met (SOP ORL-007 and SOP ORL-010) before analyzing samples.

- Adjust the purge gas flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

- Use autosampler to take a 5-mL aliquot of the sample. Care must be taken to remove any bubbles from the syringe. This process of taking an aliquot destroys the validity of the liquid sample for future analysis. Re-analysis must be done with duplicate VOA.

- The autosampler adds 1.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in SOP ORL-007 and SOP ORL-010.

- Inject the aliquot into a sparge tube.

- Purge for 11.0 minutes at room temperature in the sparge tube.

♦ Sample desorption.

- Non-cryogenic interface - After the recommended purge (see above), place the purge-and-trap system in the desorb mode and preheat the trap to 190 °C without a flow of carrier gas passing through the trap. Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition.

♦ Trap Reconditioning.

- After desorbing the sample, recondition the trap by baking it at 210 °C for 3 minutes.

3. This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035A.

- ♦ The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007 and SOP ORL-010).
- ♦ Take 5mL's of organic-free reagent water and add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in SOP ORL-007 and SOP ORL-010.
- ♦ Measure out a 100µL aliquot of the methanol phase of the sample.
- ♦ Quickly inject the 5-mL reagent water with standard mixture and 100µL of sample into a 40-mL vial and place cap with septum on it and tighten.
- ♦ Purge for 11.0 minutes at room temperature in the 40ml vial.
- ♦ Desorb the sample and recondition the trap.

4. This section provides guidance on the analysis of Low Concentration Samples prepared by Method 5035.

- ♦ The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007 and SOP ORL-010).
- ♦ Internal standards, surrogates and matrix spikes (if applicable) must be added automatically by the autosampler or manually by puncturing the septum using a small gauge needle.
- ♦ Prior to purging the sample is preheated to 40°C for 1.5 minute while being agitated by the magnetic stir bar.
- ♦ Purge for 11.0 minutes at 40°C while being agitated by the magnetic stir bar in the 40ml vial.
- ♦ Desorb the sample and recondition the trap.

5. Tedlar Bag Air Analysis

- ♦ The GC or GC/MS system must be set up as in specific determinative method (SOP ORL-007 and SOP ORL-010).

- To a 40 ml VOA bottle add 5 ml reagent water and add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in SOP ORL-007 and SOP ORL-010.

- Take a gas tight syringe with a needle fixed to the tip. Draw in a small volume of DI water into the syringe. This will provide a bubbling effect to show air is being drawn in from the bag.

- Insert the needle of the syringe through the septa of the Tedlar Bag and with draw 5 cc into the syringe.

- Bubble into 40 ml VOA bottle with 5 ml of DI water and surrogates and internal standards then cap promptly.

- Purge for 11.0 minutes at room temperature in the 40ml vial.

- Desorb the sample and recondition the trap.

6. Sample analysis. The samples prepared by this method will be analyzed according to SOP ORL-007 and SOP ORL-010.

8.0 QUALITY CONTROL

Refer to method SOP ORL-007 and SOP ORL-010 for specific quality control procedures. Quality control items employed and evaluated are provided in Table 1 and Table 2. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

11.0 SAFETY

Eye protection and gloves must be worn while performing Volatile analyses. Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

- Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run. Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

Method Blank (MB): an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (LCS) (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory

or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (also known as Spiked Sample or Fortified Sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

14.0 REFERENCES

Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

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Table 1 Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
BFB	12-hour	Method-based	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	Method-based	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Lab-based	A failed LCS must be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS must be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	n/a	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) must result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard	All samples	Method-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate
Surrogate Standard	All samples	Lab-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample must be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Tune Check	Prior to ICAL and prior To each 12-hour period of sample analysis	Specific ion abundance criteria of BFB or DFTPP from method.	Retune instrument and verify.	Flagging criteria is not appropriate.	No samples shall be analyzed without a valid tune.
Performance Check (Method 8270 only)	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation ≤ 20% for DDT. Benzidine and pentachlorophenol shall be present at their normal responses and shall not exceed a tailing factor of 2.	Correct problem, then repeat performance checks.	Flagging is not appropriate.	No sample shall be analyzed until performance check is within criteria. The DDT breakdown and Benzidine/Pentachlorophenol tailing factors are considered overall system checks to evaluate injector port inertness and column performance and are required regardless of the reported analyte list.
Initial calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	Each analyte must meet one of the three options below: Option 1. RSD for each analyte ≤ 15%;. Option 2: linear least squares regression $r^2 \geq 0.99$; Option 3:non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging criteria is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. No samples shall be analyzed until ICAL has passed. If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements must also be met.
Retention time window position establishment and surrogate	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and surrogate.
Evaluation of relative retention times (RRT)	With each sample.	RRT of each reported analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	After maintenance is performed which may affect retention times, RRTs may be updated based on the daily CCV. RRTs shall be compared with the most recently updated RRTs.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within ± 20% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within ± 20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	NA
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > $1/10^{th}$ the amount measured in any sample or $1/10^{th}$ the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	MSD: Must contain all surrogates and all analytes to be reported. The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed..	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present,	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

Table 2: Quality Control Items, Frequency, and Corrective Action for DoD Projects					
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**	**Comments**
			reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative..		

DoD Appendix C LCS Limits
Method 8260 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	125
71-55-6	1,1,1-Trichloroethane	73	130
79-34-5	1,1,2,2-Tetrachloroethane	70	124
79-00-5	1,1,2-Trichloroethane	78	121
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	66	136
75-34-3	1,1-Dichloroethane	76	125
75-35-4	1,1-Dichloroethene	70	131
563-58-6	1,1-Dichloropropene	76	125
87-61-6	1,2,3-Trichlorobenzene	66	130
96-18-4	1,2,3-Trichloropropane	73	125
526-73-8	1,2,3-Trimethlybenzene	82	118
120-82-1	1,2,4-Trichlorobenzene	67	129
95-63-6	1,2,4-Trimethylbenzene	75	123
96-12-8	1,2-Dibromo-3-chloropropane	61	132
106-93-4	1,2-Dibromoethane	78	122
95-50-1	1,2-Dichlorobenzene	78	121
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	71	136
540-59-0	1,2-Dichloroethene	78	122
78-87-5	1,2-Dichloropropane	76	123
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	64	132
108-70-3	1,3,5-Trichlorobenzene	71	128
108-67-8	1,3,5-Trimethylbenzene	73	124
541-73-1	1,3-Dichlorobenzene	77	121
142-28-9	1,3-Dichloropropane	77	121
542-75-6	1,3-Dichloropropene	77	126
106-46-7	1,4-Dichlorobenzene	75	120
105-05-5	1,4-Diethylbenzene	79	114
123-91-1	1,4-Dioxane	55	138
544-10-5	1-Chlorohexane	71	130
594-20-7	2,2-Dichloropropane	67	133

78-93-3	2-Butanone (MEK)	51	148
126-99-8	2-Chloro-1,3-butadiene	65	133
110-75-8	2-Chloroethyl vinyl ether	43	149
95-49-8	Chlorotoluene	75	122
591-78-6	2-Hexanone	53	145
79-46-9	2-Nitropropane	47	150
67-63-0	2-Propanol [Isopropyl alcohol]	60	140
460-00-4	4-Bromofluorobenzene	79	119
106-43-4	4-Chlorotoluene	72	124
108-10-1	4-Methyl-2-pentanone [MIBK]	65	135
67-64-1	Acetone	36	164
75-05-8	Acetonitrile	54	143
107-02-8	Acrolein [Propenal]	47	155
107-13-1	Acrylonitrile	65	134
107-05-1	Allyl chloride	68	135
71-43-2	Benzene	77	121
100-44-7	Benzyl chloride	64	120
108-86-1	Bromobenzene	78	121
74-97-5	Bromochloromethane	78	125
75-27-4	Bromodichloromethane	75	127
75-25-2	Bromoform	67	132
74-83-9	Bromomethane	53	143
75-15-0	Carbon disulfide	63	132
56-23-5	Carbon tetrachloride	70	135
108-90-7	Chlorobenzene	79	120
124-48-1	Chlorodibromomethane	74	126
75-00-3	Chloroethane	59	139
67-66-3	Chloroform	78	123
74-87-3	Chloromethane	50	136
156-59-2	cis-1,2-Dichloroethene	77	123
10061-01-5	cis-1,3-Dichloropropene	74	126
1476-11-5	cis-1,4-Dichloro-2-butene	69	143
110-82-7	Cyclohexane	67	131
108-94-1	Cyclohexanone	30	156
1868-53-7	Dibromofluoromethane	78	119

74-95-3	Dibromomethane	78	125
75-71-8	Dichlorodifluoromethane [Freon-12]	29	149
75-43-4	Dichlorofluoromethane	47	155
60-29-7	Diethyl ether	71	129
108-20-3	Diisopropyl ether	69	127
64-17-5	Ethanol	45	159
141-78-6	Ethyl acetate	52	139
97-63-2	Ethyl methacrylate	69	129
637-92-3	Ethyl tert-butyl ether	72	126
100-41-4	Ethylbenzene	76	122
462-06-6	Fluorobenzene	81	114
142-82-5	Heptane	49	138
87-68-3	Hexachlorobutadiene	61	135
67-72-1	Hexachloroethane	72	133
110-54-3	Hexane	45	142
74-88-4	Iodomethane	71	131
78-83-1	Isobutyl alcohol	60	135
108-21-4	Isopropyl acetate [Acetic acid]	58	131
98-82-8	Isopropylbenzene	68	134
179601-23-1	m/p-Xylene [3/4-Xylene]	77	124
126-98-7	Methacrylonitrile	66	132
79-20-9	Methyl acetate	53	144
80-62-6	Methyl methacrylate	63	134
1634-04-4	Methyl tert-butyl ether [MTBE]	73	125
108-87-2	Methylcyclohexane	66	133
75-09-2	Methylene chloride	70	128
123-86-4	n-Butyl acetate	62	128
71-36-3	n-Butyl alcohol	55	131
104-51-8	n-Butylbenzene	70	128
103-65-1	n-Propylbenzene	73	125
91-20-3	Naphthalene	62	129
95-47-6	o-Xylene	77	123
99-87-6	p-Isopropyltoluene [p-Cymene]	73	127
76-01-7	Pentachloroethane	69	135
107-12-0	Propionitrile [Ethyl cyanide]	68	134

135-98-8	sec-Butylbenzene	73	126
100-42-5	Styrene	76	124
994-05-8	tert-Amyl methyl ether [TAME]	73	126
75-65-0	tert-Butyl alcohol	68	133
98-06-6	tert-Butylbenzene	73	125
127-18-4	Tertachloroethene	73	128
109-99-9	Tetrahydrofuran	61	135
108-88-3	Toluene	77	121
2037-26-5	Toluene-d8	85	116
156-60-5	trans-1,2-Dichloroethene	74	125
10061-02-6	trans-1,3-Dichloropropene	71	130
110-57-6	trans-1,4-Dichloro-2-butene	62	136
79-01-6	Trichloroethene	77	123
75-69-4	Trichlorofluoromethane [Freon-11]	62	140
108-05-4	Vinyl acetate	50	151
75-01-4	Vinyl chloride	56	135
1330-20-7	Xylene [total]	78	124

DoD Appendix C LCS Limits
Method 8260 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	124
71-55-6	1,1,1-Trichloroethane	74	131
79-34-5	1,1,2,2-Tetrachloroethane	71	121
79-00-5	1,1,2-Trichloroethane	80	119
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	70	136
75-34-3	1,1-Dichloroethane	77	125
75-35-4	1,1-Dichloroethene	71	131
563-58-6	1,1-Dichloropropene	79	125
87-61-6	1,2,3-Trichlorobenzene	69	129
96-18-4	1,2,3-Trichloropropane	73	122
526-73-8	1,2,3-Trimethlybenzene	82	120
120-82-1	1,2,4-Trichlorobenzene	69	130
95-63-6	1,2,4-Trimethylbenzene	76	124

96-12-8	1,2-Dibromo-3-chloropropane	62	128
106-93-4	1,2-Dibromoethane	77	121
95-50-1	1,2-Dichlorobenzene	80	119
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	81	118
540-59-0	1,2-Dichloroethene	79	121
78-87-5	1,2-Dichloropropane	78	122
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	70	136
108-70-3	1,3,5-Trichlorobenzene	75	130
108-67-8	1,3,5-Trimethylbenzene	75	124
106-99-0	1,3-Butadiene	43	158
541-73-1	1,3-Dichlorobenzene	80	119
142-28-9	1,3-Dichloropropane	80	119
542-75-6	1,3-Dichloropropene	77	123
106-46-7	1,4-Dichlorobenzene	79	118
105-05-5	1,4-Diethylbenzene	79	118
123-91-1	1,4-Dioxane	59	139
544-10-5	1-Chlorohexane	76	124
540-84-1	2,2,4-Trimethylpentane [Isooctane]	58	132
594-20-7	2,2-Dichloropropane	60	139
75-85-4	2-Butanol	66	120
78-93-3	2-Butanone (MEK)	56	143
126-99-8	2-Chloro-1,3-butadiene	65	135
110-75-8	2-Chloroethyl vinyl ether	51	139
95-49-8	Chlorotoluene	79	122
591-78-6	2-Hexanone	57	139
91-57-6	2-Methylnaphthalene	17	142
79-46-9	2-Nitropropane	49	136
67-63-0	2-Propanol [Isopropyl alcohol]	56	142
624-95-3	3,3-Dimethyl-1-butanol	49	133
460-00-4	4-Bromofluorobenzene	85	114
106-43-4	4-Chlorotoluene	78	122
108-10-1	4-Methyl-2-pentanone [MIBK]	67	130
67-64-1	Acetone	39	160
75-05-8	Acetonitrile	50	142

107-02-8	Acrolein [Propenal]	39	155
107-13-1	Acrylonitrile	63	135
107-05-1	Allyl chloride	68	130
71-43-2	Benzene	79	120
100-44-7	Benzyl chloride	42	138
108-86-1	Bromobenzene	80	120
74-97-5	Bromochloromethane	78	123
75-27-4	Bromodichloromethane	79	125
75-25-2	Bromoform	66	130
74-83-9	Bromomethane	53	141
75-15-0	Carbon disulfide	64	133
56-23-5	Carbon tetrachloride	72	136
108-90-7	Chlorobenzene	82	118
124-48-1	Chlorodibromomethane	74	126
75-45-6	Chlorodifluoromethane	40	129
75-00-3	Chloroethane	60	138
67-66-3	Chloroform	79	124
74-87-3	Chloromethane	50	139
156-59-2	cis-1,2-Dichloroethene	78	123
10061-01-5	cis-1,3-Dichloropropene	75	124
1476-11-5	cis-1,4-Dichloro-2-butene	57	146
110-82-7	Cyclohexane	71	130
1868-53-7	Dibromofluoromethane	80	119
74-95-3	Dibromomethane	79	123
75-71-8	Dichlorodifluoromethane [Freon-12]	32	152
75-43-4	Dichlorofluoromethane	72	131
60-29-7	Diethyl ether	68	129
108-20-3	Diisopropyl ether	67	128
64-17-5	Ethanol	48	151
141-78-6	Ethyl acetate	55	138
97-63-2	Ethyl methacrylate	72	126
637-92-3	Ethyl tert-butyl ether	70	127
100-41-4	Ethylbenzene	79	121
462-06-6	Fluorobenzene	80	116
142-82-5	Heptane	49	140

87-68-3	Hexachlorobutadiene	66	134
67-72-1	Hexachloroethane	72	134
110-54-3	Hexane	48	143
74-88-4	Iodomethane	69	131
78-83-1	Isobutyl alcohol	63	133
108-21-4	Isopropyl acetate [Acetic acid]	63	133
98-82-8	Isopropylbenzene	72	131
179601-23-1	m/p-Xylene [3/4-Xylene]	80	121
126-98-7	Methacrylonitrile	63	133
79-20-9	Methyl acetate	56	136
80-62-6	Methyl methacrylate	67	128
1634-04-4	Methyl tert-butyl ether [MTBE]	71	124
108-87-2	Methylcyclohexane	72	132
75-09-2	Methylene chloride	74	124
123-86-4	n-Butyl acetate	69	125
71-36-3	n-Butyl alcohol	59	131
104-51-8	n-Butylbenzene	75	128
109-60-4	n-Propyl acetate	76	126
103-65-1	n-Propylbenzene	76	126
91-20-3	Naphthalene	61	128
95-47-6	o-Xylene	78	122
99-87-6	p-Isopropyltoluene [p-Cymene]	77	127
76-01-7	Pentachloroethane	69	133
109-66-0	Pentane	16	134
107-12-0	Propionitrile [Ethyl cyanide]	64	136
135-98-8	sec-Butylbenzene	77	126
100-42-5	Styrene	78	123
994-05-8	tert-Amyl methyl ether [TAME]	68	128
75-65-0	tert-Butyl alcohol	68	129
762-75-4	tert-Butyl formate	65	132
98-06-6	tert-Butylbenzene	78	124
127-18-4	Tertachloroethene	74	129
109-99-9	Tetrahydrofuran	57	133
108-88-3	Toluene	80	121
2037-26-5	Toluene-d8	89	112

156-60-5	trans-1,2-Dichloroethene	75	124
10061-02-6	trans-1,3-Dichloropropene	73	127
110-57-6	trans-1,4-Dichloro-2-butene	43	140
79-01-6	Trichloroethene	79	123
75-69-4	Trichlorofluoromethane [Freon-11]	65	141
108-05-4	Vinyl acetate	54	146
75-01-4	Vinyl chloride	58	137
1330-20-7	Xylene [total]	79	121

Figure 1: Volatiles Sample Preparation

VOLATILES
Sample Prep

Date: _____
Analyst: _____
Batch QC ID#: _____

#	Merit #	Matrix	Surrogate ID	Vol. (ul)	Spike ID	Vol. (ul)	Time Start / End	PH	Notes
	BFB								
	SPCC								
	LCS								
	LCSD								
	BLK								
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									

Reviewed by: _____

Date: _____

FIGURE 2. METHOD 5035A (LOW LEVEL) EXTRACTION SHEET

Method 5035A (Low Level)
Extraction Sheet

Analyst: _____
Date: _____
Batch QC ID #_____

Merit Number	Tare wt (g)	Vial wt (g)	Sample wt.(g)	Time Start / End	Decontaminated	Decontamination Date	Notes

Figure 3. Method 5035A (High Level) Extraction Sheet

Method 5035A (High Level)
Extraction Sheet

Analyst: _____
Date: _____
Batch QC ID#_____

Merit Number	Tare wt (g)	Vial wt (g)	Sample wt.(g)	Methanol (mL)	Sonicate (min)	Time Start / End	Notes

Reviewed By: _____
Date: _____

Methanol Lot: _____

STANDARD OPERATING PROCEDURE

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
METHOD SW-846 8260C

APPROVALS:

Barbara Ball

01/17/18

QA Officer Date

Mayra Mushaly

01/17/18

Technical Director Date

Number	Description of Change	Date
001-011	Previous revisions not documented	
0012	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
013	Updated to method 8260C	9/4/13
014	Updated to comply with DoD QSM 5.0 standards.	04/01/16
015	Updated to comply with DoD QSM 5.1 standards.	01/17/18
016		
017		
018		
019		

1.0 SCOPE AND APPLICATION

This SOP is used to determine volatile organic compounds (VOC) in a variety of matrices, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. See Table 1 for a list of compounds (along with their characteristic ions) that have been evaluated.

There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by SW-846 Methods 5030C (aqueous samples) and 5035A (solid, waste, and oil samples), are the most commonly used technique for volatile organic analytes. SW-846 Method 5000 provides general information on the selection of other introduction methods.

The practical quantitation limit (PQL) for an individual compound is instrument dependent and also dependent on the choice of the sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 50 μg/kg (wet weight) for solid samples and 1 μg/L for ground water. When lower reportable detection limits (RDLs) are required, the mass spectrometer (MS) can be set to selective ion monitoring (SIM) to achieve limits approximately 20 times lower then obtainable using the full scan method. Regardless of the sample matrix, PQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

Method Detection Limits (MDL) and Practical Quantitation Limits (PQL) are available in Merit's LIMs system.

This SOP is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF THE METHOD

VOC are introduced into the gas chromatograph by the purge-and-trap method or by other methods. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer interfaced to the gas chromatograph.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra

with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five point (or more) calibration curve.

The method includes specific calibration and quality control steps that supersede the general requirements provided in SW-846 Method 8000.

3.0 INTERFERENCES

Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds will be concentrated in the trap during the purge operation.

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to allow the system to be cleaned as well as to demonstrate the ultimate absence of cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

4.0 APPARATUS AND MATERIALS

Gas chromatograph/mass spectrometer system

- Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
- 20 m × 0.18 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 1-μm film thickness, or equivalent.
- Mass spectrometer capable of scanning from 35 to 200 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-bromofluorobenzene (BFB) which meets the criteria in Table 4.
- GC/MS interface - The capillary column is interfaced through a direct connection to the GC/MS system.

- Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

Purge-and-trap device.

Microsyringes - 2 to 500-μL.

Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

Glass bottles - 40-mL, with PTFE-lined screw-caps.

pH paper.

5.0 REAGENTS

Reagent grade inorganic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.

Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

Stock standard solutions.

- Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.
- Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a high-concentration stock solution).
- Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.
- Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicate a problem.

Internal standard solutions - The internal standards used are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4 (see Table 2). Internal standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 μg/L (i.e. 10μL per 5000μL purge volume). For SIM (selective ion monitoring) analysis, internal standards are the same, but with concentrations at 0.1 ppb (μg/L).

Calibration standards - A minimum of five calibration standards are prepared at different concentrations. The lowest calibration standard corresponds to a sample concentration at or below the standard reporting

limit. The remaining standards should represent the working range of the GC/MS system. Each standard should contain each analyte for quantitation by this method. For DoD projects, each standard shall contain all target compounds.

Surrogate standards - The surrogates used are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Surrogate standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 μg/L, or less. For SIM (selective ion monitoring) analysis, surrogate standards are the same, but with concentrations at 0.1 ppb (μg/L).

Matrix spike (MS), matrix spike duplicate (MSD) and laboratory control standards (LCS) - Matrix spiking solutions are prepared using the same standards as those used for the calibration.For DoD projects, matrix spiking solutions shall contain all target compounds.

- Matrix spiking mixes for individual analytes are created at 100 mg/L and spiked into samples at 50 μg/L (*i.e.* 2.50μL per 5000μL purge volume).
- For SIM (selective ion monitoring) analysis, compounds of interest are spiked at concentrations of 0.1 ppb (μg/L).

Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

6.0 SAMPLE HANDLING AND PRESERVATION

Unanalyzed samples are refrigerated at 4 ± 2 degrees Celsius in sealed vials or containers.

Aqueous samples are preserved to a pH <2with HCl and/or $Na_2S_2O_3$ (unless unpreserved requested) and collected in a 40 ml. Preserved samples must be analyzed within 14 days from sample collection; unpreserved samples must be analyzed within 7 days from sample collection.

Soil samples collected Encore™ Samplers must be preserved within 48 hours and analyzed within 14 days. Soil samples collected in glass jars shall be kept refrigerated and analyzed within 14 days from sample collection. For additional information on sample collection, handling and preservation for soil samples see SOP #ORL-005.

7.0 PROCEDURE

Sample introduction.

- Direct injection - This method of introduction is used only rarely, generally when the compounds of interest exhibit poor purging efficiency. Quantitation in this case, if required, is generally subject to external standard calibration procedures (*cf*. Method 8000).

- Purge-and-trap - This is generally used for sample introduction for both soil and water samples. All samples, standards, spikes, and blanks are introduced into the GC/MS system in an identical manner (see Merit SOP# ORL-005).

GC/MS operating conditions - see Table 3 for routine operating conditions for VOC analysis.

- For SIM, the MS is put into the SIM mode. Based on compounds of interest, the time windows are set within the run (i.e. for internal standards, surrogate standards, compounds). For each time window, corresponding to a compound, including internal and surrogate standards, a minimum of 3 ions are chosen for qualitative analysis. One ion (primary ion), generally the most abundant ion is used for quantitative analysis.

Initial calibration.

- Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for 4-bromofluorobenzene. Analysis does not begin until these criteria are met.

    - In the absence of any other manipulations, evaluate the mass spectrum of the peak apex or the scan immediately preceding or following from the total ion chromatogram for the BFB peak. This is the default approach used.

    - If the above evaluation is adversely affected by ion peak asymmetry, average the three highest intensity scans of the peak or average the mass spectrum ranging from the 10% initial peak intensity to the tailing 10% peak intensity level from the total ion chromatogram for the BFB peak.

    - If the above evaluation is adversely affected by background contamination, perform a background subtraction with a spectrum within 20 scans of the BFB peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.

    - The BFB mass intensity criteria in Table 4 are used as tuning acceptance criteria.

- All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must use the identical mass spectrometer instrument conditions, Exception: for SIM, tune is run using full scan acquisition and subsequent samples are acquired using SIM.

♦ Purge and analyze each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary. The purge volume must be the same for all standards and sample extracts. Table 5 details the dilutions necessary to create a set of calibration standards. Figure 1 shows a chromatogram of a midpoint calibration standard.

♦ Calculate response factors (*RF*s) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.

♦ System performance check compounds (SPCCs).

- A system performance check must be performed to ensure that minimum *RF*s are met before the calibration curve is used. For volatiles, the SPCCs are: chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene, and 1,1,2,2-tetrachloroethane (Table 2). No response factor criteria are applied to SIM analysis.
- The minimum acceptable average *RF* for these compounds is 0.1 (for chloromethane, 1,1-dichloroethane, and bromoform) and 0.3 (for chlorobenzene and 1,1,2,2-tetrachloroethane). These SPCCs typically have low *RF*s and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.
- It is also recommended that a minimum response factor for the most common target analytes as noted in Table 2b, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration level is important in demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed, some compounds will fail to meet this criteria. In particular, poor performers such as ketones and 1,2-dibromo-3-chloropropane are likely to fail this criteria but have been demonstrated to perform adequately overall.

- If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination in the purge-and-trap system, excessively high or low purge flow rates, and active sites in the column or chromatographic system. Replacing the calibration standards, clipping and/or replacing the column will likely solve this problem.

♦ Calibration check compounds (CCCs).

- The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is in addition to the successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.
- Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 20% for each target analyte. However, the RSD for each individual CCC compound (1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride; see Table 2) must be less than or equal to 30%.If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.

♦ Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. This is accomplished by setting the retention time extraction windows in the Chemstation software.

♦ Linearity of target analytes - If the %RSD of any target analytes is 20% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

- Refer to SW-846 Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. The coefficient of determination for any regression fit should be ≥0.99. In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters.

- When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc*.
- The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and the quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve. The recalculated concentration of the low calibration point should be within 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives. For analytes which do not meet the minimum quantitation calibration re-fitting criteria reporting those analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.
- The initial calibration curve should be verified immediately after performing the standard analyses using a second source standard at a concentration near the midpoint of the calibration range. The acceptance limits are 70-130% or project specific. Analytes that fail this criteria are considered estimated values.
- The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e*. average RF or regression coefficients), and the appropriate calibration quality metric (*i.e*. %RSD or COD).

♦ GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

♦ Prior to the analysis of samples or calibration standards, purge the BFB standard into the GC/MS system. The resultant mass spectrum for BFB must meet the criteria given in Table 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the BFB.

♦ The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint

concentration for the calibration range of the GC/MS (50 μg/L; this represents 2.50 μL of the 100 mg/L calibration standard solution in a 5mL purge volume). A concentration of 0.1μg/L is analyzed for SIM procedures. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the SPCC and CCC compounds. In addition the internal standards should be within 10s of those in the midpoint calibration standard and the responses should be 50-200% of those in the midpoint calibration standard.

- A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants. A method blank/wash sample is also run after calibration check/spike samples and prior to analytical samples in order to eliminate carryover contamination from the purge-and-trap system.
- System performance check compounds (SPCCs).
  - A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet the minimum response factors given above. This is the same check that is applied during the initial calibration (see §7.3.4.2).
  - Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 2b . This is the same check that is applied during the initial calibration and exceptions are noted above.
  - If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.
- Calibration check compounds (CCCs).
  - After the system performance check is met, the CCCs listed in Table 2 are used to check the validity of the initial calibration. Percent drift is used to evaluate the CCC response and it must be ≤20%.
  - All target compounds of interest must be evaluated using a 20% variability criterion. If the percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation

limit. For situations when a failed compound is present, the concentration is an estimated value.Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = \left|C - C_{spike}\right| / C_{spike}$.

- Problems similar to those listed under initial calibration could affect the calibration verification. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

GC/MS analysis of samples.

- Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.
- Use a 5 mL syringe to take a 5 mL aliquot from the sample vial. Be sure to eliminate any air bubbles from within the syringe. Table 5 has a list of commonly used dilutions as well as the required amount of sample, water, and internal standard for each dilution.
- Add 10 μL of 25 mg/L internal/surrogate standard mixture to each sample. For SIM analysis, internal and surrogate standards are spiked at 0.1μg/L.
- If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.
- The Extracted Ion Current Profile (EICP) area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Table 6a and 6b). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.

Qualitative analysis.

- The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Figures 1a and 1b. Compounds are identified when the following criteria are met.
  - Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound specific retention time.
  - The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.
  - The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)
  - Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
  - Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
  - Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.
  - In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of

continued uncertainty, the analyst should preferentially make a conservative judgment and accept an identified hit, allowing the potential for a false positive.

- For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:
  - Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
  - The relative intensities of the major ions should agree within ± 20%.
  - Molecular ions present in the reference spectrum should be present in the sample spectrum.
  - Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
  - Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Quantitative analysis.

- Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.
- The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1 C_s/C_i + k_2 C_s/C_i$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th}-order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv$ <RF>, while k_0, $k_2 \equiv 0$.
- The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the tentatively identified compound (TIC) areas for the nearest internal standard and target compound. The resulting concentration should be reported

indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

- Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-xylene).

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 6a and 6b. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. Control limits for surrogates and matrix spikes are listed in Table 7. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Laboratory specific performance data is provided for Merit's LIMs system. Each sample batch contains a method blank, laboratory control sample and matrix spike samples. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention shall be paid (but not limited) to:

a. Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

b. Hydrochloric acid is corrosive. Extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

4-Bromofluorobenzene (BFB), is used to verify that the GC/MS is properly tuned and ready for calibration and sample analyses. BFB is directly injected at 25-50 ng and precedes all other analyses. A twelve hour analysis time window is used before another BFB injection is required.

An Initial Calibration Verification standard (ICV) is analyzed before the analysis of samples as a check on the calibration curve. The ICV shall be of a second source, meaning a separate vendor and/or lot # shall be used to prepare this standard. A second source is needed to validate the integrity and concentration of the standards used for calibration.

An Initial Calibration Blank (ICB) is also analyzed before samples to confirm that the deionized water (DI H2O) used for standards, blanks, and dilutions are free from contamination. An ICB for soil samples also includes organic free sand and/or methanol used for standard and QC preparation, as well as sample dilutions and volume adjustments; the control sand and methanol must also be documented as free from contamination.

A Calibration Check Verification standard (CCV) is analyzed at the beginning of each sequence (following the BFB injection) shift and every 12 hour shift thereafter. A CCV is made up from the same standards used for calibration and is used to ensure that the calibration and retention times are stable.

An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run. Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

Internal standards (ISTD) are added to each sample, blank, spike, and check standard. The ISTDs used are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. The ISTD is used for internal calibration as a reference peak and to check purging efficiency.

Surrogate standards (SSTD) are also added to each sample, blank, spike, and check standard. The SSTDs used are Toluene-d_4, 4-Bromofluorobenzene, 1,2-Dichloroethane-d_4, and Dibromofluoromethane. The SSTD is used as matrix interference and as a method control check.

Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

A Continuing Calibration Blank (CCB) is analyzed every 12 hour shift after the MB has been analyzed and before sample reanalyzes to ensure the system is still free from contamination.

Instrument blanks are analyzed whenever instrument contamination is a suspected possibility. The purpose of an IB is to prevent carry over from a standard, spike, or contaminated sample into another sample or blank. The acceptance criteria for an IB is the same as for a MB or CCB (for example: if an IB contains detections above acceptance criteria and a MB and/or sample following the IB exhibit the same contamination above acceptance criteria, then the instrument shall be considered contaminated). The samples and/or MBs shall be reanalyzed after the instrument is confirmed free from contamination.

Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with all target compounds and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

Matrix Spike (MS): An aliquot of sample spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

14.0 REFERENCES

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Table 1. Summary of Retention Times† and Characteristic Ions for Volatile Organics

#	**Compound**	t_R (*min*)	$t_R/t_{R,I}$ (-)	$t_R-t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
1)	PENTAFLUOROBENZENE	3.58	1.000	0.00	168	99	37	
2)	1,2-DICHLOROETHANE-D4	3.8	1.061	0.22	65	102	104	
3)	1,1,2-Trichloro-1,2,2-trifluoroethane	1.9	0.531	-1.68	101	151	103	
4)	Diethyl ether (*)	1.7	0.475	-1.88	74	59	45	
5)	Acetone (*)	1.89	0.528	-1.69	58	43	44	
6)	Methyl iodide (iodomethane)	1.97	0.550	-1.61	142	141	127	
7)	Carbon disulfide (*)	2.01	0.561	-1.57	76	78	44	
8)	Methyl Acetate	2.09	0.584	-1.49	43	74	59	
9)	tert-Methyl butyl ether (MTBE)	2.37	0.662	-1.21	73	57	41	43
10	Acrylonitrile (*)	2.39	0.668	-1.19	52	53	54	
11	2-Butanone (MEK) (*)	3.23	0.902	-0.35	43	72	57	
12	Dichlorodifluoromethane	1.17	0.327	-2.41	85	87	50	
13	Chloromethane (SPCC)	1.25	0.349	-2.33	50	52	49	
14	Vinyl Chloride (CCC)	1.32	0.369	-2.26	62	64	61	
15	Bromomethane	1.44	0.402	-2.14	94	96	81	
16	Chloroethane	1.46	0.408	-2.12	64	66	49	51
17	Acrolein	1.82	0.508	-1.76	56	55	53	
18	Trichlorofluoromethane	1.66	0.464	-1.92	101	103	66	105
19	1,1-Dichloroethene (CCC/MS)	1.86	0.520	-1.72	61	96	63	98
20	Methylene Chloride	2.19	0.612	-1.39	84	49	86	51
21	trans-1,2-Dichloroethene	2.38	0.665	-1.20	61	96	63	98
22	1,1-Dichloroethane (SPCC)	2.73	0.763	-0.85	63	65	83	
23	cis-1,2-Dichloroethene	3.21	0.897	-0.37	96	61	98	
24	Tetrahydrofuran	3.42	0.955	-0.16	42	41	71	
25	Chloroform (CCC)	3.46	0.966	-0.12	83	85	47	
26	Bromochloromethane	3.4	0.950	-0.18	130	49	93	128
27	1,1,1-Trichloroethane	3.57	0.997	-0.01	97	99	61	
28	1,1-Dichloropropene	3.67	1.025	0.09	75	77	110	
29	Cyclohexane	3.63	1.014	0.05	56	84	41	

#	Compound	t_R (*min*)	$t_R/t_{R,I}$ (-)	$t_R-t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
30	1,4-DIFLUOROBENZENE	4.07	1.000	0.00	114	88	57	
31	TOLUENE-D8	4.95	1.216	0.88	98	100	70	
32	4-Methyl-2-pentanone (MIBK)	4.9	1.204	0.83	58	85	100	43
33	2-Hexanone (*)	5.37	1.319	1.30	58	43	85	100
34	2-chloroethylvinyl ether	4.73	1.162	0.66	63	106	65	
35	Carbon Tetrachloride	3.67	0.902	-0.40	117	119	121	
36	Benzene (MS)	3.82	0.939	-0.25	78	77	51	
37	1,2-Dichloroethane	3.85	0.946	-0.22	62	98	100	64
38	Trichloroethene (MS)	4.23	1.039	0.16	95	132	130	134
39	1,2-Dichloropropane (CCC)	4.38	1.076	0.31	63	76	62	
40	Bromodichloromethane	4.56	1.120	0.49	83	85	127	129
41	Methyl Cyclohexane	4.33	1.064	0.26	55	83	41	98
42	Dibromomethane	4.47	1.098	0.40	174	93	172	79
43	cis-1,3-Dichloropropene	4.82	1.184	0.75	75	77	110	
44	Toluene (CCC/MS)	4.99	1.226	0.92	91	92	65	
45	trans-1,3-Dichloropropene	5.13	1.260	1.06	75	110	77	
46	1,1,2-Trichloroethane	5.24	1.287	1.17	83	97	99	85
47	Tetrachloroethene	5.29	1.300	1.22	166	129	164	
48	CHLOROBENZENE-D5	5.76	1.000	0.00	82	117	119	
49	4BROMOFLUOROBENZENE	6.38	1.108	0.62	174	95	176	
50	trans-1,4-Dichloro-2-butene	6.49	1.127	0.73	53	89	124	75
51	Dibromochloromethane	5.46	0.948	-0.30	129	127	79	
52	1,2-Dibromoethane	5.52	0.958	-0.24	107	109	81	
53	Chlorobenzene (SPCC/MS)	5.77	1.002	0.01	112	77	114	
54	1,1,1,2-Tetrachloroethane	5.82	1.010	0.06	131	133	117	119
55	Ethylbenzene (CCC)	5.82	1.010	0.06	91	106	77	
56	p,m-Xylene	5.88	1.021	0.12	106	91	77	
57	o-Xylene	6.09	1.057	0.33	91	106	77	
58	Styrene	6.1	1.059	0.34	104	78	103	
59	Isopropylbenzene	6.28	1.090	0.52	105	120	77	
60	Bromoform (SPCC)	6.23	1.082	0.47	173	171	175	
61	1,1,2,2-Tetrachloroethane	6.47	1.123	0.71	83	85	131	133

#	Compound	t_R (*min*)	$t_R/t_{R,I}$ (-)	$t_R-t_{R,I}$ (*min*)	1^0 *m/z*	2^0 *m/z*	3^0 *m/z*	4^0 *m/z*
62	1,2,3-Trichloropropane	6.49	1.127	0.73	110	75	97	61
63	n-Propylbenzene	6.5	1.128	0.74	91	120	105	
64	Bromobenzene	6.46	1.122	0.70	156	77	158	
65	1,3,5-Trimethylbenzene	6.59	1.144	0.83	120	105	77	
66	tert-Butylbenzene	6.76	1.174	1.00	91	119	134	
67	1,2,4-Trimethylbenzene	6.79	1.179	1.03	120	105	77	
68	1,4-DICHLOROBENZENE-D4	6.99	1.000	0.00	152	150	115	
69	sec-Butylbenzene	6.87	0.983	-0.12	105	134	91	
70	p-Isopropyltoluene	6.95	0.994	-0.04	119	91	134	
71	1,3-Dichlorobenzene	6.95	0.994	-0.04	146	148	111	
72	1,4-Dichlorobenzene	7	1.001	0.01	146	148	111	
73	1,2-Dichlorobenzene	7.2	1.030	0.21	146	148	111	
74	1,2,3-Trimethylbenzene	7.01	1.003	0.02	105	120	77	
75	n-Butylbenzene	7.16	1.024	0.17	91	92	134	
76	Hexachloroethane	7.32	1.047	0.33	201	117	166	
77	1,2-Dibromo-3-Chloropropan	7.61	1.089	0.62	157	155	75	159
78	1,2,4-Trichlorobenzene	8.02	1.147	1.03	182	180	145	109
79	Hexachlorobutadiene	8.09	1.157	1.10	225	227	223	190
80	1,2,3-Trichlorobenzene	8.27	1.183	1.28	180	182	145	109
81	Naphthalene	8.15	1.166	1.16	128	102	127	129
82	2-Methylnaphthalene	8.72	1.247	1.73	142	141	115	

†: Absolute retention times (t_R) listed are from calibration FT060808.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e*. new, clipped, *etc*.), but the differential retention times (t_R - $t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

Table 2. Summary of Applicable Performance Compounds - Volatile Organics Analysis

#†	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	PENTAFLUOROBENZENE			✔		
2	1,2-DICHLOROETHANE-D4				✔	
11	Chloromethane (SPCC)		✔			
12	Vinyl Chloride (CCC)	✔				
16	1,1-Dichloroethene (CCC/MS)	✔				✔
19	1,1-Dichloroethane (SPCC)		✔			
21	Chloroform (CCC)	✔				
25	1,4-DIFLUOROBENZENE			✔		
26	TOLUENE-D8				✔	
30	Benzene (MS)					✔
32	Trichloroethene (MS)					✔
33	1,2-Dichloropropane (CCC)	✔				
37	Toluene (CCC/MS)	✔				✔
42	CHLOROBENZENE-D5			✔		
43	4-BROMOFLUOROBENZENE-				✔	
47	Chlorobenzene (SPCC/MS)		✔			✔
49	Ethylbenzene (CCC)	✔				
54	Bromoform (SPCC)		✔			
55	1,1,2,2-Tetrachloroethane (SPCC)		✔			
62	1,4-DICHLOROBENZENE-D4			✔		

†: Compound identification numbers listed are from calibration FR010910.M.

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

Key

CCC: Calibration Check Compound

SPCC: System Performance Check Compound

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

MS: Matrix Spiking Compound

Table 2b. Recommended Minimum Relative Response Factor Criteria For Initial And Continuing Calibration Verification.

Volatile Compounds	Minimum Response Factor (RF)[a]
Dichlorodifluoromethane	0.100
Chloromethane	0.100
Vinyl chloride	0.100
Bromomethane	0.100
Chloroethane	0.100
Trichlorofluoromethane	0.100
1,1-Dichloroethene	0.100
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100
Acetone	0.100
Carbon disulfide	0.100
Methyl Acetate	0.100
Methylene chloride	0.100
trans-1,2-Dichloroethene	0.100
cis-1,2-Dichloroethene	0.100
Methyl tert-Butyl Ether	0.100
1,1-Dichloroethane	0.200
2-Butanone	0.100
Chloroform	0.200
1,1,1-Trichloroethane	0.100
Cyclohexane	0.100
Carbon tetrachloride	0.100
Benzene	0.500
1,2-Dichloroethane	0.100
Trichloroethene	0.200
Methylcyclohexane	0.100
1,2-Dichloropropane	0.100
Bromodichloromethane	0.200
cis-1,3-Dichloropropene	0.200
trans-1,3-Dichloropropene	0.100
4-Methyl-2-pentanone	0.100
Toluene	0.400
1,1,2-Trichloroethane	0.100
Tetrachloroethene	0.200
2-Hexanone	0.100
Dibromochloromethane	0.100
1,2-Dibromoethane	0.100
Chlorobenzene	0.500

Volatile Compounds	Minimum Response Factor (RF)[a]
Ethylbenzene	0.100
meta-/para-Xylene	0.100
ortho-Xylene	0.300
Styrene	0.300
Bromoform	0.100
Isopropylbenzene	0.100
1,1,2,2-Tetrachloroethane	0.300
1,3-Dichlorobenzene	0.600
1,4-Dichlorobenzene	0.500
1,2-Dichlorobenzene	0.400
1,2-Dibromo-3-chloropropane	0.050
1,2,4-Trichlorobenzene	0.200

[a] The Project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed.

Table 3. GC/MS Operating Conditions - Volatile Organics Analysis

Operating Parameter	**Volatiles Analysis**
Chromatographic Column	DB 624, *L* = 20 *m*, *ID* = 0.18 *mm*
Carrier Gas	Helium (He)
Temperature Program	T_0 = 30°C, hold 2.0 *min* dT/dt_1 = 32°C/*min* T_1 = 195°C dT/dt_2 = 30°C/*min* T_2 = 235°C
Injector Temperature	250°C
Detector Temperature	280°C
Purge Volume	5 *mL*
Mass Scanning Range	35 *m/z* - 250 *m/z*
Mass Scanning Rate	2.0 *Hz*

Note: the above is subject to change based on GC and/or sample conditions.

Table 4. BFB Tune Evaluation Criteria

Target *m/z*	**Relative *m/z***	**LCL (%)**	**UCL (%)**
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5.0	9.0
173	174	0	2.0
174	95	50	120
175	174	4.0	9.0
176	174	93	101
177	176	5.0	9.0

Table 5. Commonly Used Dilutions for Sample Preparation

Dilution	Sample Volume (μL)	H_2O Volume (μL)	ISD/SSD Volume (μL)	Total Volume (μL)
1:1	5000	0	10.0	5010
2:1	2500	2500	10.0	5010
5:1	1000	4000	10.0	5010
10:1	500	4500	10.0	5010
20:1	250	4750	10.0	5010
50:1	100	4900	10.0	5010
100:1	50	4950	10.0	5010
200:1	25	4975	10.0	5010
500:1	10	5000	10.0	5020
1000:1	5.0	5000	10.0	5015
2500:1	2.0	5000	10.0	5012

General "*n*:1" dilution: (5000/*n*) μL of Sample

(5000 - 5000/*n*) μL H_2O

10 μL Internal/Surrogate Standard (ISD/SSD) at 25 mg/L

Table 6a. Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
BFB	12-hour	Table 5	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	SPCC- section 7.34 CCC- section 7.3.5	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Table 7	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	<RL	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) should result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard	All samples	Section 7.5.5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged

QC Item	Frequency	Acceptance Criteria	Corrective Action
			appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate
Surrogate Standard	All samples	Table 7	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 6b. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within ± 20% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within ± 20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed	If corrective action fails in field samples, data must be qualified and explained in the case	NA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		+100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	while system was malfunctioning is mandatory.	narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10th the amount measured in any sample or 1/10th the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
				associated preparatory batch.	
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes ≤ 20% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	MSD: Must contain all surrogates and all analytes to be reported. The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed..	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative..		
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within ± 20% of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within ± 20% of true value. All reported analytes and surrogates within ± 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			necessary; then reanalyze all associated samples since the last acceptable CCV.		
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time ± 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	NA
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > $1/10^{th}$ the amount measured in any sample or $1/10^{th}$ the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

DoD Appendix C LCS Limits
Method 8260 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	125
71-55-6	1,1,1-Trichloroethane	73	130
79-34-5	1,1,2,2-Tetrachloroethane	70	124
79-00-5	1,1,2-Trichloroethane	78	121
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	66	136
75-34-3	1,1-Dichloroethane	76	125
75-35-4	1,1-Dichloroethene	70	131
563-58-6	1,1-Dichloropropene	76	125
87-61-6	1,2,3-Trichlorobenzene	66	130
96-18-4	1,2,3-Trichloropropane	73	125
526-73-8	1,2,3-Trimethlybenzene	82	118
120-82-1	1,2,4-Trichlorobenzene	67	129
95-63-6	1,2,4-Trimethylbenzene	75	123
96-12-8	1,2-Dibromo-3-chloropropane	61	132
106-93-4	1,2-Dibromoethane	78	122
95-50-1	1,2-Dichlorobenzene	78	121
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	71	136
540-59-0	1,2-Dichloroethene	78	122
78-87-5	1,2-Dichloropropane	76	123
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	64	132
108-70-3	1,3,5-Trichlorobenzene	71	128
108-67-8	1,3,5-Trimethylbenzene	73	124
541-73-1	1,3-Dichlorobenzene	77	121
142-28-9	1,3-Dichloropropane	77	121
542-75-6	1,3-Dichloropropene	77	126
106-46-7	1,4-Dichlorobenzene	75	120
105-05-5	1,4-Diethylbenzene	79	114

123-91-1	1,4-Dioxane	55	138
544-10-5	1-Chlorohexane	71	130
594-20-7	2,2-Dichloropropane	67	133
78-93-3	2-Butanone (MEK)	51	148
126-99-8	2-Chloro-1,3-butadiene	65	133
110-75-8	2-Chloroethyl vinyl ether	43	149
95-49-8	Chlorotoluene	75	122
591-78-6	2-Hexanone	53	145
79-46-9	2-Nitropropane	47	150
67-63-0	2-Propanol [Isopropyl alcohol]	60	140
460-00-4	4-Bromofluorobenzene	79	119
106-43-4	4-Chlorotoluene	72	124
108-10-1	4-Methyl-2-pentanone [MIBK]	65	135
67-64-1	Acetone	36	164
75-05-8	Acetonitrile	54	143
107-02-8	Acrolein [Propenal]	47	155
107-13-1	Acrylonitrile	65	134
107-05-1	Allyl chloride	68	135
71-43-2	Benzene	77	121
100-44-7	Benzyl chloride	64	120
108-86-1	Bromobenzene	78	121
74-97-5	Bromochloromethane	78	125
75-27-4	Bromodichloromethane	75	127
75-25-2	Bromoform	67	132
74-83-9	Bromomethane	53	143
75-15-0	Carbon disulfide	63	132
56-23-5	Carbon tetrachloride	70	135
108-90-7	Chlorobenzene	79	120
124-48-1	Chlorodibromomethane	74	126
75-00-3	Chloroethane	59	139
67-66-3	Chloroform	78	123
74-87-3	Chloromethane	50	136
156-59-2	cis-1,2-Dichloroethene	77	123

10061-01-5	cis-1,3-Dichloropropene	74	126
1476-11-5	cis-1,4-Dichloro-2-butene	69	143
110-82-7	Cyclohexane	67	131
108-94-1	Cyclohexanone	30	156
1868-53-7	Dibromofluoromethane	78	119
74-95-3	Dibromomethane	78	125
75-71-8	Dichlorodifluoromethane [Freon-12]	29	149
75-43-4	Dichlorofluoromethane	47	155
60-29-7	Diethyl ether	71	129
108-20-3	Diisopropyl ether	69	127
64-17-5	Ethanol	45	159
141-78-6	Ethyl acetate	52	139
97-63-2	Ethyl methacrylate	69	129
637-92-3	Ethyl tert-butyl ether	72	126
100-41-4	Ethylbenzene	76	122
462-06-6	Fluorobenzene	81	114
142-82-5	Heptane	49	138
87-68-3	Hexachlorobutadiene	61	135
67-72-1	Hexachloroethane	72	133
110-54-3	Hexane	45	142
74-88-4	Iodomethane	71	131
78-83-1	Isobutyl alcohol	60	135
108-21-4	Isopropyl acetate [Acetic acid]	58	131
98-82-8	Isopropylbenzene	68	134
179601-23-1	m/p-Xylene [3/4-Xylene]	77	124
126-98-7	Methacrylonitrile	66	132
79-20-9	Methyl acetate	53	144
80-62-6	Methyl methacrylate	63	134
1634-04-4	Methyl tert-butyl ether [MTBE]	73	125
108-87-2	Methylcyclohexane	66	133
75-09-2	Methylene chloride	70	128
123-86-4	n-Butyl acetate	62	128
71-36-3	n-Butyl alcohol	55	131

104-51-8	n-Butylbenzene	70	128
103-65-1	n-Propylbenzene	73	125
91-20-3	Naphthalene	62	129
95-47-6	o-Xylene	77	123
99-87-6	p-Isopropyltoluene [p-Cymene]	73	127
76-01-7	Pentachloroethane	69	135
107-12-0	Propionitrile [Ethyl cyanide]	68	134
135-98-8	sec-Butylbenzene	73	126
100-42-5	Styrene	76	124
994-05-8	tert-Amyl methyl ether [TAME]	73	126
75-65-0	tert-Butyl alcohol	68	133
98-06-6	tert-Butylbenzene	73	125
127-18-4	Tertachloroethene	73	128
109-99-9	Tetrahydrofuran	61	135
108-88-3	Toluene	77	121
2037-26-5	Toluene-d8	85	116
156-60-5	trans-1,2-Dichloroethene	74	125
10061-02-6	trans-1,3-Dichloropropene	71	130
110-57-6	trans-1,4-Dichloro-2-butene	62	136
79-01-6	Trichloroethene	77	123
75-69-4	Trichlorofluoromethane [Freon-11]	62	140
108-05-4	Vinyl acetate	50	151
75-01-4	Vinyl chloride	56	135
1330-20-7	Xylene [total]	78	124

DoD Appendix C LCS Limits
Method 8260 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	124
71-55-6	1,1,1-Trichloroethane	74	131
79-34-5	1,1,2,2-Tetrachloroethane	71	121
79-00-5	1,1,2-Trichloroethane	80	119
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane	70	136

	[Freon-113]		
75-34-3	1,1-Dichloroethane	77	125
75-35-4	1,1-Dichloroethene	71	131
563-58-6	1,1-Dichloropropene	79	125
87-61-6	1,2,3-Trichlorobenzene	69	129
96-18-4	1,2,3-Trichloropropane	73	122
526-73-8	1,2,3-Trimethlybenzene	82	120
120-82-1	1,2,4-Trichlorobenzene	69	130
95-63-6	1,2,4-Trimethylbenzene	76	124
96-12-8	1,2-Dibromo-3-chloropropane	62	128
106-93-4	1,2-Dibromoethane	77	121
95-50-1	1,2-Dichlorobenzene	80	119
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	81	118
540-59-0	1,2-Dichloroethene	79	121
78-87-5	1,2-Dichloropropane	78	122
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	70	136
108-70-3	1,3,5-Trichlorobenzene	75	130
108-67-8	1,3,5-Trimethylbenzene	75	124
106-99-0	1,3-Butadiene	43	158
541-73-1	1,3-Dichlorobenzene	80	119
142-28-9	1,3-Dichloropropane	80	119
542-75-6	1,3-Dichloropropene	77	123
106-46-7	1,4-Dichlorobenzene	79	118
105-05-5	1,4-Diethylbenzene	79	118
123-91-1	1,4-Dioxane	59	139
544-10-5	1-Chlorohexane	76	124
540-84-1	2,2,4-Trimethylpentane [Isooctane]	58	132
594-20-7	2,2-Dichloropropane	60	139
75-85-4	2-Butanol	66	120
78-93-3	2-Butanone (MEK)	56	143
126-99-8	2-Chloro-1,3-butadiene	65	135

110-75-8	2-Chloroethyl vinyl ether	51	139
95-49-8	Chlorotoluene	79	122
591-78-6	2-Hexanone	57	139
91-57-6	2-Methylnaphthalene	17	142
79-46-9	2-Nitropropane	49	136
67-63-0	2-Propanol [Isopropyl alcohol]	56	142
624-95-3	3,3-Dimethyl-1-butanol	49	133
460-00-4	4-Bromofluorobenzene	85	114
106-43-4	4-Chlorotoluene	78	122
108-10-1	4-Methyl-2-pentanone [MIBK]	67	130
67-64-1	Acetone	39	160
75-05-8	Acetonitrile	50	142
107-02-8	Acrolein [Propenal]	39	155
107-13-1	Acrylonitrile	63	135
107-05-1	Allyl chloride	68	130
71-43-2	Benzene	79	120
100-44-7	Benzyl chloride	42	138
108-86-1	Bromobenzene	80	120
74-97-5	Bromochloromethane	78	123
75-27-4	Bromodichloromethane	79	125
75-25-2	Bromoform	66	130
74-83-9	Bromomethane	53	141
75-15-0	Carbon disulfide	64	133
56-23-5	Carbon tetrachloride	72	136
108-90-7	Chlorobenzene	82	118
124-48-1	Chlorodibromomethane	74	126
75-45-6	Chlorodifluoromethane	40	129
75-00-3	Chloroethane	60	138
67-66-3	Chloroform	79	124
74-87-3	Chloromethane	50	139
156-59-2	cis-1,2-Dichloroethene	78	123
10061-01-5	cis-1,3-Dichloropropene	75	124
1476-11-5	cis-1,4-Dichloro-2-butene	57	146

110-82-7	Cyclohexane	71	130
1868-53-7	Dibromofluoromethane	80	119
74-95-3	Dibromomethane	79	123
75-71-8	Dichlorodifluoromethane [Freon-12]	32	152
75-43-4	Dichlorofluoromethane	72	131
60-29-7	Diethyl ether	68	129
108-20-3	Diisopropyl ether	67	128
64-17-5	Ethanol	48	151
141-78-6	Ethyl acetate	55	138
97-63-2	Ethyl methacrylate	72	126
637-92-3	Ethyl tert-butyl ether	70	127
100-41-4	Ethylbenzene	79	121
462-06-6	Fluorobenzene	80	116
142-82-5	Heptane	49	140
87-68-3	Hexachlorobutadiene	66	134
67-72-1	Hexachloroethane	72	134
110-54-3	Hexane	48	143
74-88-4	Iodomethane	69	131
78-83-1	Isobutyl alcohol	63	133
108-21-4	Isopropyl acetate [Acetic acid]	63	133
98-82-8	Isopropylbenzene	72	131
179601-23-1	m/p-Xylene [3/4-Xylene]	80	121
126-98-7	Methacrylonitrile	63	133
79-20-9	Methyl acetate	56	136
80-62-6	Methyl methacrylate	67	128
1634-04-4	Methyl tert-butyl ether [MTBE]	71	124
108-87-2	Methylcyclohexane	72	132
75-09-2	Methylene chloride	74	124
123-86-4	n-Butyl acetate	69	125
71-36-3	n-Butyl alcohol	59	131
104-51-8	n-Butylbenzene	75	128
109-60-4	n-Propyl acetate	76	126
103-65-1	n-Propylbenzene	76	126

91-20-3	Naphthalene	61	128
95-47-6	o-Xylene	78	122
99-87-6	p-Isopropyltoluene [p-Cymene]	77	127
76-01-7	Pentachloroethane	69	133
109-66-0	Pentane	16	134
107-12-0	Propionitrile [Ethyl cyanide]	64	136
135-98-8	sec-Butylbenzene	77	126
100-42-5	Styrene	78	123
994-05-8	tert-Amyl methyl ether [TAME]	68	128
75-65-0	tert-Butyl alcohol	68	129
762-75-4	tert-Butyl formate	65	132
98-06-6	tert-Butylbenzene	78	124
127-18-4	Tertachloroethene	74	129
109-99-9	Tetrahydrofuran	57	133
108-88-3	Toluene	80	121
2037-26-5	Toluene-d8	89	112
156-60-5	trans-1,2-Dichloroethene	75	124
10061-02-6	trans-1,3-Dichloropropene	73	127
110-57-6	trans-1,4-Dichloro-2-butene	43	140
79-01-6	Trichloroethene	79	123
75-69-4	Trichlorofluoromethane [Freon-11]	65	141
108-05-4	Vinyl acetate	54	146
75-01-4	Vinyl chloride	58	137
1330-20-7	Xylene [total]	79	121

Table 7. Summary of Control Limits: Surrogate and Matrix Spiking Compounds Percent Recovery[†]

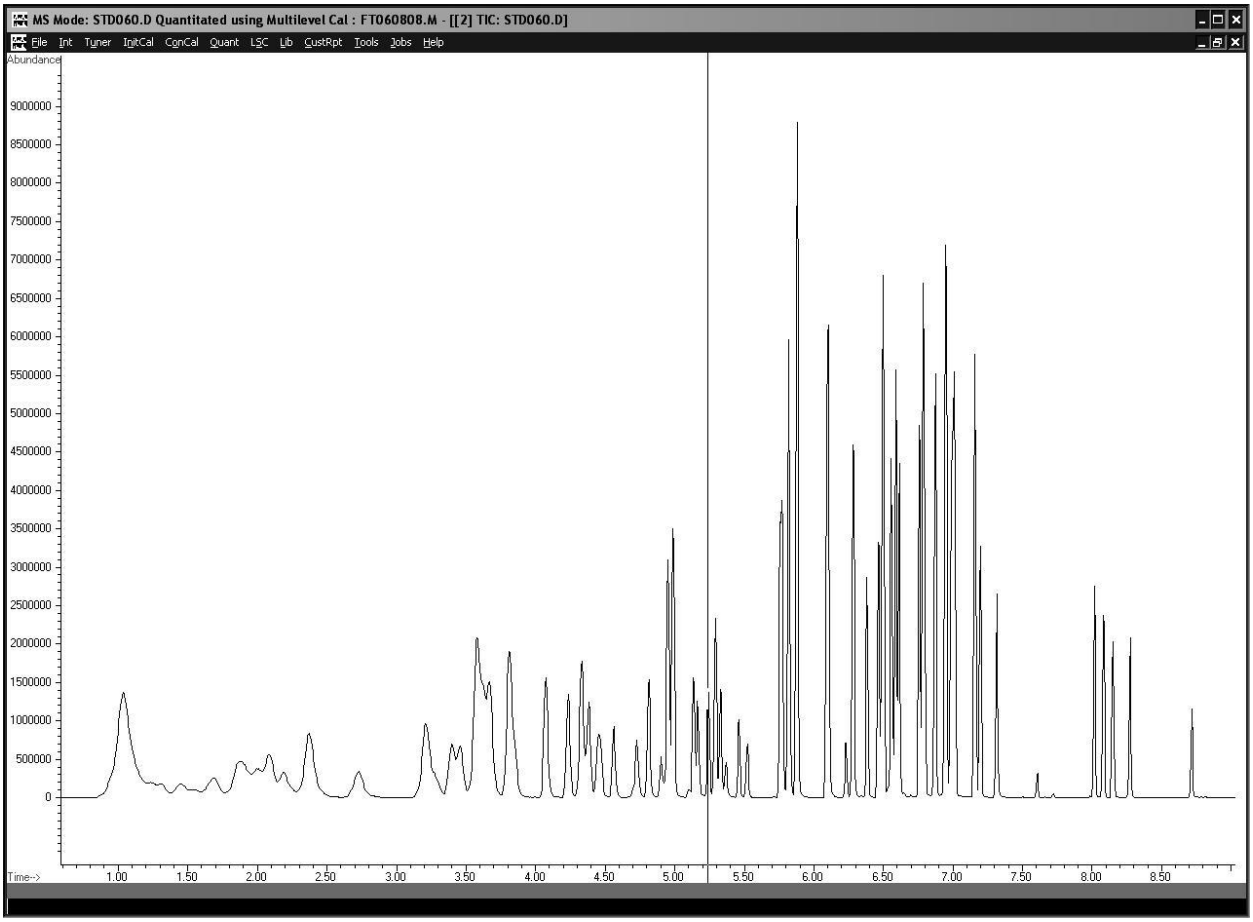
#[‡]	COMPOUND	Water Matrix		Solid Matrix	
		LCL (%)	UCL (%)	LCL (%)	UCL (%)
2	1,2-DICHLOROETHANE-D4	66.4	124.8	70.0	136.3
26	TOLUENE-D8	82.5	118.4	84.0	138.0
43	4BROMOFLUOROBENZENE	78.4	119.6	59.0	122.8
16	1,1-Dichloroethene (CCC/MS)	59.9	145.0	59.0	172.0
30	Benzene (MS)	73.7	127.0	66.0	142.0
32	Trichloroethene (MS)	71.0	121.2	62.0	137.0
37	Toluene (CCC/MS)	71.4	127.6	59.0	139.0
47	Chlorobenzene (SPCC/MS)	75.0	130.0	60.0	133.0
n/a	Gasoline Range Organics	70.0	130.0	70.0	130.0

[†]: Results based on recovery data from 2001.

[‡]: Compound identification numbers listed are from calibration FR010910.M.

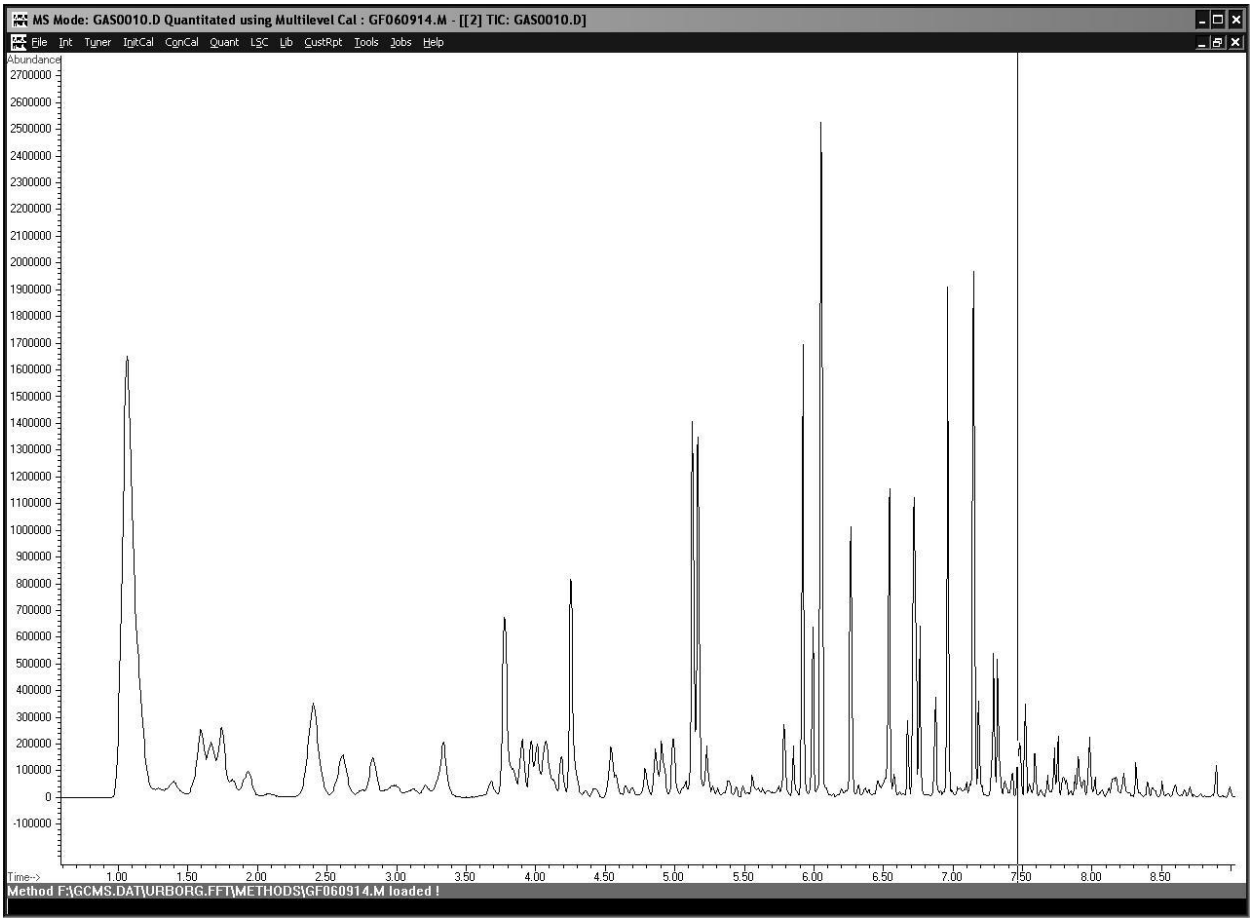
: For DoD projects, all target compounds must be included in the spikes. LCS acceptance criteria specified in the DoD QSM or in-house LCS control limits shall be used.

Figure 1. Example Total Ion Chromatogram for a Midpoint VOA Calibration Standard†



†: Data file Std060.D (60 μg/L). GC/MS acquisition parameters are given by Table 4.

Figure 2. Example Total Ion Chromatogram for a Gasoline Range Organics Calibration Standard†



†:GAS_010.D from calibration GF060914.M (1.0 mg/L). GC/MS acquisition parameters are given by Table 4.

Appendix C
Laboratory Reference Data
TestAmerica and Pace

TESTAMERICA

Analysis Group	Method Description	Method Code	Prep Metho	Analyte Description	CAS Number	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
Table 1.5 chlorinated organics	Volatile Organic Compounds (GC/MS)	8260B	5030B	1,1,1-Trichloroethane	71-55-6	64	147	35	57	156	13		
				1,1,2,2-Tetrachloroethane	79-34-5	58	122	35	51	123	17		
				1,1,2-Trichloroethane	79-00-5	76	121	35	68	127	11		
				1,1-Dichloroethane	75-34-3	74	120	35	69	122	11		
				1,1-Dichloroethene	75-35-4	65	127	35	62	127	14		
				1,2-Dichlorobenzene	95-50-1	80	120	35	70	120	19		
				1,2-Dichloroethane	107-06-2	68	133	35	64	138	11		
				1,2-Dichloropropane	78-87-5	78	127	35	72	131	12		
				1,3-Dichlorobenzene	541-73-1	80	120	35	71	120	18		
				1,4-Dichlorobenzene	106-46-7	80	120	35	72	120	17		
				2-Chloroethyl vinyl ether	110-75-8	58	123	35	10	120	35		
				Benzene	71-43-2	79	120	35	69	127	10		
				Bromoform	75-25-2	55	145	35	61	135	13		
				Bromomethane	74-83-9	17	158	35	10	148	35		
				Carbon tetrachloride	56-23-5	55	171	35	53	175	17		
				Chlorobenzene	108-90-7	80	120	35	76	120	12		
				Chloroethane	75-00-3	10	149	35	10	141	35		
				Chloroform	67-66-3	80	120	35	74	125	11		
				Chloromethane	74-87-3	59	124	35	34	127	25		
				cis-1,3-Dichloropropene	10061-01-5	75	120	35	68	120	13		
				Bromodichloromethane	75-27-4	79	125	35	75	128	13		
				Dichlorodifluoromethane	75-71-8	42	141	35	45	130	34		
				Ethylbenzene	100-41-4	80	120	35	72	121	15		
				Methylene Chloride	75-09-2	64	140	35	52	137	12		
				Tetrachloroethene	127-18-4	80	122	35	69	126	18		
				Toluene	108-88-3	78	120	35	69	125	14		
				trans-1,2-Dichloroethene	156-60-5	74	124	35	66	131	11		
				trans-1,3-Dichloropropene	10061-02-6	67	120	35	59	120	14		
				Trichlorofluoromethane	75-69-4	27	176	35	28	172	26		
				Vinyl chloride	75-01-4	65	124	35	55	123	12		
				Dibromochloromethane	124-48-1	64	129	35	62	131	15		
				1,2-Dichloroethane-d4 (Surr)	17060-07-0			35				61	138
				4-Bromofluorobenzene (Surr)	460-00-4			35				69	120
				Toluene-d8 (Surr)	2037-26-5			35				73	120
				Dibromofluoromethane (Surr)	1868-53-7			35				69	124

Soils	Metals (ICP)	6010B	3050B	Aluminum	7429-90-5	80	120	20	75	125	20		
				Antimony	7440-36-0	80	120	20	75	125	20		
				Barium	7440-39-3	80	120	20	75	125	20		
				Beryllium	7440-41-7	80	120	20	75	125	20		
				Calcium	7440-70-2	80	120	20	75	125	20		
				Cadmium	7440-43-9	80	120	20	75	125	20		
				Cobalt	7440-48-4	80	120	20	75	125	20		
				Chromium	7440-47-3	80	120	20	75	125	20		
				Copper	7440-50-8	80	120	20	75	125	20		
				Iron	7439-89-6	80	120	20	75	125	20		
				Potassium	7440-09-7	80	120	20	75	125	20		
				Magnesium	7439-95-4	80	120	20	75	125	20		
				Manganese	7439-96-5	80	120	20	75	125	20		
				Silver	7440-22-4	80	120	20	75	125	20		
				Sodium	7440-23-5	80	120	20	75	125	20		
				Nickel	7440-02-0	80	120	20	75	125	20		
				Vanadium	7440-62-2	80	120	20	75	125	20		
				Zinc	7440-66-6	80	120	20	75	125	20		
				Arsenic	7440-38-2	80	120	20	75	125	20		
				Lead	7439-92-1	80	120	20	75	125	20		
				Selenium	7782-49-2	80	120	20	75	125	20		
				Thallium	7440-28-0	80	120	20	75	125	20		

Soils	Mercury (CVAA)	7471A	7471A_Prep	Mercury	7439-97-6	80	120	20	80	120	20		

Soils	Polychlorinated Biphenyls (PCBs) by Gas	8082A	3540C	Aroclor-1016	12674-11-2	47	120	30	31	120	30		
				Aroclor-1221	11104-28-2								
				Aroclor-1232	11141-16-5								
				Aroclor-1242	53469-21-9								
				Aroclor-1248	12672-29-6								
				Aroclor-1254	11097-69-1								
				Aroclor-1260	11096-82-5	46	120	30	21	122	30		
				Aroclor-1262	37324-23-5								
				Aroclor-1268	11100-14-4								
				Tetrachloro-m-xylene	877-09-8							14	128
				DCB Decachlorobiphenyl	2051-24-3							10	132

TESTAMERICA

Analysis Group	Method Description	Method Code	Prep Metho	Analyte Description	CAS Number	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
Soils	Semivolatile Organic Compounds (GC/M	8270C	3540C	1,1'-Biphenyl	92-52-4	48	120	40	33	120	33		
				bis (2-chloroisopropyl) ether	108-60-1	37	120	40	26	120	31		
				2,4,5-Trichlorophenol	95-95-4	34	120	40	20	120	38		
				2,4,6-Trichlorophenol	88-06-2	19	120	40	19	120	36		
				2,4-Dichlorophenol	120-83-2	48	120	40	32	120	32		
				2,4-Dimethylphenol	105-67-9	37	120	40	28	120	35		
				2,4-Dinitrophenol	51-28-5	10	120	40	10	120	40		
				2,4-Dinitrotoluene	121-14-2	53	120	40	38	120	27		
				2,6-Dinitrotoluene	606-20-2	54	120	40	43	120	31		
				2-Chloronaphthalene	91-58-7	49	120	40	35	120	30		
				2-Chlorophenol	95-57-8	50	120	40	30	120	37		
				2-Methylnaphthalene	91-57-6	49	120	40	31	120	33		
				2-Methylphenol	95-48-7	49	120	40	31	120	36		
				2-Nitroaniline	88-74-4	46	120	40	29	120	31		
				2-Nitrophenol	88-75-5	46	120	40	26	120	38		
				3,3'-Dichlorobenzidine	91-94-1	40	120	40	10	120	40		
				3-Nitroaniline	99-09-2	48	120	40	21	120	40		
				4,6-Dinitro-2-methylphenol	534-52-1	18	120	40	10	120	40		
				4-Bromophenyl phenyl ether	101-55-3	51	120	40	44	120	40		
				4-Chloro-3-methylphenol	59-50-7	47	120	40	31	120	25		
				4-Chloroaniline	106-47-8	37	120	40	15	120	36		
				4-Chlorophenyl phenyl ether	7005-72-3	49	120	40	41	120	40		
				4-Nitroaniline	100-01-6	49	120	40	23	120	40		
				4-Nitrophenol	100-02-7	42	120	40	32	120	31		
				Acenaphthene	83-32-9	48	120	40	36	120	28		
				Acenaphthylene	208-96-8	46	120	40	35	120	26		
				Acetophenone	98-86-2	46	120	40	31	120	40		
				Anthracene	120-12-7	51	120	40	42	120	32		
				Atrazine	1912-24-9	57	120	40	41	120	26		
				Benzaldehyde	100-52-7	48	120	40	28	120	40		
				Benzo[a]anthracene	56-55-3	53	120	40	35	120	40		
				Benzo[a]pyrene	50-32-8	50	120	40	33	120	40		
				Benzo[b]fluoranthene	205-99-2	48	120	40	26	120	40		
				Benzo[g,h,i]perylene	191-24-2	50	120	40	16	120	40		
				Benzo[k]fluoranthene	207-08-9	51	120	40	33	120	40		
				Bis(2-chloroethoxy)methane	111-91-1	50	120	40	36	120	33		
				Bis(2-chloroethyl)ether	111-44-4	48	120	40	33	120	36		
				Bis(2-ethylhexyl) phthalate	117-81-7	52	120	40	40	120	28		
				Butyl benzyl phthalate	85-68-7	53	120	40	46	120	39		
				Caprolactam	105-60-2	59	120	40	33	128	40		
				Carbazole	86-74-8	56	120	40	35	120	34		
				Chrysene	218-01-9	54	120	40	33	120	40		
				Dibenz(a,h)anthracene	53-70-3	48	120	40	30	120	40		
				Dibenzofuran	132-64-9	49	120	40	37	120	28		
				Diethyl phthalate	84-66-2	52	120	40	44	120	26		
				Dimethyl phthalate	131-11-3	53	120	40	42	120	35		
				Di-n-butyl phthalate	84-74-2	56	120	40	45	120	28		
				Di-n-octyl phthalate	117-84-0	42	120	40	35	120	33		
				Fluoranthene	206-44-0	53	120	40	26	121	40		
				Fluorene	86-73-7	50	120	40	36	120	28		
				Hexachlorobenzene	118-74-1	46	120	40	36	120	25		
				Hexachlorobutadiene	87-68-3	44	120	40	31	120	35		
				Hexachlorocyclopentadiene	77-47-4	14	120	40	10	120	40		
				Hexachloroethane	67-72-1	45	120	40	15	120	40		
				Indeno[1,2,3-cd]pyrene	193-39-5	49	120	40	24	120	40		
				Isophorone	78-59-1	47	120	40	34	120	32		
				Naphthalene	91-20-3	48	120	40	29	120	34		
				Nitrobenzene	98-95-3	48	120	40	33	120	40		
				N-Nitrosodi-n-propylamine	621-64-7	49	120	40	32	120	32		
				N-Nitrosodiphenylamine	86-30-6	53	120	40	29	120	30		
				Pentachlorophenol	87-86-5	14	120	40	10	120	40		
				Phenol	108-95-2	49	120	40	21	120	40		
				Phenanthrene	85-01-8	52	120	40	28	120	40		
				Pyrene	129-00-0	55	120	40	28	120	40		
				3 & 4 Methylphenol	15831-10-4	50	120	40	33	120	29		
				2-Fluorobiphenyl (Surr)	321-60-8			40				32	120
				2-Fluorophenol (Surr)	367-12-4			40				29	120
				2,4,6-Tribromophenol (Surr)	118-79-6			40				10	120
				Nitrobenzene-d5 (Surr)	4165-60-0			40				30	120
				Phenol-d5 (Surr)	4165-62-2			40				29	120
				Terphenyl-d14 (Surr)	1718-51-0			40				41	120
Soils	Volatile Organic Compounds (GC/MS)	8260B	5035A_FM	Acetone	67-64-1	24	125	40	15	127	40		
				Benzene	71-43-2	77	120	40	33	127	40		

TESTAMERICA

Analysis Group	Method Description	Method Code	Prep Metho	Analyte Description	CAS Number	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
				Dichlorobromomethane	75-27-4	61	132	40	22	127	40		
				Bromoform	75-25-2	40	140	40	10	120	40		
				Bromomethane	74-83-9	10	153	40	13	138	40		
				2-Butanone (MEK)	78-93-3	51	120	40	29	127	40		
				Carbon disulfide	75-15-0	17	163	40	15	131	40		
				Carbon tetrachloride	56-23-5	43	144	40	17	127	40		
				Chlorobenzene	108-90-7	76	120	40	15	122	40		
				Chloroethane	75-00-3	10	166	40	15	148	40		
				Chloroform	67-66-3	74	120	40	41	121	40		
				Chloromethane	74-87-3	41	124	40	33	122	40		
				1,1-Dichloroethane	75-34-3	72	120	40	41	122	40		
				1,2-Dichloroethane	107-06-2	71	120	40	35	122	40		
				1,1-Dichloroethene	75-35-4	58	130	40	30	139	40		
				1,2-Dichloropropane	78-87-5	78	122	40	38	130	40		
				cis-1,3-Dichloropropene	10061-01-5	66	126	40	13	127	40		
				trans-1,3-Dichloropropene	10061-02-6	55	121	40	11	120	40		
				Ethylbenzene	100-41-4	76	120	40	18	126	40		
				2-Hexanone	591-78-6	52	129	40	21	136	40		
				Methylene Chloride	75-09-2	64	126	40	34	134	40		
				4-Methyl-2-pentanone (MIBK)	108-10-1	65	131	40	16	164	40		
				Styrene	100-42-5	80	120	40	10	128	40		
				1,1,2,2-Tetrachloroethane	79-34-5	78	120	40	16	157	40		
				Tetrachloroethene	127-18-4	68	122	40	17	126	40		
				Toluene	108-88-3	74	120	40	29	127	40		
				Trichloroethene	79-01-6	73	123	40	10	160	40		
				Vinyl chloride	75-01-4	49	131	40	31	134	40		
				Xylenes, Total	1330-20-7	78	120	40	10	137	40		
				1,1,1-Trichloroethane	71-55-6	60	136	40	33	130	40		
				1,1,2-Trichloroethane	79-00-5	80	120	40	19	137	40		
				Cyclohexane	110-82-7	66	129	40	22	135	40		
				1,2-Dibromo-3-Chloropropane	96-12-8	40	133	40	10	128	40		
				Ethylene Dibromide	106-93-4	80	120	40	25	137	40		
				Dichlorodifluoromethane	75-71-8	15	127	40	10	126	40		
				cis-1,2-Dichloroethene	156-59-2	78	120	40	46	120	40		
				trans-1,2-Dichloroethene	156-60-5	74	124	40	32	134	40		
				Isopropylbenzene	98-82-8	76	124	40	10	128	40		
				Methyl acetate	79-20-9	63	126	40	14	151	40		
				Methyl tert-butyl ether	1634-04-4	68	129	40	49	134	40		
				1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	64	125	40	26	130	40		
				1,2,4-Trichlorobenzene	120-82-1	60	124	40	10	120	40		
				1,2-Dichlorobenzene	95-50-1	75	120	40	10	120	40		
				1,3-Dichlorobenzene	541-73-1	72	120	40	10	120	40		
				1,4-Dichlorobenzene	106-46-7	71	120	40	10	120	40		
				Trichlorofluoromethane	75-69-4	28	152	40	24	137	40		
				Chlorodibromomethane	124-48-1	46	125	40	19	120	40		
				Methylcyclohexane	108-87-2	71	126	40	13	134	40		
				m-Xylene & p-Xylene	179601-23-1	78	120	40	10	136	40		
				o-Xylene	95-47-6	77	120	40	17	128	40		
				1,2-Dichloroethane-d4 (Surr)	17060-07-0			40				64	144
				4-Bromofluorobenzene (Surr)	460-00-4			40				58	142
				Toluene-d8 (Surr)	2037-26-5			40				61	137
				Dibromofluoromethane (Surr)	1868-53-7			40				31	155
Soils	Volatile Organic Compounds (GC/MS)	8260B	5035A_FW	Acetone	67-64-1	24	125	40	15	127	40		
				Benzene	71-43-2	77	120	40	33	127	40		
				Dichlorobromomethane	75-27-4	61	132	40	22	127	40		
				Bromoform	75-25-2	40	140	40	10	120	40		
				Bromomethane	74-83-9	10	153	40	13	138	40		
				2-Butanone (MEK)	78-93-3	51	120	40	29	127	40		
				Carbon disulfide	75-15-0	17	163	40	15	131	40		
				Carbon tetrachloride	56-23-5	43	144	40	17	127	40		
				Chlorobenzene	108-90-7	76	120	40	15	122	40		
				Chloroethane	75-00-3	10	166	40	15	148	40		
				Chloroform	67-66-3	74	120	40	41	121	40		
				Chloromethane	74-87-3	41	124	40	33	122	40		
				1,1-Dichloroethane	75-34-3	72	120	40	41	122	40		
				1,2-Dichloroethane	107-06-2	71	120	40	35	122	40		
				1,1-Dichloroethene	75-35-4	58	130	40	30	139	40		
				1,2-Dichloropropane	78-87-5	78	122	40	38	130	40		
				cis-1,3-Dichloropropene	10061-01-5	66	126	40	13	127	40		
				trans-1,3-Dichloropropene	10061-02-6	55	121	40	11	120	40		
				Ethylbenzene	100-41-4	76	120	40	18	126	40		
				2-Hexanone	591-78-6	52	129	40	21	136	40		
				Methylene Chloride	75-09-2	64	126	40	34	134	40		

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Analysis Group	Method Description	Method Code	Prep Metho	Analyte Description	CAS Number	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
				4-Methyl-2-pentanone (MIBK)	108-10-1	65	131	40	16	164	40		
				Styrene	100-42-5	80	120	40	10	128	40		
				1,1,2,2-Tetrachloroethane	79-34-5	78	120	40	16	157	40		
				Tetrachloroethene	127-18-4	68	122	40	17	126	40		
				Toluene	108-88-3	74	120	40	29	127	40		
				Trichloroethene	79-01-6	73	123	40	10	160	40		
				Vinyl chloride	75-01-4	49	131	40	31	134	40		
				Xylenes, Total	1330-20-7	78	120	40	10	137	40		
				1,1,1-Trichloroethane	71-55-6	60	136	40	33	130	40		
				1,1,2-Trichloroethane	79-00-5	80	120	40	19	137	40		
				Cyclohexane	110-82-7	66	129	40	22	135	40		
				1,2-Dibromo-3-Chloropropane	96-12-8	40	133	40	10	128	40		
				Ethylene Dibromide	106-93-4	80	120	40	25	137	40		
				Dichlorodifluoromethane	75-71-8	15	127	40	10	126	40		
				cis-1,2-Dichloroethene	156-59-2	78	120	40	46	120	40		
				trans-1,2-Dichloroethene	156-60-5	74	124	40	32	134	40		
				Isopropylbenzene	98-82-8	76	124	40	10	128	40		
				Methyl acetate	79-20-9	63	126	40	14	151	40		
				Methyl tert-butyl ether	1634-04-4	68	129	40	49	134	40		
				1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	64	125	40	26	130	40		
				1,2,4-Trichlorobenzene	120-82-1	60	124	40	10	120	40		
				1,2-Dichlorobenzene	95-50-1	75	120	40	10	120	40		
				1,3-Dichlorobenzene	541-73-1	72	120	40	10	120	40		
				1,4-Dichlorobenzene	106-46-7	71	120	40	10	120	40		
				Trichlorofluoromethane	75-69-4	28	152	40	24	137	40		
				Chlorodibromomethane	124-48-1	46	125	40	19	120	40		
				Methylcyclohexane	108-87-2	71	126	40	13	134	40		
				m-Xylene & p-Xylene	179601-23-1	78	120	40	10	136	40		
				o-Xylene	95-47-6	77	120	40	17	128	40		
				1,2-Dichloroethane-d4 (Surr)	17060-07-0			40				61	127
				4-Bromofluorobenzene (Surr)	460-00-4			40				61	132
				Toluene-d8 (Surr)	2037-26-5			40				66	125
				Dibromofluoromethane (Surr)	1868-53-7			40				43	131
Waters TCL TAL	Semivolatile Organic Compounds (GC/M	8270C	3510C_Acid	1,1'-Biphenyl	92-52-4	53	120	35	45	120	26		
				bis (2-chloroisopropyl) ether	108-60-1	45	120	35	44	120	34		
				2,4,5-Trichlorophenol	95-95-4	54	120	35	20	120	33		
				2,4,6-Trichlorophenol	88-06-2	54	120	35	40	120	29		
				2,4-Dichlorophenol	120-83-2	55	120	35	19	121	34		
				2,4-Dimethylphenol	105-67-9	52	120	35	16	120	35		
				2,4-Dinitrophenol	51-28-5	12	120	35	10	120	35		
				2,4-Dinitrotoluene	121-14-2	60	120	35	49	120	26		
				2,6-Dinitrotoluene	606-20-2	60	120	35	48	120	25		
				2-Chloronaphthalene	91-58-7	53	120	35	42	120	28		
				2-Chlorophenol	95-57-8	53	120	35	29	120	35		
				2-Methylnaphthalene	91-57-6	54	120	35	43	120	30		
				2-Methylphenol	95-48-7	46	120	35	18	120	35		
				2-Nitroaniline	88-74-4	51	120	35	35	120	28		
				2-Nitrophenol	88-75-5	54	120	35	43	120	35		
				3,3'-Dichlorobenzidine	91-94-1	57	120	35	10	120	35		
				3-Nitroaniline	99-09-2	53	120	35	10	120	35		
				4,6-Dinitro-2-methylphenol	534-52-1	36	120	35	10	120	35		
				4-Bromophenyl phenyl ether	101-55-3	54	120	35	41	120	27		
				4-Chloro-3-methylphenol	59-50-7	54	120	35	32	120	32		
				4-Chloroaniline	106-47-8	10	120	35	10	120	35		
				4-Chlorophenyl phenyl ether	7005-72-3	56	120	35	43	120	27		
				4-Nitroaniline	100-01-6	55	120	35	10	120	35		
				4-Nitrophenol	100-02-7	10	120	35	10	120	35		
				Acenaphthene	83-32-9	54	120	35	35	120	35		
				Acenaphthylene	208-96-8	53	120	35	36	120	35		
				Acetophenone	98-86-2	56	120	35	42	120	31		
				Anthracene	120-12-7	56	120	35	35	120	35		
				Atrazine	1912-24-9	61	127	35	47	121	25		
				Benzaldehyde	100-52-7	47	134	35	46	120	35		
				Benzo[a]anthracene	56-55-3	54	120	35	16	120	35		
				Benzo[a]pyrene	50-32-8	54	120	35	10	120	35		
				Benzo[b]fluoranthene	205-99-2	53	120	35	10	120	35		
				Benzo[g,h,i]perylene	191-24-2	55	120	35	10	120	35		
				Benzo[k]fluoranthene	207-08-9	55	120	35	10	120	35		
				Bis(2-chloroethoxy)methane	111-91-1	56	120	35	44	120	32		
				Bis(2-chloroethyl)ether	111-44-4	51	120	35	42	120	35		
				Bis(2-ethylhexyl) phthalate	117-81-7	50	120	35	15	120	35		
				Butyl benzyl phthalate	85-68-7	51	120	35	39	120	30		
				Caprolactam	105-60-2	10	120	35	10	120	33		

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Analysis Group	Method Description	Method Code	Prep Metho	Analyte Description	CAS Number	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
				Carbazole	86-74-8	62	120	35	55	120	24		
				Chrysene	218-01-9	56	120	35	14	120	35		
				Dibenz(a,h)anthracene	53-70-3	52	120	35	10	120	35		
				Dibenzofuran	132-64-9	55	120	35	46	120	25		
				Diethyl phthalate	84-66-2	42	132	35	49	120	24		
				Dimethyl phthalate	131-11-3	56	120	35	47	120	24		
				Di-n-butyl phthalate	84-74-2	61	120	35	42	120	27		
				Di-n-octyl phthalate	117-84-0	58	120	35	13	120	35		
				Fluoranthene	206-44-0	58	120	35	28	120	35		
				Fluorene	86-73-7	56	120	35	36	120	35		
				Hexachlorobenzene	118-74-1	51	120	35	31	120	26		
				Hexachlorobutadiene	87-68-3	44	120	35	30	120	35		
				Hexachlorocyclopentadiene	77-47-4	19	120	35	10	120	35		
				Hexachloroethane	67-72-1	44	120	35	12	120	35		
				Indeno[1,2,3-cd]pyrene	193-39-5	54	120	35	10	120	35		
				Isophorone	78-59-1	55	120	35	45	120	33		
				Naphthalene	91-20-3	53	120	35	32	120	35		
				Nitrobenzene	98-95-3	55	120	35	48	120	35		
				N-Nitrosodi-n-propylamine	621-64-7	53	120	35	45	120	33		
				N-Nitrosodiphenylamine	86-30-6	55	120	35	39	120	35		
				Pentachlorophenol	87-86-5	30	120	35	20	120	24		
				Phenol	108-95-2	10	120	35	10	120	35		
				Phenanthrene	85-01-8	55	120	35	36	120	35		
				Pyrene	129-00-0	57	120	35	28	120	35		
				3 & 4 Methylphenol	15831-10-4	40	120	35	15	120	35		
				2-Fluorobiphenyl (Surr)	321-60-8			35				38	120
				2-Fluorophenol (Surr)	367-12-4			35				10	120
				2,4,6-Tribromophenol (Surr)	118-79-6			35				28	120
				Nitrobenzene-d5 (Surr)	4165-60-0			35				32	120
				Phenol-d5 (Surr)	4165-62-2			35				10	120
				Terphenyl-d14 (Surr)	1718-51-0			35				23	127
Waters TCL TAL	Metals (ICP)	6010B	3005A	Aluminum	7429-90-5	80	120	20	75	125	20		
				Antimony	7440-36-0	80	120	20	75	125	20		
				Barium	7440-39-3	80	120	20	75	125	20		
				Beryllium	7440-41-7	80	120	20	75	125	20		
				Calcium	7440-70-2	80	120	20	75	125	20		
				Cadmium	7440-43-9	80	120	20	75	125	20		
				Cobalt	7440-48-4	80	120	20	75	125	20		
				Chromium	7440-47-3	80	120	20	75	125	20		
				Copper	7440-50-8	80	120	20	75	125	20		
				Iron	7439-89-6	80	120	20	75	125	20		
				Potassium	7440-09-7	80	120	20	75	125	20		
				Magnesium	7439-95-4	80	120	20	75	125	20		
				Manganese	7439-96-5	80	120	20	75	125	20		
				Silver	7440-22-4	80	120	20	75	125	20		
				Sodium	7440-23-5	80	120	20	75	125	20		
				Nickel	7440-02-0	80	120	20	75	125	20		
				Vanadium	7440-62-2	80	120	20	75	125	20		
				Zinc	7440-66-6	80	120	20	75	125	20		
				Arsenic	7440-38-2	80	120	20	75	125	20		
				Lead	7439-92-1	80	120	20	75	125	20		
				Selenium	7782-49-2	80	120	20	75	125	20		
				Thallium	7440-28-0	80	120	20	75	125	20		
Waters TCL TAL	Mercury (CVAA)	7470A	7470A_Prep	Mercury	7439-97-6	80	120	20	80	120	20		
Waters TCL TAL	Volatile Organic Compounds (GC/MS)	8260B	5030B	Acetone	67-64-1	35	131	35	19	133	35		
				Benzene	71-43-2	79	120	35	69	127	10		
				Dichlorobromomethane	75-27-4	79	125	35	75	128	13		
				Bromoform	75-25-2	55	145	35	61	135	13		
				Bromomethane	74-83-9	17	158	35	10	148	35		
				2-Butanone (MEK)	78-93-3	43	149	35	34	153	23		
				Carbon disulfide	75-15-0	49	141	35	46	143	18		
				Carbon tetrachloride	56-23-5	55	171	35	53	175	17		
				Chlorobenzene	108-90-7	80	120	35	76	120	12		
				Chloroethane	75-00-3	10	149	35	10	141	35		
				Chloroform	67-66-3	80	120	35	74	125	11		
				Chloromethane	74-87-3	59	124	35	34	127	25		
				1,1-Dichloroethane	75-34-3	74	120	35	69	122	11		
				1,2-Dichloroethane	107-06-2	68	133	35	64	138	11		
				1,1-Dichloroethene	75-35-4	65	127	35	62	127	14		
				1,2-Dichloropropane	78-87-5	78	127	35	72	131	12		
				cis-1,3-Dichloropropene	10061-01-5	75	120	35	68	120	13		

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Analysis Group	Method Description	Method Code	Prep Metho	Analyte Description	CAS Number	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
				trans-1,3-Dichloropropene	10061-02-6	67	120	35	59	120	14		
				Ethylbenzene	100-41-4	80	120	35	72	121	15		
				2-Hexanone	591-78-6	28	169	35	21	184	12		
				Methylene Chloride	75-09-2	64	140	35	52	137	12		
				4-Methyl-2-pentanone (MIBK)	108-10-1	53	144	35	53	147	16		
				Styrene	100-42-5	80	121	35	74	125	14		
				1,1,2,2-Tetrachloroethane	79-34-5	58	122	35	51	123	17		
				Tetrachloroethene	127-18-4	80	122	35	69	126	18		
				Toluene	108-88-3	78	120	35	69	125	14		
				Trichloroethene	79-01-6	76	124	35	68	129	12		
				Vinyl chloride	75-01-4	65	124	35	55	123	12		
				Xylenes, Total	1330-20-7	80	120	35	71	122	14		
				1,1,1-Trichloroethane	71-55-6	64	147	35	57	156	13		
				1,1,2-Trichloroethane	79-00-5	76	121	35	68	127	11		
				Cyclohexane	110-82-7	66	135	35	56	135	35		
				1,2-Dibromo-3-Chloropropane	96-12-8	50	130	35	48	130	31		
				Ethylene Dibromide	106-93-4	80	120	35	73	121	12		
				Dichlorodifluoromethane	75-71-8	42	141	35	45	130	34		
				cis-1,2-Dichloroethene	156-59-2	77	120	35	69	127	11		
				trans-1,2-Dichloroethene	156-60-5	74	124	35	66	131	11		
				Isopropylbenzene	98-82-8	80	128	35	70	132	16		
				Methyl acetate	79-20-9	63	137	35	52	139	14		
				Methyl tert-butyl ether	1634-04-4	73	120	35	67	125	12		
				1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	65	144	35	58	137	35		
				1,2,4-Trichlorobenzene	120-82-1	34	141	35	26	138	35		
				1,2-Dichlorobenzene	95-50-1	80	120	35	70	120	19		
				1,3-Dichlorobenzene	541-73-1	80	120	35	71	120	18		
				1,4-Dichlorobenzene	106-46-7	80	120	35	72	120	17		
				Trichlorofluoromethane	75-69-4	27	176	35	28	172	26		
				Chlorodibromomethane	124-48-1	64	129	35	62	131	15		
				Methylcyclohexane	108-87-2	63	141	35	46	139	35		
				m-Xylene & p-Xylene	179601-23-1	80	120	35	70	121	15		
				o-Xylene	95-47-6	80	120	35	71	125	15		
				1,2-Dichloroethane-d4 (Surr)	17060-07-0			35				61	138
				4-Bromofluorobenzene (Surr)	460-00-4			35				69	120
				Toluene-d8 (Surr)	2037-26-5			35				73	120
				Dibromofluoromethane (Surr)	1868-53-7			35				69	124
Waters TCL TAL	Polychlorinated Biphenyls (PCBs) by Gas	8082A	3520C	Aroclor-1016	12674-11-2	28	120	30	14	120	30		
				Aroclor-1221	11104-28-2								
				Aroclor-1232	11141-16-5								
				Aroclor-1242	53469-21-9								
				Aroclor-1248	12672-29-6								
				Aroclor-1254	11097-69-1								
				Aroclor-1260	11096-82-5	30	120	30	10	120	30		
				Aroclor-1262	37324-23-5								
				Aroclor-1268	11100-14-4								
				Tetrachloro-m-xylene	877-09-8							22	120
				DCB Decachlorobiphenyl	2051-24-3							10	120

Analytical Method Details - Pace Analytical Services, LLC

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD	CAS #
Polychlorinated Biphenyls (PCBs) by EPA Method 608 in Waste Water								
USEPA-608	PCB-1016	-	20	55-117	20	50-114	20	12674-11-2
USEPA-608	PCB-1221	-	20	70-130	20	15-178	20	11104-28-2
USEPA-608	PCB-1232	-	20	49-133	20	10-215	20	11141-16-5
USEPA-608	PCB-1242	-	20	67-101	20	39-150	20	53469-21-9
USEPA-608	PCB-1248	-	20	65-123	20	38-158	20	12672-29-6
USEPA-608	PCB-1254	-	20	54-118	20	29-131	20	11097-69-1
USEPA-608	PCB-1260	-	20	46-132	20	8-127	20	11096-82-5
USEPA-608	Total PCBs	-	20	70-130	20	70-130	20	1336-36-3
USEPA-608	Decachlorobi	30-138	-	-	-	-	-	2051-24-3
USEPA-608	Tetrachloro-m	29-117	-	-	-	-	-	877-09-8
Polychlorinated Biphenyls (PCBs) by EPA Method 8082A in Soil								
USEPA-8082	PCB-1016	-	-	49-128	30	68-129	30	12674-11-2
USEPA-8082	PCB-1221	-	-	54-157	30	58-147	30	11104-28-2
USEPA-8082	PCB-1232	-	-	51-149	30	71-130	30	11141-16-5
USEPA-8082	PCB-1242	-	-	50-139	30	73-118	30	53469-21-9
USEPA-8082	PCB-1248	-	-	42-168	30	55-139	30	12672-29-6
USEPA-8082	PCB-1254	-	-	47-148	30	71-133	30	11097-69-1
USEPA-8082	PCB-1260	-	-	48-138	30	60-140	30	11096-82-5
USEPA-8082	Total PCBs	-	-	-	-	-	-	1336-36-3
USEPA-8082	Decachlorobi	45-135	-	-	-	-	-	2051-24-3
USEPA-8082	Tetrachloro-m	56-123	-	-	-	-	-	877-09-8
Polychlorinated Biphenyls (PCBs) by EPA Method 8082A in Water								
USEPA-8082	PCB-1016	-	-	56-120	30	58-120	30	12674-11-2
USEPA-8082	PCB-1221	-	-	70-130	30	66-117	30	11104-28-2
USEPA-8082	PCB-1232	-	-	75-122	30	63-139	30	11141-16-5
USEPA-8082	PCB-1242	-	-	41-134	30	62-124	30	53469-21-9
USEPA-8082	PCB-1248	-	-	46-155	30	44-146	30	12672-29-6
USEPA-8082	PCB-1254	-	-	60-117	30	76-121	30	11097-69-1
USEPA-8082	PCB-1260	-	-	61-136	30	62-131	30	11096-82-5
USEPA-8082	Total PCBs	-	-	-	-	-	-	1336-36-3
USEPA-8082	Decachlorobi	52-139	-	-	-	-	-	2051-24-3
USEPA-8082	Tetrachloro-m	26-118	-	-	-	-	-	877-09-8

MERIT TYPICAL REPORTING LIMITS, METHOD REPORTING DETECTION LIMITS (RDLs)
Precision and Accuracy

MERIT LABS Compound	EPA Method	SW-846 Method	Accuracy LCL %	Accuracy UCL %	Precision RPD %	Lowest Criteria	Accuracy LCL %	Accuracy UCL %	Precision RPD %
Volatiles	**624.1**	**8260C**							
Acetone	624.1	8260C	30%	162%	30	15,000	25%	155%	30
Benzene	624.1	8260C	80%	125%	30	100	75%	129%	30
Bromochloromethane	624.1	8260C	78%	121%	30		72%	123%	30
Bromodichloromethane	624.1	8260C	80%	128%	30	2,000	77%	128%	30
Bromoform	624.1	8260C	69%	128%	30	2,000	55%	137%	30
Bromomethane	624.1	8260C	57%	151%	30	200	10%	157%	30
2-Butanone	624.1	8260C	44%	134%	30	44,000	39%	137%	30
Carbon Disulfide	624.1	8260C	64%	137%	30	16,000	57%	123%	30
Carbon Tetrachloride	624.1	8260C	73%	133%	30	100	73%	136%	30
Chlorobenzene	624.1	8260C	79%	123%	30	940	74%	128%	30
Chloroethane	624.1	8260C	53%	149%	30	8,600	10%	169%	30
Chloroform	624.1	8260C	78%	124%	30	2,000	75%	123%	30
Chloromethane	624.1	8260C	24%	167%	30	5,200	30%	153%	30
Cyclohexane	624.1	8260C	10%	169%	30	NA	42%	147%	30
Dibromochloromethane	624.1	8260C	75%	127%	30	2,000	69%	133%	30
1,2-Dibromo-3-chloropropane	624.1	8260C	21%	189%	30	4	54%	156%	30
1,2-Dibromoethane	624.1	8260C	70%	134%	30	10	71%	129%	30
Dichlordifluoromethane	624.1	8260C	10%	223%	30	95,000	10%	172%	30
1,2-Dichlorobenzene	624.1	8260C	10%	166%	30	360	74%	133%	30
1,3-Dichlorobenzene	624.1	8260C	77%	131%	30	170	77%	131%	30
1,4-Dichlorobenzene	624.1	8260C	21%	138%	30	290	33%	126%	30
1,1-Dichloroethane	624.1	8260C	72%	126%	30	18,000	73%	123%	30
1,2-Dichloroethane	624.1	8260C	76%	126%	30	100	73%	125%	30
1,1-Dichloroethene	624.1	8260C	70%	139%	30	140	59%	138%	30
cis-1,2-Dichloroethene	624.1	8260C	77%	122%	30	1,400	75%	121%	30
trans-1,2-Dichloroethene	624.1	8260C	74%	129%	30	2,000	73%	129%	30
1,2-Dichloropropane	624.1	8260C	79%	126%	30	100	78%	124%	30
cis-1,3-Dichloropropene	624.1	8260C	80%	130%	30	420	79%	128%	30
trans-1,3-Dichloropropene	624.1	8260C	74%	131%	30	420	75%	130%	30
1,4-Dioxane (SIMS)	624.1	8260C	70%	130%	30		70%	130%	30
Ethylbenzene	624.1	8260C	80%	129%	30	360	78%	130%	30
2-Hexanone	624.1	8260C	55%	137%	30	20,000	46%	142%	30
Isopropylbenzene	624.1	8260C	74%	122%	30	91,000	70%	128%	30
Methyl Acetate	624.1	8260C	65%	125%	30	NA	54%	134%	30
Methyl Cyclohexane	624.1	8260C	77%	131%	30	NA	54%	148%	30
4-Methyl-2-pentanone	624.1	8260C	72%	125%	30	36,000	60%	134%	30
Methyl tert-butyl ether	624.1	8260C	73%	122%	30	800	68%	124%	30
Methylene Chloride	624.1	8260C	73%	121%	30	100	71%	122%	30
Styrene	624.1	8260C	70%	127%	30	2,200	71%	119%	30
1,1,2,2-Tetrachloroethane	624.1	8260C	80%	126%	30	170	65%	135%	30
Tetrachloroethene	624.1	8260C	75%	125%	30	100	73%	125%	30
Toluene	624.1	8260C	60%	125%	30	2,800	75%	129%	30
1,1,1-Trichloroethane	624.1	8260C	79%	131%	30	4,000	74%	129%	30
1,1,2-Trichloroethane	624.1	8260C	79%	123%	30	100	71%	126%	30
Trichloroethene	624.1	8260C	80%	124%	30	100	74%	128%	30
1,2,3-Trichlorobenzene	624.1	8260C	75%	131%	30		59%	158%	30
1,2,4-Trichlorobenzene	624.1	8260C	27%	143%	30	1,800	37%	131%	30
Trichlorofluoromethane	624.1	8260C	60%	152%	30	52,000	26%	138%	30
Trifluorotrichloroethane	624.1	8260C	75%	136%	30	550,000	57%	138%	30
Vinyl Chloride	624.1	8260C	44%	149%	30	40	45%	139%	30
m&p-Xylene	624.1	8260C	79%	132%	30		80%	132%	30
o-Xylene	624.1	8260C	80%	131%	30		79%	132%	30

MERIT TYPICAL REPORTING LIMITS, METHOD REPORTING DETECTION LIMITS (RDLs)
Precision and Accuracy

MERIT LABS			Accuracy		Precision	Lowest	Accuracy		Precision
Compound	EPA Method	SW-846 Method	LCL %	UCL %	RPD %	Criteria	LCL %	UCL %	RPD %
Semivolatiles	**625.1**	**8270D**							
Acenaphthene	625.1	8270D	35%	125%	30	4,400	48%	125%	30
Acenaphthylene	625.1	8270D	17%	141%	30	5,900	10%	162%	30
Acetophenone	625.1	8270D	48%	106%	30	30,000	64%	113%	30
Anthracene	625.1	8270D	38%	116%	30	41,000	35%	127%	30
Atrazine	625.1	8270D	53%	143%	30	NA	62%	153%	30
1,1-Biphenyl	625.1	8270D	50%	111%	30	NA	60%	132%	30
Benzaldehyde	625.1	8270D	36%	137%	30	NA	33%	154%	30
Benzo(a)anthracene	625.1	8270D	41%	116%	30	20,000	49%	112%	30
Benzo(a)pyrene	625.1	8270D	51%	133%	30	2,000	58%	133%	30
Benzo(b)fluoranthene	625.1	8270D	43%	119%	30	20,000	39%	132%	30
Benzo(g,h,i)perylene	625.1	8270D	37%	122%	30	2,500,000	39%	136%	30
Benzo(k)fluoranthene	625.1	8270D	41%	117%	30	200,000	35%	131%	30
bis(2-Chloroethoxy)methane	625.1	8270D	48%	105%	30	NA	66%	113%	30
bis(2-Chloroethyl)ether	625.1	8270D	43%	102%	30	330	62%	107%	30
bis(2-Chloroisopropyl)ether	625.1	8270D	33%	106%	30		62%	115%	30
bis(2-Ethylhexyl)phthalate	625.1	8270D	45%	126%	30	2,800,000	72%	120%	30
4-Bromophenyl-phenylether	625.1	8270D	45%	117%	30	NA	51%	141%	30
Butylbenzylphthalate	625.1	8270D	47%	122%	30	26,000	66%	120%	30
Caprolactam	625.1	8270D	10%	113%	30	120,000	51%	121%	30
Carbazole	625.1	8270D	44%	129%	30	1,100	31%	164%	30
4-Chloro-3-Methylphenol	625.1	8270D	39%	123%	30	5,800	53%	122%	30
4-Chloroaniline	625.1	8270D	33%	89%	30	NA	21%	87%	30
2-Chloronaphthalene	625.1	8270D	50%	108%	30	NA	59%	125%	30
2-Chlorophenol	625.1	8270D	36%	114%	30	440	49%	113%	30
4-Chlorophenyl-phenylether	625.1	8270D	52%	117%	30	NA	59%	133%	30
Chrysene	625.1	8270D	29%	137%	30	2,000,000	28%	150%	30
2-Methylphenol	625.1	8270D	39%	109%	30	1,400	37%	120%	30
3-, 4-Methylphenol	625.1	8270D	36%	115%	30	1,400	35%	128%	30
Di-n-Butylphthalate	625.1	8270D	48%	122%	30	11,000	64%	140%	30
Di-n-Octylphthalate	625.1	8270D	46%	123%	30	6,900,000	71%	127%	30
Dibenzo(a,h)anthracene	625.1	8270D	34%	132%	30	2,000	45%	132%	30
Dibenzofuran	625.1	8270D	52%	112%	30	1,700	62%	131%	30
3,3'-Dichlorobenzidine	625.1	8270D	37%	97%	30	2,000	39%	88%	30
2,4-Dichlorophenol	625.1	8270D	58%	116%	30	380	66%	120%	30
Diethylphthalate	625.1	8270D	48%	118%	30	110,000	64%	132%	30
Dimethylphthalate	625.1	8270D	49%	118%	30	NA	62%	131%	30
2,4-Dimethylphenol	625.1	8270D	43%	115%	30	7,400	67%	115%	30
4,6-Dinitro-2-methylphenol	625.1	8270D	19%	149%	30	1,700	37%	135%	30
2,4-Dinitrophenol	625.1	8270D	10%	171%	30	NA	10%	130%	30
2,4-Dinitrotoluene	625.1	8270D	36%	127%	30	430	42%	126%	30
2,6-Dinitrotoluene	625.1	8270D	48%	119%	30	NA	58%	137%	30
Fluoranthene	625.1	8270D	43%	128%	30	5,500	52%	134%	30
Fluorene	625.1	8270D	37%	110%	30	5,300	38%	125%	30
Hexachlorobenzene	625.1	8270D	45%	119%	30	1,800	48%	135%	30
Hexachlorobutadiene	625.1	8270D	30%	119%	30	330	60%	106%	30
Hexachlorocyclopentadiene	625.1	8270D	10%	272%	30	320,000	18%	285%	30
Hexachloroethane	625.1	8270D	24%	138%	30	430	56%	129%	30
Indeno(1,2,3-cd)pyrene	625.1	8270D	42%	117%	30	20,000	45%	132%	30
Isophorone	625.1	8270D	45%	108%	30	11,000	61%	126%	30
2-Methylnaphthalene	625.1	8270D	26%	166%	30	57,000	10%	176%	30
Naphthalene	625.1	8270D	33%	136%	30	870	39%	129%	30
2-Nitroaniline	625.1	8270D	53%	120%	30	NA	61%	138%	30
3-Nitroaniline	625.1	8270D	42%	109%	30	NA	44%	115%	30
4-Nitroaniline	625.1	8270D	46%	120%	30	NA	42%	120%	30
Nitrobenzene	625.1	8270D	42%	110%	30	330	65%	110%	30
2-Nitrophenol	625.1	8270D	54%	110%	30	400	64%	115%	30
4-Nitrophenol	625.1	8270D	15%	122%	30	NA	34%	122%	30
N-Nitroso-di-n-propylamine	625.1	8270D	36%	109%	30	330	47%	113%	30
N-Nitrosodiphenylamine	625.1	8270D	10%	104%	30	5,400	10%	115%	30
Pentachlorophenol	625.1	8270D	10%	139%	30	22	22%	124%	30
Phenanthrene	625.1	8270D	32%	123%	30	2,300	29%	133%	30
Phenol	625.1	8270D	10%	130%	30	4,200	46%	117%	30
Pyrene	625.1	8270D	38%	131%	30	480,000	49%	134%	30
2,4,5-Trichlorophenol	625.1	8270D	49%	119%	30	39,000	54%	137%	30
2,4,6-Trichlorophenol	625.1	8270D	48%	117%	30	330	55%	133%	30
1,2,4,5-Tetrachlorobenzene	625.1	8270D	70%	130%	30		70%	130%	30
2,3,4,6-Tetrachlorophenol	625.1	8270D	70%	130%	30	330	70%	130%	30

MERIT TYPICAL REPORTING LIMITS, METHOD REPORTING DETECTION LIMITS (RDLs)
Precision and Accuracy

MERIT LABS Compound	EPA Method	SW-846 Method	Accuracy LCL %	Accuracy UCL %	Precision RPD %	Lowest Criteria	Accuracy LCL %	Accuracy UCL %	Precision RPD %
PCBs (Aroclor-Specific)	**608.3**	**8082A**							
Aroclor-1016	608.3	8082A	50%	125%	20	20,000	50%	125%	20
Aroclor-1221	608.3	8082A	50%	125%	20		50%	125%	20
Aroclor-1232	608.3	8082A	50%	125%	20		50%	125%	20
Aroclor-1242	608.3	8082A	50%	125%	20	20,000	50%	125%	20
Aroclor-1248	608.3	8082A	50%	125%	20	20,000	50%	125%	20
Aroclor-1254	608.3	8082A	50%	125%	20	20,000	50%	125%	20
Aroclor-1260	608.3	8082A	50%	125%	20	20,000	50%	125%	20
Total PCBs	608.3	8082A	50%	125%	20		50%	125%	20
Metals	**200.8**	**6020A**							
Aluminum	200.8	6020A	85%	115%	20		85%	115%	20
Antimony	200.8	6020A	85%	115%	20		85%	115%	20
Arsenic	200.8	6020A	85%	115%	20	7,600	85%	115%	20
Barium	200.8	6020A	85%	115%	20	1,300,000	85%	115%	20
Beryllium	200.8	6020A	85%	115%	20		85%	115%	20
Cadmium	200.8	6020A	85%	115%	20	6,000	85%	115%	20
Calcium	200.8	6020A	85%	115%	20		85%	115%	20
Chromium	200.8	6020A	85%	115%	20	3,300	85%	115%	20
Cobalt	200.8	6020A	85%	115%	20		85%	115%	20
Copper	200.8	6020A	85%	115%	20		85%	115%	20
Cyanide (total)	335.4	N/A	90%	110%	20		90%	110%	15
Iron	200.8	6020A	85%	115%	20		85%	115%	20
Lead-Total	200.8	6020A	85%	115%	20		85%	115%	20
Magnesium	200.8	6020A	85%	115%	20		85%	115%	20
Manganese	200.8	6020A	85%	115%	20		85%	115%	20
Mercury	245.1	7471B	85%	115%	20	100	85%	115%	20
Nickel	200.8	6020A	85%	115%	20		85%	115%	20
Potassium	200.8	6020A	85%	115%	20		85%	115%	20
Selenium	200.8	6020A	85%	115%	20	400	85%	115%	20
Silver	200.8	6020A	85%	115%	20	500	85%	115%	20
Sodium	200.8	6020A	85%	115%	20		85%	115%	20
Thallium	200.8	6020A	85%	115%	20		85%	115%	20
Vanadium	200.8	6020A	85%	115%	20	500	85%	115%	20
Zinc	200.8	6020A	85%	115%	20		85%	115%	20
Conventional									
Total Suspended Solids (TSS)		SM2540D	90%	110%	5		NA	NA	NA
Chloride	300.0/325.3		90%	110%	15		NA	NA	NA
Conductivity	120.1		90%	110%	15		NA	NA	NA
Oil & Grease (HEM)	1664A		78%	114%	NA		NA	NA	NA
Sulfide		SM4500-S2 D	90%	110%	15		90%	110%	15
TCLP									
Benzene		8260C	80%	125%	30	100	NA	NA	NA
Carbon Tetrachloride		8260C	73%	133%	30	100	NA	NA	NA
Chlorobenzene		8260C	79%	123%	30	940	NA	NA	NA
Chloroform		8260C	78%	124%	30	2,000	NA	NA	NA
1,4-Dichlorobenzene		8260C	21%	138%	30	290	NA	NA	NA
1,1-Dichloroethene		8260C	70%	139%	30	140	NA	NA	NA
1,2-Dichloroethane		8260C	76%	126%	30	100	NA	NA	NA
2-Butanone		8260C	44%	134%	30	44,000	NA	NA	NA
Tetrachloroethene		8260C	75%	125%	30	100	NA	NA	NA
Trichloroethene		8260C	80%	124%	30	100	NA	NA	NA
Vinyl Chloride		8260C	44%	149%	30	40	NA	NA	NA
2-Methylphenol		8270D	39%	109%	30	1,400	NA	NA	NA
3-, 4-Methylphenol		8270D	36%	115%	30	1,400	NA	NA	NA
2,4-Dinitrotoluene		8270D	36%	127%	30	430	NA	NA	NA
Hexachlorobenzene		8270D	45%	119%	30	1,800	NA	NA	NA
Hexachlorobutadiene		8270D	30%	119%	30	330	NA	NA	NA
Hexachloroethane		8270D	24%	138%	30	430	NA	NA	NA
Nitrobenzene		8270D	42%	110%	30	330	NA	NA	NA
Pentachlorophenol		8270D	10%	139%	30	22	NA	NA	NA
Pyridine		8270D	10%	120%	30	480,000	NA	NA	NA
2,4,5-Trichlorophenol		8270D	49%	119%	30	39,000	NA	NA	NA
2,4,6-Trichlorophenol		8270D	48%	117%	30	330	NA	NA	NA
Arsenic		6020A	85%	115%	20	7,600	NA	NA	NA
Barium		6020A	85%	115%	20	1,300,000	NA	NA	NA
Cadmium		6020A	85%	115%	20	6,000	NA	NA	NA
Chromium		6020A	85%	115%	20	3,300	NA	NA	NA
Lead		6020A	85%	115%	20		NA	NA	NA
Mercury		7471B	85%	115%	20	100	NA	NA	NA
Selenium		6020A	85%	115%	20	400	NA	NA	NA
Silver		6020A	85%	115%	20	500	NA	NA	NA

Appendix D
Field Analytical Standard Operating Procedures

Appendix D

Table of Contents

Field SOPs

Title	SOP Number
Procedures for Measuring pH/T/Conductivity/DO/ORP	Field S.O.P. No. 1
Procedures for Measuring Turbidity	Field S.O.P. No. 2
Soil Headspace VOC Screening	Field S.O.P. No. 3

Field S.O.P. No. 1

Procedures for Calibration and Use of the YSI 556 MPS Flow Cell Meter

The YSI 556 MPS Flow Cell is used to measure pH, temperature, conductivity, DO, and ORP.

1. Calibration Procedure

The YSI meter will be calibrated daily

1) Check pH 7 buffer reading. Calibrate if greater than ± 0.2. PH is a two point calibration but always start with the seven standard.
2) Fill calibration cup with pH 7.0 buffer and attach to probe with probes facing down.
3) Press ESC to enter into main menu and use down arrow key to highlight calibration menu. Press ↵ to accept.
4) Use ↓key to highlight pH symbol and press enter ↵
5) Select 2 point calibration and use number pad to enter 7.0 and push ↵ to accept value. Push ↵ again to calibrate.
6) Repeat these steps to calibrate your pH value to 4.0 or 10.0
7) Press ESC to return to the calibration screen.
8) Check conductivity standard near the expected range. Calibrate if greater than ±0.5%. Conductivity is a one point calibration.
9) Fill calibration cup with 1.413 mS standard and attach to probe with probes facing up.
10) Press ESC to return to the calibration screen.
11) Use the ↑or ↓to select SpC and press ↵
12) Use the number key pad to enter 1.413 and push ↵ to accept value. Push ↵ again to calibrate.
13) Check ORP standard. Press ESC to return to the calibration screen.
14) Use the ↑or ↓to select ORP and press ↵
15) Use the number key pad to enter the value and push ↵ to accept. Push ↵ again to calibrate
16) To calibrate DO, see manual for instructions

2. Operation Procedure

1) Calibrate meter.
2) Rinse probe in distilled/deionized water
3) Place probe into flow meter assembly and secure.
4) Once attached begin purging and allow 5 to 10 minutes to pass before collecting first reading.

5) Log results in field notebook.

6) Rinse probe off with distilled/deionized water after each location.

7) If the electrodes become coated with foreign compounds, the probe should be cleaned with a detergent solution and then rinsed with distilled/deionized water.

3. Maintenance Procedure

1) Replace batteries on a regular basis.

2) Store electrode in wet, protective casing when not in use

3) Keep records of usage, maintenance, calibration, and of any problems and repair.

4) A replacement meter will be available on-site or ready for overnight shipment.

5) Meter will be sent back to manufacturer for service when needed.

4. Quality Control

1) The quality control standard must be analyzed daily. The standard must be within ±0.2 for pH, ±10% for conductivity, ±10% for ORP, and ±1 degree Celsius of the true value or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standards in the field logbook.

2) Duplicate a minimum of 1 out of 10 readings. If less than 10 samples are analyzed, a duplicate is still required. Duplicate values are to be within ±15% of each other. If outside this range, reanalyze the samples. If still outside the acceptance range, recollect sample and reanalyze. If still out, replace probe.

Field S.O.P. No. 2

Procedures for Calibration and Use of the Lamotte 2020 Meter

The Lamotte 2020 is used to measure turbidity

1. Calibration Procedure

The Lamotte meter will be calculated daily

1) Check outside of reference standard bottles for cleanliness and condensation then wipe with lint free cloth
2) Open lid and align arrows.
3) Insert the reference standard and index (10 or 1.0 NTU)
4) Press the read button. (If the value displayed is not the same as the standard, continue the calibration procedure).
5) Push the CAL button for 5 seconds until CAL is displayed.
6) Release the CAL button and the display will flash.
7) Press the up and/or down arrows until the value of the standard is displayed.
8) Push the CAL button again to store the calibration.
9) The instrument is now ready to use.
10) Turn the meter off by pressing the READ button for at least 1 second

2. Operation Procedure

1) Push the READ button. The instrument is now ready to read sample turbidity
2) Fill the vial with sample, wipe vial clean and insert into meter with both arrows aligning (on jar and meter), and close lid.
3) Reading should stabilize within 5 seconds.
4) Take reading and log results in field notebook.
5) Rinse out sample vial before next sample.

3. Maintenance Procedure

1) Replace battery when ER1 (very low battery) or BAT (low battery) message is displayed.
2) Send to manufacturer for replacement of lamp or other calibration difficulties.
3) Recalibrate meter after replacing battery.
4) Keep records of usage, maintenance, calibration, problems, and repairs.

4. Quality Control

1) Duplicate 1 out of 10 readings. If less than 10 readings are analyzed, a duplicate is still required. Duplicate must be ±5%

2) If the results are outside the control limits, wipe of sample vial, reinsert in meter and repeat measurement. If the results are still outside of the control limits, recollect sample and repeat measurement. If the results are still outside of the control limits, recalibrate and repeat measurements for all readings since last calibration.

3) Calibration check results must be ±5% of the true value. If the result is outside, refill sample vial, wipe clean, and check again. If still outside the control limit, recalibrate the meter and analyze all readings analyzed since the last in-control calibration.

Field S.O.P. No. 3

Soil Headspace VOC Screening

Scope and Application:	This method is applicable to screening VOCs in the headspace above a soil sample.
Method:	Photoionization
Sensitivity:	Approximately 0.5 ppm depending on background
Optimum Range:	Background to 2,000 ppm
Sample Handling:	Determined on site

1. Reagents and Apparatus

1. HNu Model PI 101 Photoionizer or Photovac MicroTIP Photoionization Detector;
2. Calibration gas - 100 ppmv isobutylene;
3. Calibration apparatus and tubing;
4. Battery rechargers;
5. Ultraviolet Light Source Lamps - 10.6 eV (Photovac), 11.7 or 10.2 eV (HNu).

2. Calibration

2.1 Calibration of the HNu

1. Connect the analyzer to the regulator and calibration gas cylinder with a short segment (butt connection) of tubing. The calibration gas consists of a mixture of isobutylene and zero air. Isobutylene is non-toxic and safe to use in confined areas. There are no listed exposure levels at any concentration.

   It is important that the tubing be clean since contaminated tubing will affect the calibration reading. A cylinder containing less than 30 psig pressure will not be used as readings below that level can deviate up to ten percent from the rated value.

   Turn the function switch to the STANDBY position. Turn the zero knob until the meter needle rests at 0.
2. With the SPAN setting and the function switch at the same positions as listed in the Application Data Sheet or Calibration Report, open the valve on the cylinder until a steady reading is obtained.
3. If the reading is the same as the recorded data, the analyzer calibration for the original species of interest is still correct.
4. If the reading has changed, adjust the SPAN setting until the reading is the same.
5. Shut off the cylinder as soon as the reading is established.
6. Record and maintain this new SPAN setting.
7. Background organic vapor readings should be measured prior to any soil screening.

2.2 Calibration of MicroTip

1. Connect the supplied regulator to the span gas cylinder. Hand tighten the fittings. Observe proper handling techniques for all gases.
2. Open the valve on the gas bag by turning the valve stem fully counterclockwise.
3. Attach the nut to the regulator. Hand tighten the fittings.
4. Turn the regulator knob counterclockwise about half a turn to start the flow of gas.
5. Fill the gas bag about half full and then close the regulator fully clockwise to turn off the flow of gas.
6. Disconnect the bag from the adapter and empty it. Flush the bag a few times with the span gas and then fill it.
7. Close the gas bag by turning the valve clockwise.
8. Press SETUP and select the desired Cal Memory with the arrow keys and press ENTER. Press EXIT to leave Setup.
9. Press CAL and enter the desired response factor. Use Table 2 from the manual to find the correct response factor. If the compound is not in Table 2 or you are not looking specifically for one compound then enter 1.00.

   The concentration detected by MicroTIP will be multiplied by the response factor before it is displayed and logged.
10. Expose MicroTIP to zero air. Press ENTER and MicroTIP sets its zero point.
11. MicroTIP then asks for the span gas concentration. Enter the known span gas concentration and then connect the span gas bag adapter to the inlet.
12. Press ENTER and MicroTIP sets its sensitivity.
13. When MicroTIP's display reverts to normal, MicroTIP is calibrated and ready for use. Remove the span gas bag from the inlet.

3. Procedure:

1. Calibrate meter using the correct calibration procedure for the meter used.
2. Insert probe into the headspace above the soil sample that has been placed in a sealed polyethylene bag (Ziploc or equivalent) or jar. The sample should be allowed to equilibrate for a minimum of 10 minutes at ambient temperature prior to taking PID reading.
3. Take the highest reading from the meter or readout of the instrument.
4. Record the reading in the field log book.
5. Recheck calibration with calibration gas after a minimum of every 10 samples and after the last sample.

4. Quality Control:

1. Calibration check results must be ±10% of the true value. If the result is outside of ±10%, recalibrate the meter as specified above.
2. Duplicate samples are not analyzed since the headspace VOC readings will vary considerably.

5. Interferences and Limitations:

Extremely humid conditions will cause a negative bias to the reading. The photoionization detection principle used by the instruments will not detect all VOCs. The instrument is most sensitive to aromatic, alkene and alkyne VOCs.

Appendix E
Field Audit Checklist

Appendix E Field Audit Checklist

Briefing with Project Manager

Signature of Auditor _____ Date of Audit _____

Project Manager _____ Project No. _____

Project Location _____

Type of Investigation (authority, agency) _____

Yes _____ No _____ N/A ____ 1. Was a project plan prepared? If yes, what items are addressed in the plan?

_____

_____

_____

Yes _____ No _____ N/A ____ 2. Were additional instructions given to project participants (i.e., changes in the project plan)? If yes, describe these changes.

_____

_____

_____

Yes _____ No _____ N/A ____ 3. Is there a written list of sampling locations and descriptions? If yes, describe where documents are.

_____

_____

_____

Yes _____ No _____ N/A ____ 4. Is there a map of sampling locations? If yes, where is the map?

_____

_____

_____

Field Observations

Yes _____ No _____ N/A ____ 1. Are the number, frequency, and types of field measurements and observations taken as specified in the project plan or as directed by the project manager? If yes, where are they recorded?

Yes _____ No _____ N/A ____ 2. Are samples collected in the types of containers specified for each type of analysis? If no, what kind of sample containers are used?

Yes _____ No _____ N/A ____ 3. Are samples preserved as required? If no or N/A, explain.

Yes _____ No _____ N/A ____ 4. Are the number, frequency, and types of samples collected as specified in the project plan or as directed by the project manager? If no, explain why not.

Yes _____ No _____ N/A ____ 5. Are samples packed for preservation when required (i.e., packed in ice, etc.)? If no or N/A, explain why.

Yes _____ No _____ N/A ____ 6. Is sample custody maintained? How?

Document Control

Yes _____ No _____ N/A ____ 1. Are samples identified with sample tags? If no, how are samples identified?

Yes _____ No _____ N/A ____ 2. Are sample tags completed (e.g., station no., location, date, time, analyses, signatures on samples, type, preservatives, etc.)? If yes, describe types of information recorded.

Yes _____ No _____ N/A ____ 3. Are samples collected listed on a chain of custody record? If yes, describe the type of chain of custody record used and what information is recorded.

Yes _____ No _____ N/A ____ 4. If used, are sample tag numbers recorded on chain of custody documents?

Yes _____ No _____ N/A ____ 5. Does information on sample tags and chain of custody records match?

Yes _____ No _____ N/A ____ 6. Does the chain of custody record indicate the method of sample shipment?

Document Control-(cont'd)

Yes _____ No _____ N/A ____ 7. Is the chain of custody record included with the samples in the shipping container?

Yes _____ No _____ N/A ____ 8. If used, do the sample traffic reports agree with the sample tags?

Yes _____ No _____ N/A ____ 9. If used, are blank samples identified?

Yes _____ No _____ N/A ____ 10. If collected, are duplicate samples identified on sample tags and chain of custody records?

Yes _____ No _____ N/A ____ 11. If used, are spiked samples identified?

Yes _____ No _____ N/A ____ 12. Are logbooks signed by the individual who checked out the logbook from the project coordinator?

Yes _____ No _____ N/A ____ 13. Are logbooks dated upon receipt from the project coordinator?

Document Control-(cont'd)

Yes _____ No _____ N/A ____ 14. Are logbooks project-specific (by logbook or by page)?

Yes _____ No _____ N/A ____ 15. Are logbook entries dated and identified by the author?

Yes _____ No _____ N/A ____ 16. Are photographs documented in logbooks (e.g., time, date, description of subject, photographer, etc.)?

Yes _____ No _____ N/A ____ 17. If film from a self-developing camera is used, are photos matched with logbook documentation?

Yes _____ No _____ N/A ____ 18. Are sample tag numbers recorded? If yes, describe where they are recorded.

Yes _____ No _____ N/A ____ 19. Are calibration of pH meters, conductivity meters, etc., documented? If yes, describe where this is documented.

Yes _____ No _____ N/A ____ 20. Are amendments to the project plan documented? If yes, describe where the amendments are documented.

Debriefing with Project Manager

Yes _____ No _____ N/A ____ 1. Was a debriefing held with project manager and/or other participants?

Yes _____ No _____ N/A ____ 2. Were any recommendations made to the project participants during the debriefing? If yes, list recommendations.

Appendix F
Laboratory Audit Checklist

Appendix F Laboratory Audit Checklist

Signature of Auditor _____ Date of Audit _____

Project Manager _____ Project No. _____

Project Location _____

Type of Investigation _____
(authority, agency)

The enclosed laboratory audit checklists are organized into the categories by laboratory functional area. The attached audit checklists have been numbered according to the following outline:

1.0 Sample Management

2.0 Organic Sample Preparation

3.0 Gas Chromatography

4.0 Mass Spectrometry

5.0 Metals Preparation

6.0 Metals Analysis

7.0 Wet Chemistry

8.0 Report Generation

9.0 Computer Systems

Special Checklists

Form A Laboratory Temperature Monitoring Checklist

Form B Laboratory Notebook Checklist

Form C Laboratory Balance Checklist

Form D Reagent and Analytical Standards Checklist

Form E Laboratory Safety Checklist

1. Sample Management

Shipment of Sample Bottles and Coolers

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comments
		Is there a standard operating procedure (SOP) describing preparation and shipment of sample coolers?	
		Are sample bottles precleaned and is cleaning documented?	
		Are cooler shipment records maintained?	
		Are coolers and bottles sent out under chain of custody (COC)?	
		Are preservatives provided with the cooler?	
		Are sample collectors supplied with preservatives and sampling instructions for their use?	
		Is there a SOP describing the amount and concentration of preservation agents added to bottles?	
		Are COC forms provided along with instructions for proper completion?	
		Are trip blanks included with the cooler?	
		If so, is the purity of the trip blank water checked before shipment and can it be documented?	
		Does the laboratory only utilize new sample containers?	

Receipt and Storage of Samples

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory quality assurance (QA) program?	
		Is there a written SOP readily available to the log-in personnel?	
		Is the SOP followed as written?	
		If discrepancies are noted between COC records and the samples, are they documented and appropriate personnel notified?	
		Is the pH checked on all appropriate incoming samples and documented?	
		Is the pH check done in such a manner that avoids sample contamination?	
		Is hydrogen chloride (HCl) preservation utilized for volatile sample preservation? If not, is a 7-day hold time being applied?	
		Are incoming volatile vials checked for the presence of air bubbles?	
		If air bubbles are detected, is the client notified?	
		If there a mechanism to receive samples after normal work hours and weekends?	
		Is the filing system for original custody forms and paperwork traceable?	
		Is a fume hood available for opening of hazardous samples?	
		Are eyewashes and/or showers available in the immediate area?	
		Is there a central log-in notebook, and is it document controlled?	
		Are unique laboratory sample identification numbers assigned and properly recorded on sample container labels and sample log-in documentation?	
		Is there a SOP describing how the lab handles samples with short holding times?	
		Are samples checked for proper preservation upon receipt? (Required by New Jersey).	
		If samples are not properly preserved, is there a SOP describing how it is handled?	
		Are files maintained for log-in documentation?	
		Are all samples and extracts stored in a secure manner? (Locked refrigerators and freezers).	
		Are all samples and extracts stored in separate storage units?	
		Is there limited access to sample and extract storage areas?	
		Is there an internal custody procedure for samples and extracts, and is it documented in a SOP? If so, where are records filed?	
		Is there a procedure for documenting where samples and extracts are stored?	
		Are volatile samples stored separately from other samples or extracts?	

Y	N	Item	Comment
		Are volatile water samples stored separately from soil volatile samples?	
		Are refrigerator holding blanks utilized to monitor potential sample contamination in each volatile sample storage unit?	
		Are standards or reagents stored with samples or extracts?	
		Are samples maintained in a cooled condition until holding time expires?	
		Are archived samples stored in a secure manner?	
		Is there a policy describing how long samples are held after a report is issued?	
		Are samples being held after report issuance maintained in a cooled condition?	
		Is there a SOP describing the archival and disposal of samples and sample extracts?	
		Does the disposal SOP describe how the lab disposes of samples of unknown content?	
		Is there a record of when every sample has been discarded?	
		Do supervisory personnel review the paperwork in the department, and is this review documented?	

2. Organic Sample Preparation

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Are the following QC samples processed with each analytical batch?	
		Method Blank	
		Quality Control (QC) Check Sample	
		Matrix Spike	
		Matrix Spike Duplicate	
		Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
		Are gas lines checked for leaks each time a tank is changed?	
		If the lab utilizes desiccators, do they appear to be properly maintained?	
		Is there an SOP for glassware washing, and is it posted in the washing area?	
		Are operating manuals available to the analysts for all major equipment?	
		Is there a record of instrument servicing maintained in a logbook, and is it document controlled?	
		Is appropriate corrective action taken if a surrogate is outside of acceptable limits?	
		Are boiling chips kept to a minimum size to prevent volumetric distortion and minimize sample contamination potential? (Only one boiling chip, the size of a grain of salt, should be used).	
		Are graduated cylinders utilized for measuring out sample volumes for water extractions?	
		Are amber screw cap vials utilized for solvent extracts? (Screw cap vials prevent solvent losses associated with crimp top vials).	
		If the volume of solvent extracts is reduced utilizing gas blowdown systems, do the gas lines contain molecular sieves to remove contaminants from the gas supply?	

Y	N	Item	Comment
		Are surrogates added to samples utilizing Class A pipets in a manner to ensure quantitative transfer of the surrogates?	
		Are various dry reagents such as florisil, sodium sulfate, and glass wool or thimbles pre-extracted prior to use?	
		Is florisil PR 60/100 mesh utilized, and is it stored in a dark glass bottle with foil-lined cap and initially activated at 676 ^{o}C and at 130 ^{o}C before use?	
		Is anhydrous sodium sulfate used, which is dried at 400 ^{o}C for 4 hours and stored at 130 ^{o}C before use?	
		Are only approved solvent lot numbers being utilized by the laboratory?	
		Is laboratory glassware rotated so that method blanks are truly representative of the effectiveness of routine glassware cleaning procedures? (Dedicated glassware must not be used for QC samples, and only one blank can be extracted per batch).	
		When utilizing liquid/liquid continuous extractors, is <u>all</u> the solvent remaining after extraction in both the extractor and the boiling flask concentrated down to the final volume?	
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the corporate QA program?	

3. Gas Chromatography (GC)

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Are gas lines checked for leaks each time a tank is changed?	
		Are instruments properly vented or are appropriate traps in place?	
		Can the lab demonstrate the absence of volatile organics in the lab reagent water?	
		Are SOPs available detailing the procedures used in this area?	
		Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
		Are operating manuals available to the analysts for all major equipment?	
		Is there a record of instrument servicing maintained in a logbook, and is it document controlled?	
		Are volatile analyses being conducted using the appropriate packed or capillary columns as specified by the particular method?	
		Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low level sample?	
		Is quantitation correct for the method (based upon the average response factor [RF] of a calibration curve or the RF from a continuing calibration standard)?	
		Is the initial calibration conducted at five or three concentrations as appropriate for the method?	
		Are all reported results within the calibration range of the highest and lowest standard?	
		Are calibrations performed at the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	

Y	N	Item	Comment
		Is a method blank run with every batch of samples?	
		Are there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is appropriate corrective action taken if a surrogate is outside of acceptance limits?	
		Is appropriate corrective action taken if internal standard area is outside of acceptance limits?	
		Is a run log maintained for all instrumentation?	
		Are GC identifications confirmed on a second dissimilar column?	
		Are polychlorinated biphenyls (PCB) identifications performed by manual pattern recognition?	
		Is a sufficient number of peaks used to calculate a PCB result (minimum of three)?	
		Are various extract clean-up techniques such as copper, florisil, alumina, sulfuric acid used routinely?	
		Do gas lines contain molecular sieves or other filters to remove contaminants from the gas supply?	
		If 25-milliliter (mL) purge vessels are utilized for methods normally requiring a 5-mL purge, have method detection limit (MDL) studies been performed to verify that required MDLs are achieved?	

4. Mass Spectrometry (MS)

Volatile GC/MS Area

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Are the following QC samples processed with each analytical batch?	
		Method Blank	
		QC Check Sample	
		Matrix Spike	
		Matrix Spike Duplicate	
		Are gas lines checked for leaks each time a tank is changed?	
		Are the instruments properly vented or are appropriate traps in place?	
		Can the lab demonstrate the absence of volatile organics in the lab reagent water?	
		Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
		Is the laboratory utilizing the most recent version of the EPA/NIH mass spectral database? If not what version is being used?	
		Are operating manuals available to the analysis for all major equipment?	
		Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
		Are volatile analyses being conducted using the appropriate packed or capillary columns as specified by the particular method?	

Y	N	Item	Comment
		Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low level sample?	
		Is the initial calibration conducted at five or three concentrations as appropriate for the method?	
		Is quantitation correct for the method (based upon the average RF of a calibration curve or the RF from a continuing calibration standard)?	
		Are calibrations and tuning performed according the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	
		Is appropriate corrective action taken if a continuing calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Are there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is the appropriate corrective action taken if a surrogate is outside of acceptance limits?	
		Is the appropriate corrective action taken if internal standard area is outside of acceptance limits?	
		Are library searches examined by the mass spectrometry expert before results are reported and is there documentation of this review?	
		Is a run log maintained for all instrumentation and is it documented controlled?	
		Is raw data stored in a secure manner under appropriate conditions to prevent loss of data?	
		Are the reported results within the calibration range of the highest and lowest standard?	
		Are appropriate dilutions performed?	
		Do gas lines contain molecular sieves or other filters to remove contaminants in gas supply?	
		If 25-mL purge vessels are utilized for methods normally requiring a 5-mL purge, have MDL studies been performed to verify that required MDLs are achieved?	

4.0 Mass Spectrometry (MS) (cont'd)

Semi-volatile GC/MS Area

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Are gas lines checked for leaks each time a tank is changed?	
		Are the instruments properly vented or are appropriate traps in place?	
		Can the lab demonstrate the absence of volatile organics in the lab reagent water?	
		Are the solvent storage cabinets properly vented as appropriate to avoid possible laboratory contamination?	
		Is the laboratory utilizing the most recent version of the EPA/NIH mass spectral database? If not what version is being used?	
		Are operating manuals available to the analysis for all major equipment?	
		Is there a record of instrument servicing maintained in a logbook and is it document controlled?	
		Are volatile analyses being conducted using the appropriate packed or capillary columns as specified by the particular method?	
		Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low-level sample?	
		Is the initial calibration conducted at five or three concentrations as appropriate for the method?	
		Is quantitation correct for the method (based upon the average RF of a calibration curve or the RF from a continuing calibration standard)?	

Y	N	Item	Comment
		Are calibrations and tuning performed according the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	
		Is appropriate corrective action taken if a continuing calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Are there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is the appropriate corrective action taken if a surrogate is outside of acceptance limits?	
		Is the appropriate corrective action taken if internal standard area is outside of acceptance limits?	
		Are library searches examined by the MS expert before results are reported, and is there documentation of this review?	
		Is a run log maintained for all instrumentation and is it documented controlled?	
		Is raw data stored in a secure manner under appropriate conditions to prevent loss of data?	
		Are the reported results within the calibration range of the highest and lowest standard?	
		Are appropriate dilutions performed?	
		Do gas lines contain molecular sieves or other filters to remove contaminants in gas supply?	

5. Metals Preparation

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Is the storage area for acids properly ventilated?	
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
Are the following QC samples processed with each analytical batch?			
		Method Blank	
		QC Check Sample	
		Matrix Spike	
		Matrix Spike Duplicate or Matrix Duplicate	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Is there a SOP for glassware washing, and is it posted in the washing area?	
		Are high purity trace metal grade acids utilized for preservation and digestion of samples for metals?	
		Is glassware for metals analysis acid washed?	
		If automatic dispensers are utilized for acids, are they properly maintained?	
		Does the lab ensure that powder-free gloves are used to avoid possible zinc contamination of samples?	
		Are operating manuals available to the analysts for all major equipment?	
		Is there a record of instrument servicing maintained in a logbook, and is it document controlled?	
		Is a digestion log maintained for all samples, and is it document controlled?	
		Is an acid digestion performed for drinking water samples requiring total metals?	
		Are samples for dissolved metals digested after filtration?	EPA required, except for drinking water where turbidity is below a certain level.

6. Metals Analysis

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Are gas lines checked for leaks each time a tank is changed?	
		Are vents above AA units functioning properly (200 ft^3/min.)?	
		Are SOPs available detailing the procedures used in this area?	
		Are operating manuals available to the analysis for all major equipment?	
		Is there a record of instrument servicing maintained in a logbook, and is it document controlled?	
		Is there a policy in place concerning carryover prevention in the event a high level sample precedes a relatively low-level sample?	
		Are calibrations performed according the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	
		Are continuing calibrations run at an adequate frequency?	
		Is appropriate corrective action taken if a continuing calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Is appropriate corrective action taken if a continuing calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Are there specified acceptance limits for the method blank?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is a run log maintained for all instrumentation and is it documented controlled?	
		Are post-digestion spikes performed for graphic furnace analyses?	

Y	N	Item	Comment
		Is there a corrective action when PDS fail? Is it to flag results or perform standard additions?	
		Are ICP interference standards run at the required frequency specified in the method?	
		Are serial dilutions performed?	
		Are check standards run at a frequency of 10 percent for graphite furnace to monitor when the furnace should be changed?	
		For mercury analysis, is the mercury vapor safely removed from the lab atmosphere?	
		Are all reported results within the calibration range of the highest and lowest standard?	

7. Wet Chemistry

Check off which of the following items are utilized in this area and complete the associated forms.

	Refrigerators, freezers, ovens	Complete Form A
	Logbooks	Complete Form B
	Laboratory Balances	Complete Form C
	Reagents and Standards	Complete Form D
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Are the following QC samples processed with each analytical batch?	
		Method Blank	
		QC Check Sample	
		Matrix Spike	
		Matrix Spike Duplicate or Matrix Duplicate	
		If the lab utilizes desiccators, do they appear to be properly maintained?	
		Is there a SOP for glassware washing, and is it posted in the washing area?	
		Are operating manuals available to the analysts for all major equipment?	
		Is there a record of instrument servicing maintained in a logbook, and is it document controlled?	
		Is there a policy in place concerning carryover prevention in the event a high-level sample precedes a relatively low-level sample?	
		Are calibrations performed according the required frequency specified in the methods?	
		Is appropriate corrective action taken if a calibration is out of criteria?	
		Is a method blank run with every batch of samples?	
		Are there specified acceptance limits for the method banks?	
		Is there a policy stating that the laboratory does not "blank correct" sample data?	
		Is a dedicated analysis log maintained for all parameters determined, and are they document controlled?	
		Is the pH meter checked daily, or before use, by setting the meter to pH 7.0, then measuring pH at 4 and 10?	

Y	N	Item	Comment
		Is the conductivity meter calibrated daily against a 0.001M potassium chloride solution and the data recorded in a logbook?	
		Is the turbidimeter calibrated daily, or before use, with 40 nephelometric turbidity unit (NTU) formazine standard and the data recorded in a logbook?	
		Is the dissolved oxygen meter calibrated weekly against the Winkler method and data recorded in a logbook?	
		Are all reported results within the calibration range of the highest and lowest standard?	

8. Report Generation

Check off which of the following items are utilized in this area and complete the associated forms.

	Logbooks	Complete Form B
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Is there a document describing in detail the contents and order of deliverables provided with various types of reporting levels or packages?	
		Do all reports contain a cover letter and case narrative?	
		Is COC provided with all reports?	

9. Computer Systems

Check off which of the following items are utilized in this area and complete the associated forms.

	Logbooks	Complete Form B
	Safety Equipment	Complete Form E

Y	N	Item	Comment
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory QA program?	
		Are SOPs available detailing the procedures used in this area?	Obtain a listing of all procedures performed in the area. Compare the list with available SOPs, and estimate a percentage complete on the line below. Percent Compliance _____
		Are computer programs validated before use?	
		Are operating manuals available to the computer specialists for all computer equipment?	
		Is there a record of computer servicing maintained in a logbook, and is it document controlled?	
		Is the computer system backed up at a regular frequency and if so, what is the frequency? Backup copy maintained off Site?	
		Is the system protected from unauthorized access utilizing a password system?	
		Are backup power supplied utilized to prevent loss of information in the event of a power failure?	
		Is the system protected from a lightning strike?	
		If an in-house information management system is utilized, are instructions available to the users?	
		Is there a formal training program for new users?	
		Is there any mechanism to prevent computer clocks from being altered to reflect incorrect dates and times?	
		If such alteration would occur, is there a mechanism to detect it in a very timely fashion?	
		Are computer specialists at the facility familiar with the EPA computer requirements set forth in the good automated lab practices (GALP) manual?	

10. Forms

10.1 Form A – Laboratory Temperature Monitoring Checklist

Identify the Laboratory Area under Review:			
Identify the number of units in this laboratory area:			**Refrigerators:** **Freezers:** **Ovens:**
Y	**N**	**Item**	**Comment**
		Do the laboratory personnel indicate a familiarity with the requirements set forth in the laboratory SOP for temperature monitoring?	
		Are temperatures of all lab temperature units such as refrigerators, ovens, freezers, and incubators monitored daily and documented in a logbook?	
		Are all units individually identified with a unique identification number on the outside of the unit?	
		Have thermometers been calibrated against National Institute of Standards and Technology (NIST) within the last year and documented?	
		Are temperature excursion noted and appropriate action taken?	
		Does all laboratory equipment contain thermometers, which are uniquely identified?	
		Are all thermometers immersed in appropriate media?	
		Is the laboratory aware of whether the temperature has been checked routinely?	

10.2 Form B – Laboratory Notebook Checklist

Identify the Laboratory Area under Review:			
Identify the Number of Notebooks in this Area:			
Y	**N**	**Item**	**Comment**
		Do the logbooks comply with GLP standards for logbooks?	
		Are the contents of the notebook clearly identified?	
		Are lab notebooks maintained in black ink?	
		Are notebooks permanently bound and contain pre-printed and consecutively numbered pages?	
		Are lab notebooks neat, orderly, and legible?	
		Are entries noting anomalies routinely recorded?	
		Are mistakes in notebooks crossed out with one line signed and dated?	
		Do all notebooks have a unique document control number?	
		Is there evidence of secondary review of the notebook?	
		Are unused portions of pages struck out with a line or Z'd out?	

10.3 Form C – Laboratory Balance Checklist

Identify the Laboratory Area under Review:			
Identify the Number of Balances in this Area:			
Y	**N**	**Item**	**Comment**
		Are all balances being calibrated at the correct frequency?	
		Have the calibrations been conducted at the correct level?	
		Are the acceptance limits presented in the logbook?	
		Are balances and S weights maintained in a clean environment?	
		Does each balance have a unique identification number?	
		Has each balance been serviced in the past year, and is a sticker affixed to the balance?	

10.4 Form D – Laboratory Reagents and Standards Checklist

Identify the Laboratory Area under Review:			
Y	**N**	**Item**	**Comment**
		Is there a SOP describing how reagents and standards are prepared and stored?	
		Is there a mechanism for verifying a prepared standard or purchased commercial standard prior to its use in the lab?	
		Is a standards notebook maintained for all areas, which describes the preparation and standardization of standard solutions, and is it document controlled?	
		Are stock standards traceable to their source?	
		Are standards and reagents properly labelled with received date, concentration, date prepared, preparer's initials, and expiration date?	
		Are standards stored separately from samples or sample extracts?	
		Are all sources of reagent water checked daily?	
		Does water meet the conductance requirements outlined in the SOP, and is it documented?	
		Are the water quality records documents controlled?	
		Are reagent grade or higher grade chemicals used to prepare standards?	
		Is there evidence that all reagents and standards are within their expiration dates?	
		Are chemicals being used in analyses tested to ensure they contain no contaminants which may interfere with the analyses, prior to use?	

10.5 Form E – Laboratory Safety Checklist

Identify the Laboratory Area under Review:			
Y	**N**	**Item**	**Comment**
		Is there sufficient safety equipment in this area, such as fume hoods, shower, eyewash, first aid kit, etc.?	
		Is there an emergency spill kit available in the vicinity?	
		Are lab fume hoods checked monthly for proper air flow, and is it documented?	
		Is there a cut-off level for determining airflow (100 fpm)?	
		Is the interior of fume hoods maintained in a clutter-free manner?	
		Are safety glasses worn in the laboratory areas?	
		Are appropriate gloves worn suitable for the reagents used in the laboratory?	
		Are the storage areas and benchtops maintained in an orderly manner such that safety hazards are avoided?	
		Have fire extinguishers, safety showers, and eyewashes been checked for proper operation?	
		Are self-contained breathing apparatus available for use in emergency situations?	
		Is all standards preparation performed in a fume hood?	
		Are material safety data sheets (MSDS) accessible and up-to-date?	
		Are all instruments properly vented?	
		Have all personnel participated in formal safety training?	

about GHD

GHD is one of the world's leading professional services companies operating in the global markets of water, energy and resources, environment, property and buildings, and transportation. We provide engineering, environmental, and construction services to private and public sector clients.

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