



Quality Assurance Project Plan (QAPP)

for the Resource Conservation and Recovery Act (RCRA)
Area 1 Corrective Action Operations, Maintenance and
Monitoring (OM&M) Plan
Eckles Road Site
Livonia, Michigan

**Revitalizing Auto Communities
Environmental Response Trust
(RACER) Site**

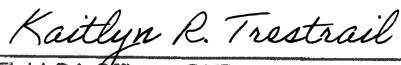


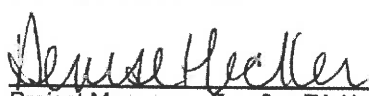


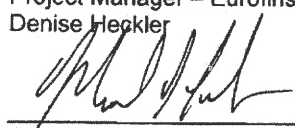
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Table of Contents

1.	Project Description	1
1.1	Introduction	1
1.1.1	Project Objectives and Decision Statement	1
1.1.2	Project Status/Phase	2
1.1.3	QAPP Preparation Guidelines	2
1.2	Facility Description	2
1.3	Site History	2
1.4	Project Objectives and Intended Data Use	3
1.4.1	Target Parameter List	3
1.4.1.1	Field Parameters	3
1.4.1.2	Laboratory Parameters	3
1.5	Sampling Locations	3
1.6	Project Schedule	3
2.	Project Organization and Responsibilities	4
2.1	Management Responsibilities	4
2.2	Quality Assurance Responsibilities	5
2.3	Laboratory Responsibilities	5
2.4	Field Responsibilities	7
3.	Quality Assurance Objectives for Measurement Data	7
3.1	Precision	8
3.1.1	Definition	8
3.1.2	Laboratory Precision Sample Objectives	8
3.1.3	Field Precision Sample Objectives	8
3.2	Accuracy	9
3.2.1	Definition	9
3.2.2	Laboratory Accuracy Sample Objectives	9
3.2.3	Field Accuracy Objectives	9
3.3	Representativeness	10
3.3.1	Definition	10
3.3.2	Measures to Ensure Representativeness of Field Data	10
3.3.3	Measures to Ensure Representativeness of Laboratory Data	10
3.4	Completeness	10
3.4.1	Definition	10
3.4.2	Field Completeness Objectives	10
3.4.3	Laboratory Completeness Objectives	10



Table of Contents

3.5	Comparability	11
3.5.1	Definition	11
3.5.2	Measures to Ensure Comparability of Field Data	11
3.5.3	Measures to Ensure Comparability of Laboratory Data	11
3.6	Decision Rules	11
3.6.1	Definition	11
3.6.2	Decision Rule Objective	11
3.7	Level of Quality Control Effort	12
4.	Special Training/Certification Sampling Procedures	13
5.	Sampling Procedures	13
5.1	Sample Containers	13
5.2	Sample Labeling	13
5.3	Field QC Sample Collection	14
5.3.1	Equipment Rinsate Blank Sample Collection	14
5.3.2	Field Duplicate Sample Collection	14
5.3.2.1	Water Samples	14
5.3.2.2	Soil and Solid Samples	14
5.3.3	MS/MSD Sample Collection	14
6.	Custody Procedures	14
6.1	Field Custody Procedures	15
6.1.1	Field Procedures	16
6.1.2	Transfer of Custody and Shipment Procedures	16
6.2	Laboratory Chain of Custody Procedures	17
6.3	Storage of Samples	17
6.4	Final Project Files Custody Procedures	18
7.	Calibration Procedures and Frequency	18
7.1	Field Instrument Calibration Procedures	18
7.2	Laboratory Instrument Calibration Procedures	19
8.	Analytical Procedures	19
8.1	Field Analytical Procedures	20
8.2	Laboratory Analytical Procedures	20
8.2.1	List of Project Target Compounds and Laboratory Detection Limits	20
8.2.2	List of Method Specific Quality Control Criteria	20



Table of Contents

9.	Internal Quality Control Checks	21
9.1	Field Quality Control	21
9.1.1	Equipment Rinsate Blanks	21
9.1.2	Trip Blanks.....	21
9.1.3	Field Duplicate Samples.....	21
9.2	Laboratory Procedures	22
10.	Data Reduction, Validation, and Reporting	22
10.1	Data Reduction	22
10.1.1	Field Data Reduction Procedures.....	22
10.1.2	Laboratory Data Reduction Procedures	23
10.2	Data Validation.....	23
10.2.1	Procedures Used to Evaluate Field Data	23
10.2.2	Procedures to Validate Laboratory Data	23
10.3	Data Reporting	25
10.3.1	Field Data Reporting.....	25
10.3.2	Laboratory Data Reporting	25
11.	Performance and System Audits.....	27
11.1	Field Performance and System Audits	27
11.1.1	Internal Field Audit Responsibilities.....	27
11.1.2	External Field Audit Responsibilities	27
11.2	Laboratory Performance and System Audits	28
11.2.1	Internal Laboratory Audit Responsibilities	28
11.2.2	External Laboratory Audit Responsibilities.....	28
12.	Preventative Maintenance.....	29
12.1	Field Instrument Preventative Maintenance	29
12.2	Laboratory Instrument Preventative Maintenance	29
13.	Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness..	30
13.1	Field Measurements	30
13.2	Laboratory Data	30
13.2.1	Precision.....	30
13.2.1.1	Accuracy.....	30
13.2.2	Completeness.....	30
13.3	Statistical Evaluations	31
13.3.1	Percent Recovery	31
13.3.2	Relative Percent Difference	31



Table of Contents

14.	Corrective Action	31
14.1	Field Corrective Action	31
14.2	Laboratory Corrective Action	32
14.3	Corrective Action During Data Validation and Data Assessment	32
15.	Quality Assurance Reports	33
16.	References	33

Figure Index

Figure 1	Organization Chart

Table Index

Table 1.1	Summary of Sampling and Analysis Program
Table 1.2	Target Compound and Target Analyte Parameter List - EurofinsTestAmerica
Table 5.1	Container, Preservation, Shipping and Packaging Requirements

Appendix Index

Appendix A	Analytical Laboratory List
Appendix B	Laboratory Standard Operating Procedures
Appendix C	Laboratory Reference Data
Appendix D	Field Analytical and Sampling Standard Operating Procedures
Appendix E	Field Audit Checklist
Appendix F	Laboratory Audit Checklist



1. Project Description

The following outlines the scope of the Resource Conservation and Recovery Act (RCRA) Corrective Action Operations, Maintenance & Monitoring (OM&M) Plan and any subsequent events, to be performed in accordance with the requirements of the RCRA Administrative Order on Consent (AOC) (effective September 29, 2011) between the United States Environmental Protection Agency (USEPA) and RACER for the Eckles Road Site (Site) (Docket No. RCRA 05-2011-0025).

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 supplemental RFI and Operation, Maintenance, and Monitoring (OMM) activities for the Eckles Road Site. 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, with the exception of soil vapor sampling related to Area of Interest (AOI) 31 - Former Fire Training Area.

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 RACER. The QAPP is a component of the overall project scope including the associated Work Plans: and ISCO PRB Remediation Plan. 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. Soil vapor and indoor air monitoring related to AOI 31 – Former Fire Training Area monitoring will be addressed under separate cover.

1.1.1 Project Objectives and Decision Statement

The primary objectives for data collection activities include:

- 1 Collect sufficient data to monitor the effectiveness of previously implemented response actions for Area 1 – Former Plating Area in-situ chemical reduction (ISCR) treatment programs, requirements of OMM Plans, and discharge permit requirements.
- 2 Collect sufficient data to monitor groundwater quality and the effectiveness of proposed remedial response activities for AOI 31 – Former Fire Training Area in-situ chemical oxidation (ISCO) remedial activities and requirements of OMM Plans. The proposed ISCO remedial activities include the injection of a sodium persulfate solution to reduce trichloroethylene (TCE) concentrations in groundwater through oxidation. The proposed ISCO injections will be conducted at multiple transects across the off-site area of TCE-impacted groundwater. Performance groundwater monitoring will be conducted to monitoring the effectiveness of the remedial activities and determine when/if additional injections may be warranted.
- 3 Define the nature and extent of Per- and Polyfluoroalkyl Substances (PFAS) constituents in environmental media (soil, groundwater, and/or surface water) at the Eckles Road Site.



The Decision Statement for the project scope is as follows:

1. Determine whether interim or final remedial actions are necessary and/or have been completed to control current unacceptable risks, if any, to human health or the environment.
2. 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 Work Plans, OMM Plans and subsequent amendments or sampling programs submitted as necessary, and periodic status reports.

1.1.3 QAPP Preparation Guidelines

As previously noted, this QAPP has been prepared to present the project specific QA/QC elements in 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 RCRA Facility Investigation (RFI) Report (CRA, March, 2005) sections

Land Use	RFI Report Section 3.7
Climate	RFI Report Section 3.2
Topography	RFI Report Section 3.1
Surface Water Hydrology	RFI Report Section 3.3
Local Geology and Hydrology	RFI Report Sections 3.4 and 3.5

1.3 Site History

The RACER Eckles Road Site history is provided in Section 2.0 of the RFI Work Plan (CRA, September 2002) and incorporated here by reference:

Current and Historical Operations	RFI Work Plan Section 2.0
Current Conditions Report Summary	RFI Work Plan Section 1.6
RFI Objectives and Strategy	RFI Report Section 2.2.4
Results of RFI Investigations	RFI Report Section 4.0



1.4 Project Objectives and Intended Data Use

1.4.1 Target Parameter List

The investigative and OMM activities include the sampling and analysis of environmental media for the presence of organic and inorganic constituents based on historical operations at the Site. The field and laboratory parameters are summarized below and presented in Table 1.1. This table may be updated when OMM programs are modified or remedial alternatives are proposed.

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

VOCs, specifically TCE, and select metals (nickel, chromium, and hexavalent chromium) are the primary target analytes. Other possible target parameters include PFAS, additional metals, sulfate/sulfide, and general/physical parameters. The basis for the selected parameter list is provided in the Work Plans.

Table 1.2 presents the estimated quantitation limits (EQL) for each compound or analyte. Method detection limit (MDL) studies have been performed by Eurofins TestAmerica (TA) 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. TA will be used as primary project laboratory network.

1.5 Sampling Locations

The Proposed Scopes of Work and Work Plans, and subsequent amendments or sampling programs provide a summary and rationale for the sample locations at the Site. 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 Manager and RACER Project Manager. Current sample collection activities include: soil/water investigative sampling, groundwater monitoring, surface water monitoring, and OMM including water treatment systems.

1.6 Project Schedule

The schedule and projected milestones are presented in the work plans.



2. Project Organization and Responsibilities

The RACER Project Manager with assistance from the designated GHD Project Manager, will have the primary responsibility for the implementation of the RFI Work Plan. The project laboratories listed in Appendix A will perform the analyses of environmental samples collected at the Site. 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

Management responsibilities are as follows:

Greg Rudloff (USEPA RCRA Corrective Action Project Manager)

The Regulatory Agency Project Manager has the overall responsibility for oversight of all phases of the Corrective Action and OM & M.

Dave Favero – RACER Project Manager

The RACER Project Manager is responsible for implementing the project, and has the authority to commit the resources necessary to meet project objectives and requirements. The RACER Project Manager's primary function is to ensure that technical, financial, and scheduling objectives are achieved successfully. The RACER Project Manager will provide the major point of contact and control matters concerning the project and represent the project team at regulatory agency meetings. The Project Manager will define project objectives and develop a detailed project schedule. The RACER 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.

Chris Meincke - GHD Project Manager

The GHD Project Manager will provide final review of significant work products and may participate in technical meetings with the USEPA or other agencies. The GHD Project Manager will ensure that overall technical quality is maintained. The GHD Project Manager will be actively involved in the direction of the project. The GHD Project Manager has overall responsibility for ensuring that the project meets RFI, individual Work Plan, and OMM objectives. The GHD Project Manager will:

1. Acquire and apply technical and other resources as needed to ensure performance within budget and schedule restraints.
2. Review work performed on each task to ensure quality, responsiveness, cost effectiveness, and timeliness.
3. Be responsible for the preparation and quality of interim and final reports.
4. Communicate with RACER about the progress of the project.

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



GHD Project Coordinator

The GHD Project Coordinator will assist 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:

1. Assisting in monitoring the RFI progress and quality
2. Preparing and reviewing RFI reports
3. Providing technical support of project activities
4. 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:

1. Assuring the application and effectiveness of the QAPP by the analytical laboratory and the project staff
2. Conducting internal QA/QC of the investigation activities
3. Providing input to the GHD Project Manager and the GHD Project Engineer as to corrective actions required resulting from the above-mentioned evaluations
4. Preparation and review of data validation and audit reports
5. 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:

1. Conducting external performance and system audits of the RFI laboratories
2. 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 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:

1. Receiving and inspecting the incoming sample containers
2. Recording the condition of the incoming sample containers
3. Signing appropriate documents
4. Verifying COC and its correctness
5. Notifying the Laboratory Project Manager and Laboratory Operations Manager of sample receipt and inspection
6. Assigning a unique identification number and customer number and entering each into the sample receiving log
7. Initiating transfer of samples to lab sections
8. 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
- Eurofins TestAmerica/West Sacramento, California



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

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 Manager. The GHD Field QA Officer works with the project Health and Safety Officer to conduct operations in compliance with the project health and safety plan (HASP). The GHD Field QA Officer will facilitate communication and coordinate efforts between the GHD Project Manager and the field team members. Other responsibilities include:

1. Developing and implementing field-related work plans, ensuring schedule compliance, and adhering to management-developed project requirements
2. Coordinating and managing field staff, including sampling and drilling
3. Performing field system audits
4. Overseeing QC for technical data provided by the field staff
5. Preparing and approving of text and graphics required for field team efforts
6. Coordinating and overseeing technical efforts of subcontractors assisting the field team
7. Identifying problems in the field, resolving difficulties in consultation with the GHD Project QA Officer, and GHD Project Manager/Coordinator, and implementing and documenting corrective action procedures
8. Will review and understand the QAPP
9. Participating in preparation of the final reports

Field Team Personnel

Field Team Personnel involved in the project scope will be responsible for:

1. Performance of field activities as detailed in the 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

All Work Plans 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, as necessary. The QAPP program will include:

1. A mechanism for ongoing control of measurements and evaluation of data quality
2. 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 SOPs and reference data provided in Appendix B and C, respectively, present the performance criteria for laboratory QC objectives. Additionally, GHDs Innovative Technology Group will prepare leachate from soils/sediments for PFAS using groundwater that is either from the Site or based on Site groundwater chemistry. The SOP is included in Appendix B.

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 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.

3.1.3 Field Precision Sample Objectives

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

The project specific criteria for field duplicates are as follows: The RPDs associated with field duplicate samples must be less than 50 and 100 percent for water and soil/solid samples, respectively. If the reported concentration in either the investigative sample or its duplicate is less than five times the reporting limit (RL), the evaluation criteria is one or two times the RL value for water and soil/solid samples, respectively.



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 Laboratory Accuracy Sample Objectives

Analytical bias will be assessed through the use of known laboratory control samples (LCS) and Site 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.

3.2.3 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.

The specific criteria for field QC blanks are defined in the Contract Laboratory Program (CLP) National Functional Guidelines documents, which are referenced in Section 10.2.2.



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 generally be biased; that is, sampling associated with the soil and groundwater will be based on the observed or known presence/absence of Site specific contaminants, and/or Site knowledge of a release. If non-biased sampling is appropriate the approach will be identified in a specific Scope of Work or Work Plan. Specific sampling technique descriptions, which allow consistency, repetitiveness, and thus representativeness, are provided as SOPs in Appendix D.

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 Site investigations 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, ng per L of media for PFAS analyses, and mg per L for inorganic analyses

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 various supplemental Work Plans and Scopes of Work, OMM Plans, and Revised



Groundwater Monitoring Plan (CRA, April 2008), and subsequent amendments or sampling programs. The decision rule for the sampling and analysis data collected is also provided as follows:

1. 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.
2. Identify action levels (e.g., EGLE Part 201 Criteria, Risk-based Screening Levels; Regional Screening Levels [RSLs]); or a reference-based standard based on a Site Conceptual Model that will be developed in consultation with USEPA.
3. If appropriate 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 to update the baseline human health and ecological risk assessment for the evaluation of 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 Site. One equipment rinsate blank, if required by use of non-disposable or non-dedicated equipment, or for investigation events including samples to be analyzed for PFAS, will be collected for every 10 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 (prepared or purchased by lab) 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. 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, discharge 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 Site. MS will be performed in duplicate



for all designated 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.. Aqueous and non-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 recorded/interactive learning 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 may be obtained throughout 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 RACER and USEPA. The field sampling SOPs provided in Appendix D describes each of the sampling tasks and objectives.

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.



The sample numbering system for the project has been designed to uniquely identify each sample from each sampling program and event. The Site-specific sample number should consist of the following, at a minimum:

GW - 081612-MP-XXX

where GW - Designates sample type (GW-water, SO-soil)

081619 - Date of collection (MMDDYY)

MP - Sampler initials

XXX - Sequential number starting with 001 each sampling event

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.

5.3.2.2 Soil and Solid Samples

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

5.3.3 MS/MSD Sample Collection

MS/MSD sample collection for aqueous and non-aqueous samples requires triple the sample volume..

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:

1. 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 bottles. The sample container, preservation methods, shipping, and packaging requirements are presented in Table 5.1.
2. 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.
3. 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).
4. 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

1. 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.
2. 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.
3. 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.

4. When samples are split with a regulatory agency and RACER 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 Site will require the representative's signature acknowledging sample receipt.
5. 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.
6. 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, oxidation reduction potential (ORP) 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.

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, with the exception of the analysis of PFAS, which does not have an approved USEPA method. The laboratory developed 537 Modified method will be used for the analysis of PFAS in soil and groundwater samples. The 537 Modified method utilizes isotope dilution which can address matrix suppression or enhancement that can be seen in non-potable water and soil samples and is very similar to the specifications of Department of Defense QSM Version 5.1, Table B-15 for the determination of PFAS analytes, for which Eurofins is certified. 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 Site. 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 are provided in Appendix B of this document and the SOPs are based on the USEPA methodology requirements promulgated in:

1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", SW-846 EPA, USEPA Office of Solid Waste, 3rd Edition and promulgated updates, 1986
2. "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, March 1983
3. "Standard Methods for the Examination of Water and Wastewater", APHA, AWWA, and WEF, 22th Edition, 2009 (with subsequent editions)
4. EPA Method 537, Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Revision 1.1, September 2009

EPA Method 537 modified is being used for this project for analysis of PFAS. As of this writing, there are two SW-846 EPA methods for PFAS analyses that will undergo review and public comment in 2019. The methods, EPA 8327 and EPA 8328, utilize different sample preparation and calibration procedures. Once one or both methods becomes final, EPA 537 modified will be replaced by one of the two methods for future PFAS scope. EPA 537 modified is similar to EPA 8328, which utilizes solid phase extraction and an isotope dilution calibration procedure.

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

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 Table 1.2. 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 7 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 ORP meter cannot be calibrated; it can only be checked for accuracy using a known solution. 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 5 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 2 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. 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, ORP 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-2017-002, January 2017, "National Functional Guidelines for Inorganic Superfund Methods Data Review", EPA 540-R-2017-001, January 2017 and "Data Review and Validation Guidelines for Perfluoroalkyl Substances (PFASs) Analyzed Using EPA Method 537", EPA 910-R-18-001, November 2018.

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 Semi-annual groundwater monitoring samples and PFAS Area 1 Characterization samples. Investigative samples



used for risk assessment purposes analyzed by TA 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 project scope, including OM & M monitoring and Post Injection sampling. 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 10.2.2. The task of reporting laboratory data by RACER 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:

1. Title Page
 - Project name and number
 - Laboratory project or lot number
 - Signature of the Laboratory QA Officer or his designee
 - Date issued
2. Table of Contents - Laboratory Report Contents
3. 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
4. Analytical Methods Summary - Methods of Sample Preparation and Analyses for Samples
5. Analytical Sample Summary - Cross-Reference Table of Laboratory Sample to Project Sample Identification Numbers
6. Shipping and Receiving Documents
 - Sample container documentation
 - Sample reception information and original COC record
7. 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) --required upon GHD request or when stage 3 validation is required



- 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)-- required upon GHD request or when stage 3 validation is required
 - MS recoveries and MD RPDs, LCS, method blank results
 - Serial dilutions, reagent blank results, and interference check standards (inorganics) required upon GHD request or when stage 3 validation is required

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.

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:

1. Field sampling records, screening results, instrument operating records
2. Sample collection
3. Handling and packaging in compliance with procedures
4. Maintenance of QA procedures
5. 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:

1. Sampling equipment decontamination procedures



2. Sample bottle preparation procedures
3. Sampling procedures
4. Examination of HASPs
5. Procedures for verification of field duplicates
6. 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:

1. Review of laboratory analytical procedures
2. Laboratory on-Facility visits
3. 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:

1. Sample receipt procedures



2. Custody, sample security, and log-in procedures
3. Review of instrument calibration logs
4. Review of QA procedures
5. Review of logbooks
6. Review of analytical SOPs
7. Personnel interviews

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

1. Comparison of resulting data to the SOP or method
2. Verification of initial and continuing calibrations within control limits
3. Verification of surrogate recoveries and instrument timing results
4. Review of extended quantitation reports for comparisons of library spectra to instrument spectra, where applicable
5. 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 3.4.



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:

R₁ = value of first result
R₂ = 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:

1. Identify/define the problem
2. Assign responsibility for investigating the problem



3. Investigate/determine the cause of the problem
4. Determine an appropriate corrective action to eliminate the problem
5. Implement the corrective action
6. Evaluate the effectiveness of the corrective action
7. Verify that the corrective action has eliminated the problem
8. Prepare a written record detailing the problem, corrective action utilized, and solution of the problem
9. Submit the Corrective Action Record (CAR) to whoever initiated the corrective action and the GHD Project QA Officer, GHD Project Manager and RACER 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 RACER 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 RACER 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

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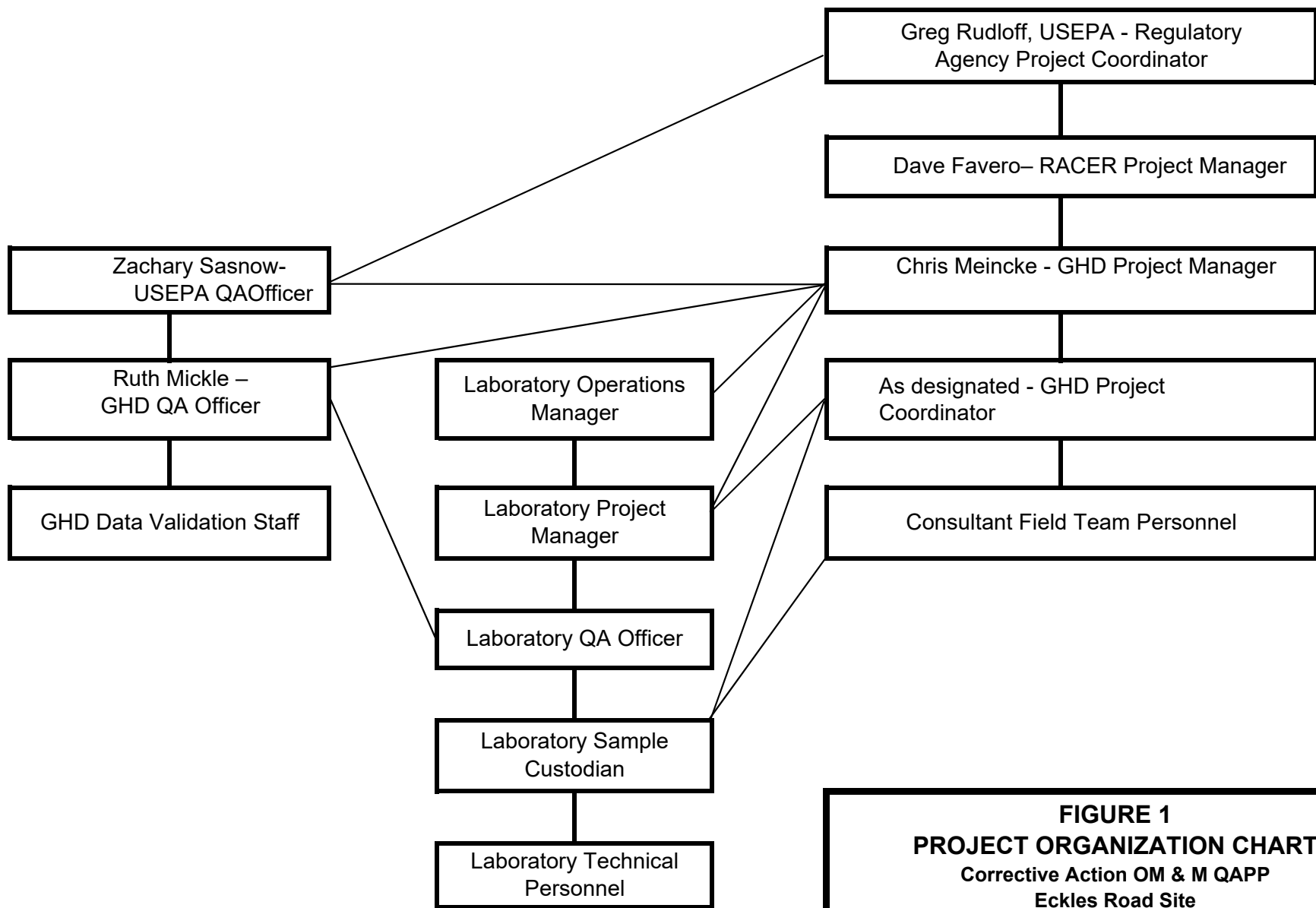


FIGURE 1
PROJECT ORGANIZATION CHART
Corrective Action OM & M QAPP
Eckles Road Site

Table 1.1

Summary of Sampling and Analysis Program
Eckles Road Site
Livonia, Michigan

Sample Matrix	Field Parameters	Laboratory Parameters	# of Samples ⁽¹⁾	Quality Control Samples			Total
				Field Blanks/Trip blank ⁽²⁾	Field Duplicates	MS/MSD ⁽³⁾	
A. OM & M Sampling -Water Water	Effluent- one monthly sample	Discharge Metals (Cr, Pb, Hg, Ni, Zn) Hexavalent Chromium Oil & Grease (HEM) TSS PP PCBs	12	--	--	--	12
			12	--	--	--	12
			12	--	--	--	12
			12	--	--	--	12
			12	--	--	--	12
	Annual monitoring	Discharge Metals (Cr, Pb, Hg, Ni, Zn) Oil & Grease (HEM) Hexavalent Chromium TSS PP VOCs PP SVOCs 2,3,7,8-TCDD Screen PP PCBs PP Pesticides	1	--	--	--	1
			1	--	--	--	1
			1	--	--	--	1
			1	--	--	--	1
			1	--	--	--	1
			1	--	--	--	1
			1	--	--	--	1
			1	--	--	--	1
			1	--	--	--	1
	Influent sampling- frequency as needed	Select Metals (Cr, Ni) Hexavalent Chromium	1	--	--	--	1
			1	--	--	--	1
B. Groundwater Semi-annual- Water	pH/ temperature, DO, Specific Conductivity, Turbidity, ORP	TCL VOC	40	2	2	2	48
		Cr, Ni, Cr VI	8	--	1	1	11
C. Post Injection Scope -Water	--	Select Metals (total & dissolved)	TBD				
		Hexavalent & Trivalent Chromium	TBD				
		Sulfate	TBD				
		Sulfide	TBD				
		Hardness	TBD				
		Alkalinity	TBD				

Table 1.1
Summary of Sampling and Analysis Program
Eckles Road Site
Livonia, Michigan

Sample Matrix	Field Parameters	Laboratory Parameters	# of Samples ⁽¹⁾	Quality Control Samples			Total
				Field Blanks/Trip blank ⁽²⁾	Field Duplicates	MS/MSD ⁽³⁾	
D. PFAS Area 1 Characterization							
Water	pH/temperature, DO, Specific Conductivity, Turbidity, ORP	PFAS	14	1	1	1	18
		Total Nickel & Chromium	14	1	1	1	18
		Hexavalent and Trivalent Chromium	14	1	1	1	18
		TOC	14	1	1	1	18
Leachate liquid	--	PFAS	1	--	--	--	1
Soil	--	PFAS	12	--	--	--	12
		TOC	12	--	--	--	12
		FOC	12	--	--	--	12
		Bulk Density	12	--	--	--	12
		TOP Assay	2	--	--	--	2

Notes:

- ⁽¹⁾ - Additional samples may be required.
- ⁽²⁾ - Field blank samples will not be required if dedicated or disposable sampling equipment is used.
- ⁽³⁾ - Matrix Spike/Matrix Spike duplicate (MS/MSD)

- DO - Dissolved Oxygen
- FOC - Fractional Organic Carbon
- ORP - Oxidation-Reduction Potential
- PFAS - Per- and Polyfluoroalkyl Substances.
- PP - Priority Pollutant
- TOC - Total Organic Carbon
- TOP - Total Oxidizable Precursor
- TBD - To be Determined
- TCL - Target Compound List
- TSS - Total Suspended Solids
- PCBs - Polychlorinated Biphenyl Compounds
- TCDD - Tetrachlorodibenzodioxin
- SVOCs - Semi-volatile Organic Compounds
- VOCs - Volatile Organic Compounds

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
Water Parameters					
TOC	Sw 9060	Total Organic Carbon	1.00	0.141	mg/L
Hex Chromium	SM 3500	Hexavalent Chromium	0.00500	0.00300	mg/L
Trivalent Chromium	SM 3500	Trivalent Chromium	0.0200	0.00200	mg/L
Total Cr	EPA 200.7	Total Chromium	0.0500	0.000625	mg/L
Total Ni	EPA 200.7	Total Nickel	0.0100	0.00220	mg/L
Sulfate	SW-845 9056	Sulfate	1.00	0.348	mg/L
Sulfide	SW-846 9030	Sulfide	3.00	1.41	mg/L
Hardness	130/SM2340C	Hardness	5.00	2.39	mg/L
Alkalinity	310/SM2320	Alkalinity	5.00	2.60	mg/L
Oil & Grease HEM	EPA-WW 1664	Oil & Grease /Hexane Extractable Material	5.00	1.02	mg/L
TSS	SM 2540 D	Total Suspended Solids	4.00	2.22	mg/L
PFAS (LC/LC/MS)	537 modified	Perfluorobutanoic acid (PFBA)	2.00	0.350	ng/L
		Perfluoropentanoic acid (PFPeA)	2.00	0.490	ng/L
		Perfluorohexanoic acid (PFHxA)	2.00	0.580	ng/L
		Perfluoroheptanoic acid (PFHpA)	2.00	0.250	ng/L
		Perfluorooctanoic acid (PFOA)	2.00	0.850	ng/L
		Perfluorononanoic acid (PFNA)	2.00	0.270	ng/L
		Perfluorodecanoic acid (PFDA)	2.00	0.310	ng/L
		Perfluoroundecanoic acid (PFUnA)	2.00	1.10	ng/L
		Perfluorododecanoic acid (PFDoA)	2.00	0.550	ng/L
		Perfluorotridecanoic acid (PFTriA)	2.00	1.30	ng/L
		Perfluorotetradecanoic acid (PFTeA)	2.00	0.290	ng/L
		Perfluorobutanesulfonic acid (PFBS)	2.00	0.200	ng/L
		Perfluorohexanesulfonic acid (PFHxS)	2.00	0.170	ng/L
		Perfluoroheptanesulfonic Acid (PFHpS)	2.00	0.190	ng/L
		Perfluorodecanesulfonic acid (PFDS)	2.00	0.320	ng/L
		Perfluorooctanesulfonic acid (PFOS)	2.00	0.540	ng/L
		Perfluorooctanesulfonamide (FOSA)	2.00	0.350	ng/L
		Perfluoropentanesulfonic acid (PFPeS)	2.00	0.300	ng/L
		Perfluorononanesulfonic acid (PFNS)	2.00	0.160	ng/L
		N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	20.0	3.10	ng/L
		N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	20.0	1.90	ng/L
		4:2 FTS	20.0	5.20	ng/L
		6:2 FTS	20.0	2.00	ng/L
		8:2 FTS	20.0	2.00	ng/L

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
PFAS TOP Water	537 modified	Perfluorobutanoic acid (PFBA)	5.00	0.880	ng/L
		Perfluoropentanoic acid (PFPeA)	5.00	1.20	ng/L
		Perfluorohexanoic acid (PFHxA)	5.00	1.40	ng/L
		Perfluoroheptanoic acid (PFHpA)	5.00	0.630	ng/L
		Perfluorooctanoic acid (PFOA)	5.00	2.10	ng/L
		Perfluorononanoic acid (PFNA)	5.00	0.680	ng/L
		Perfluorodecanoic acid (PFDA)	5.00	0.780	ng/L
		Perfluoroundecanoic acid (PFUnA)	5.00	2.80	ng/L
		Perfluorododecanoic acid (PFDoA)	5.00	1.40	ng/L
		Perfluorotridecanoic acid (PFTriA)	5.00	3.20	ng/L
		Perfluorotetradecanoic acid (PFTeA)	5.00	0.730	ng/L
		Perfluorobutanesulfonic acid (PFBS)	5.00	0.500	ng/L
		Perfluoropentanesulfonic acid (PFPeS)	5.00	0.750	ng/L
PFAS TOP Water	537 modified	Perfluorohexanesulfonic acid (PFHxS)	5.00	0.430	ng/L
		Perfluoroheptanesulfonic Acid (PFHpS)	5.00	0.480	ng/L
		Perfluorooctanesulfonic acid (PFOS)	5.00	0.800	ng/L
		Perfluorononanesulfonic acid (PFNS)	5.00	0.400	ng/L
		Perfluorodecanesulfonic acid (PFDS)	5.00	1.40	ng/L
		Perfluorooctanesulfonamide (FOSA)	40.0	0.880	ng/L
		N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	50.0	7.80	ng/L
		N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	50.0	4.80	ng/L
		4:2 FTS	50.0	13.0	ng/L
		6:2 FTS	50.0	5.00	ng/L
		8:2 FTS	50.0	5.00	ng/L
PP VOCs	EPA-MCA 624.1	Benzene	1.00	0.130	ug/L
		Ethylbenzene	1.00	0.110	ug/L
		Toluene	1.00	0.140	ug/L
		Vinyl chloride	1.00	0.200	ug/L
		Xylenes, Total	2.00	0.150	ug/L
		Dichlorobromomethane	1.00	0.170	ug/L
		Bromoform	1.00	0.760	ug/L
		Bromomethane	1.00	0.420	ug/L
		Carbon tetrachloride	1.00	0.260	ug/L
		Chlorobenzene	1.00	0.140	ug/L
		Chlorodibromomethane	1.00	0.390	ug/L
		Chloroethane	1.00	0.830	ug/L
		2-Chloroethyl vinyl ether	10.0	0.260	ug/L
		Chloroform	1.00	0.130	ug/L
		Chloromethane	1.00	0.200	ug/L
		1,2-Dichlorobenzene	1.00	0.150	ug/L

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
PP VOCs	EPA-MCA 624.1	1,3-Dichlorobenzene	1.00	0.150	ug/L
		1,4-Dichlorobenzene	1.00	0.160	ug/L
		1,1-Dichloroethane	1.00	0.170	ug/L
		1,1-Dichloroethene	1.00	0.190	ug/L
		1,2-Dichloroethane	1.00	0.210	ug/L
		trans-1,2-Dichloroethene	0.500	0.190	ug/L
		1,2-Dichloropropane	1.00	0.150	ug/L
		cis-1,3-Dichloropropene	1.00	0.610	ug/L
		trans-1,3-Dichloropropene	1.00	0.670	ug/L
		Methylene Chloride	5.00	2.62	ug/L
		1,1,2,2-Tetrachloroethane	1.00	0.130	ug/L
		Tetrachloroethene	1.00	0.150	ug/L
		1,1,1-Trichloroethane	1.00	0.240	ug/L
		1,1,2-Trichloroethane	1.00	0.0900	ug/L
		Trichloroethene	1.00	0.100	ug/L
		m-Xylene & p-Xylene	2.00	0.0800	ug/L
		o-Xylene	1.00	0.0900	ug/L
		Acrolein	20.0	2.07	ug/L
		Acrylonitrile	20.0	1.13	ug/L
		1,3-Dichloropropene, Total	2.00	1.29	ug/L
TCL VOCs	SW 8260	Acetone	10.0	5.41	ug/L
		Benzene	1.00	0.130	ug/L
		Bromodichloromethane	1.00	0.170	ug/L
		Bromoform	1.00	0.760	ug/L
		Bromomethane	1.00	0.420	ug/L
		2-Butanone (MEK)	10.0	1.16	ug/L
		Carbon disulfide	5.00	0.280	ug/L
		Carbon tetrachloride	1.00	0.260	ug/L
		Chlorobenzene	1.00	0.140	ug/L
		Chloroethane	1.00	0.830	ug/L
		Chloroform	1.00	0.130	ug/L
		Chloromethane	1.00	0.200	ug/L
		1,1-Dichloroethane	1.00	0.170	ug/L
		1,2-Dichloroethane	1.00	0.210	ug/L
		1,1-Dichloroethene	1.00	0.190	ug/L
		1,2-Dichloropropane	1.00	0.150	ug/L
		cis-1,3-Dichloropropene	1.00	0.610	ug/L
		trans-1,3-Dichloropropene	1.00	0.670	ug/L
		Ethylbenzene	1.00	0.110	ug/L
		2-Hexanone	10.0	0.540	ug/L

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
TCL VOCs	SW 8260	Methylene Chloride	5.00	2.62	ug/L
		4-Methyl-2-pentanone (MIBK)	10.0	0.420	ug/L
		Styrene	1.00	0.100	ug/L
		1,1,2,2-Tetrachloroethane	1.00	0.130	ug/L
		Tetrachloroethene	1.00	0.150	ug/L
		Toluene	1.00	0.140	ug/L
		Trichloroethene	1.00	0.100	ug/L
		Vinyl chloride	1.00	0.200	ug/L
		Xylenes, Total	2.00	0.150	ug/L
		1,1,1-Trichloroethane	1.00	0.240	ug/L
		1,1,2-Trichloroethane	1.00	0.0900	ug/L
		Cyclohexane	1.00	0.240	ug/L
		1,2-Dibromo-3-Chloropropane	1.00	0.910	ug/L
		1,2-Dibromoethane	1.00	0.120	ug/L
		Dichlorodifluoromethane	1.00	0.350	ug/L
		cis-1,2-Dichloroethene	1.00	0.160	ug/L
		trans-1,2-Dichloroethene	1.00	0.190	ug/L
		Isopropylbenzene	1.00	0.0900	ug/L
		Methyl acetate	10.0	1.72	ug/L
		Methyl tert-butyl ether	1.00	0.0700	ug/L
		1,1,2-Trichloro-1,2,2-trifluoroethane	1.00	0.410	ug/L
		1,2,4-Trichlorobenzene	1.00	0.260	ug/L
		1,2-Dichlorobenzene	1.00	0.150	ug/L
		1,3-Dichlorobenzene	1.00	0.150	ug/L
		1,4-Dichlorobenzene	1.00	0.160	ug/L
		Trichlorofluoromethane	1.00	0.450	ug/L
		Dibromochloromethane	1.00	0.390	ug/L
		Methylcyclohexane	1.00	0.330	ug/L
		m-Xylene & p-Xylene	2.00	0.0800	ug/L
		o-Xylene	1.00	0.0900	ug/L
SVOCs	EPA-MCA 625.1	Benzo[a]anthracene	10.0	0.171	ug/L
		Benzo[a]pyrene	10.0	0.173	ug/L
		Benzo[b]fluoranthene	10.0	0.154	ug/L
		Benzo[g,h,i]perylene	10.0	0.178	ug/L
		Acenaphthene	10.0	0.172	ug/L
		Acenaphthylene	10.0	0.125	ug/L
		Anthracene	10.0	0.135	ug/L
		Benzo[k]fluoranthene	10.0	0.140	ug/L
		Butyl benzyl phthalate	10.0	0.666	ug/L
		Bis(2-chloroethoxy)methane	10.0	0.455	ug/L
		Bis(2-chloroethyl)ether	10.0	0.402	ug/L

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
SVOCs	EPA-MCA 625.1	Bis(2-ethylhexyl) phthalate	10.0	2.22	ug/L
		bis (2-chloroisopropyl) ether	10.0	0.551	ug/L
		4-Bromophenyl phenyl ether	10.0	0.499	ug/L
		2-Chloronaphthalene	10.0	0.483	ug/L
		4-Chlorophenyl phenyl ether	10.0	0.551	ug/L
		Chrysene	10.0	0.186	ug/L
		Dibenz(a,h)anthracene	10.0	0.151	ug/L
		Di-n-butyl phthalate	10.0	1.80	ug/L
		3,3'-Dichlorobenzidine	10.0	1.15	ug/L
		Diethyl phthalate	10.0	3.82	ug/L
		Dimethyl phthalate	10.0	0.515	ug/L
		2,4-Dinitrotoluene	10.0	2.07	ug/L
		2,6-Dinitrotoluene	10.0	2.13	ug/L
		Di-n-octyl phthalate	10.0	0.821	ug/L
		Fluoranthene	10.0	0.160	ug/L
		Fluorene	10.0	0.169	ug/L
		Hexachlorobenzene	10.0	0.161	ug/L
		Hexachlorobutadiene	10.0	0.543	ug/L
		Hexachloroethane	10.0	0.395	ug/L
		Indeno[1,2,3-cd]pyrene	10.0	0.135	ug/L
		Isophorone	10.0	0.324	ug/L
		Naphthalene	10.0	0.109	ug/L
		Nitrobenzene	10.0	0.514	ug/L
		N-Nitrosodi-n-propylamine	10.0	0.253	ug/L
		Phenanthrene	10.0	0.167	ug/L
		Pyrene	10.0	0.175	ug/L
		1,2,4-Trichlorobenzene	10.0	0.427	ug/L
		4-Chloro-3-methylphenol	10.0	0.296	ug/L
		2-Chlorophenol	10.0	0.273	ug/L
		2,4-Dichlorophenol	10.0	0.262	ug/L
		2,4-Dimethylphenol	10.0	0.518	ug/L
		2,4-Dinitrophenol	50.0	6.21	ug/L
		4,6-Dinitro-2-methylphenol	50.0	2.82	ug/L
		2-Nitrophenol	10.0	0.564	ug/L
		4-Nitrophenol	50.0	2.17	ug/L
		Pentachlorophenol	10.0	3.10	ug/L
		Phenol	10.0	0.128	ug/L
		2,4,6-Trichlorophenol	10.0	1.80	ug/L
		Benzidine	5.00	1.88	ug/L
		Hexachlorocyclopentadiene	10.0	1.76	ug/L
		N-Nitrosodimethylamine	1.00	0.219	ug/L
		N-Nitrosodiphenylamine	10.0	0.440	ug/L
		1,2-Diphenylhydrazine	1.00	0.433	ug/L

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
2,3,7,8-TCDD Screen	EPA-MCA 625.1	2,3,7,8-TCDD	--	--	
PCBs	EPA MCA 608.3	Aroclor-1016	0.100	0.0560	ug/L
		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
Pesticides	EPA MCA 608.3	Aldrin	0.0500	0.00240	ug/L
		alpha-BHC	0.0500	0.00200	ug/L
		beta-BHC	0.0500	0.00460	ug/L
		delta-BHC	0.0500	0.00430	ug/L
		gamma-BHC (Lindane)	0.0500	0.00250	ug/L
		Chlordane (technical)	0.500	0.0465	ug/L
		4,4'-DDD	0.0500	0.00530	ug/L
		4,4'-DDE	0.0500	0.00430	ug/L
		4,4'-DDT	0.0500	0.00480	ug/L
		Dieldrin	0.0500	0.00230	ug/L
		Endosulfan I	0.0500	0.00370	ug/L
		Endosulfan II	0.0500	0.00230	ug/L
		Endosulfan sulfate	0.0500	0.00370	ug/L
		Endrin	0.0500	0.00250	ug/L
		Endrin aldehyde	0.0500	0.00460	ug/L
		Heptachlor	0.0500	0.00330	ug/L
		Heptachlor epoxide	0.0500	0.00260	ug/L
		Toxaphene	2.00	0.0581	ug/L
		Chlordane (technical) Peak 1	0.500	0.0465	ug/L
		Chlordane (technical) Peak 2	0.500	0.0465	ug/L
		Chlordane (technical) Peak 3	0.500	0.0465	ug/L
		Chlordane (technical) Peak 4	0.500	0.0465	ug/L
		Toxaphene Peak 1	2.00	0.0581	ug/L
		Toxaphene Peak 2	2.00	0.0581	ug/L
		Toxaphene Peak 3	2.00	0.0581	ug/L
		Toxaphene Peak 4	2.00	0.0581	ug/L
		Toxaphene Peak 5	2.00	0.0581	ug/L

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
Solid/soil Parameters	TOC	Lloyd_Kahn	Total Organic Carbon	1000	mg/Kg
	FOC	ASTM D_2974	Fractional Organic Carbon	-	%
	Density	ASTM D2937	Bulk Density	-	gm/cm3
PFAS (LC/LC/MS)	537 modified	Perfluorobutanoic acid (PFBA)	0.200	0.0280	ug/Kg
		Perfluoropentanoic acid (PFPeA)	0.200	0.0770	ug/Kg
		Perfluorohexanoic acid (PFHxA)	0.200	0.0420	ug/Kg
		Perfluoroheptanoic acid (PFHpA)	0.200	0.0290	ug/Kg
		Perfluorooctanoic acid (PFOA)	0.200	0.0860	ug/Kg
		Perfluorononanoic acid (PFNA)	0.200	0.0360	ug/Kg
		Perfluorodecanoic acid (PFDA)	0.200	0.0220	ug/Kg
		Perfluoroundecanoic acid (PFUnA)	0.200	0.0360	ug/Kg
		Perfluorododecanoic acid (PFDoA)	0.200	0.0670	ug/Kg
		Perfluorotridecanoic acid (PFTriA)	0.200	0.0510	ug/Kg
		Perfluorotetradecanoic acid (PFTeA)	0.200	0.0540	ug/Kg
		Perfluorobutanesulfonic acid (PFBS)	0.200	0.0250	ug/Kg
		Perfluoropentanesulfonic acid (PFPeS)	0.200	0.0200	ug/Kg
		Perfluorohexanesulfonic acid (PFHxS)	0.200	0.0310	ug/Kg
		Perfluoroheptanesulfonic Acid (PFHpS)	0.200	0.0350	ug/Kg
		Perfluorooctanesulfonic acid (PFOS)	0.500	0.200	ug/Kg
		Perfluorononanesulfonic acid (PFNS)	0.200	0.0200	ug/Kg
		Perfluorodecanesulfonic acid (PFDS)	0.200	0.0390	ug/Kg
		Perfluorooctanesulfonamide (FOSA)	0.200	0.0820	ug/Kg
		N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	2.00	0.390	ug/Kg
		N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	2.00	0.370	ug/Kg
		4:2 FTS	2.00	0.370	ug/Kg
		6:2 FTS	2.00	0.150	ug/Kg
		8:2 FTS	2.00	0.250	ug/Kg
PFAS TOP Soil	537 modified	Perfluorobutanoic acid (PFBA)	0.500	0.0700	ug/Kg
		Perfluoropentanoic acid (PFPeA)	0.500	0.190	ug/Kg
		Perfluorohexanoic acid (PFHxA)	0.500	0.110	ug/Kg
		Perfluoroheptanoic acid (PFHpA)	0.500	0.0730	ug/Kg
		Perfluorooctanoic acid (PFOA)	0.500	0.220	ug/Kg
		Perfluorononanoic acid (PFNA)	0.500	0.0900	ug/Kg
		Perfluorodecanoic acid (PFDA)	0.500	0.0550	ug/Kg
		Perfluoroundecanoic acid (PFUnA)	0.500	0.0900	ug/Kg
		Perfluorododecanoic acid (PFDoA)	0.500	0.170	ug/Kg
		Perfluorotridecanoic acid (PFTriA)	0.500	0.130	ug/Kg
		Perfluorotetradecanoic acid (PFTeA)	0.500	0.140	ug/Kg
		Perfluorobutanesulfonic acid (PFBS)	0.500	0.0630	ug/Kg
		Perfluoropentanesulfonic acid (PFPeS)	0.500	0.0500	ug/Kg
		Perfluorohexanesulfonic acid (PFHxS)	0.500	0.0780	ug/Kg
PFAS-soil, cont'd	PFAS TOP Soil	537 modified			

Table 1.2

Target Compound and Target Analyte Parameter List - Eurofins TestAmerica
Eckles Road Site
Livonia, Michigan

Method Description	Method Code	Analyte Description	Estimated Quantitation Limit (EQL)	Method Detection Limit (MDL)	Units
		Perfluoroheptanesulfonic Acid (PFHpS)	0.500	0.0880	ug/Kg
		Perfluorooctanesulfonic acid (PFOS)	1.25	0.500	ug/Kg
		Perfluorononanesulfonic acid (PFNS)	0.500	0.0500	ug/Kg
		Perfluorodecanesulfonic acid (PFDS)	0.500	0.0980	ug/Kg
		Perfluorooctanesulfonamide (FOSA)	0.500	0.210	ug/Kg
		N-methylperfluorooctanesulfonamidoacetic acid (NMeFOSAA)	5.00	0.980	ug/Kg
		N-ethylperfluorooctanesulfonamidoacetic acid (NEtFOSAA)	5.00	0.930	ug/Kg
		4:2 FTS	5.00	0.930	ug/Kg
		6:2 FTS	5.00	0.380	ug/Kg
		8:2 FTS	5.00	0.630	ug/Kg

Notes:

FOC	- Fractional Organic Carbon	PP	- Priority Pollutant
PFAS	- Per- and Polyfluoroalkyl Substances.	TCL	-Target Compound List
TOC	- Total Organic Carbon	SVOCs	- Semi-volatile Organic Compounds
TOP	- Total Oxidizable Precursor	VOCs	- Volatile Organic Compounds
		PCBs	- Polychlorinated Biphenyl Compounds

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 matrix dependent 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 basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.

Table 5.1

Container, Preservation, Shipping and Packaging Requirements
Eckles Road Site
Livonia, Michigan

Analyses	Sample Containers ¹	Preservation	Maximum Holding Time from Sample Collection ²	Volume of Sample	Shipping	Normal Packaging
Water/Liquid PFAS	bottles	Iced, 4 ± 2° C	14 days for extraction 28 days after extraction for analysis	Fill to neck of bottle	Overnight	Foam Liner or Bubble-wrap
Select Metals	One 250 ml plastic bottle	HNO ₃ to pH < 2 Iced, 4 ± 2° C	180 days for analysis (28 days - mercury)	Fill to neck of bottle	Overnight	Foam Liner or Bubble-wrap
Hexavalent/ Trivalent Chromium	One 250 ml plastic bottle	Iced, 4 ± 2° C	24 hours	Fill to neck of bottle	Overnight	Foam Liner or Bubble-wrap
TOC	Two 40ml VOC vials	H2SO4 to pH<2 Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
Sulfate	One 100 ml plastic bottle	Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
Sulfide	One 500 ml glass bottle	Iced, 4 ± 2° C (pH >9, 1M ZnAC)	7 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
Hardness	One 100 ml plastic bottle	pH < 2 and Iced, 4 ± 2° C	180 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
Alkalinity	One 250 ml plastic bottle	Iced, 4 ± 2° C	14 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
Oil & Grease (HEM)	32 oz w/ HCL glass bottle	pH < 2 and Iced, 4 ± 2° C (H ₂ SO ₄)	28 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
TSS	One 100 ml plastic bottle	Iced, 4 ± 2° C	7 days for analysis	Fill to neck of bottle	Overnight	Bubble-wrap
VOCs	3 x 40ml vials w/ HCL	pH < 2 and Iced, 4 ± 2° C	14 days for analysis	Fill to neck of bottle	Overnight	Foam Liner or Bubble-wrap
SVOCs	2 x 1000 mL amber glass bottle	Iced, 4 ± 2° C	7 days from sample collection to extraction; 40 days from extraction to completion of analysis	Fill to neck of bottle	Overnight	Bubble-wrap
2,3,7,8-TCDD Screen	2 x 1000 mL amber glass bottle	Iced, 4 ± 2° C	30 days from sample collection to extraction; - 45 days from extraction to completion of analysis	Fill to neck of bottle	Overnight	Bubble-wrap
PCBs	2 x 1000 mL amber glass bottle	Iced, 4 ± 2° C	7 days from sample collection to extraction; 40 days from extraction to completion of analysis	Fill to neck of bottle	Overnight	Bubble-wrap

Table 5.1

Container, Preservation, Shipping and Packaging Requirements
Eckles Road Site
Livonia, Michigan

Analyses	Sample Containers ¹	Preservation	Maximum Holding Time from Sample Collection ²	Volume of Sample	Shipping	Normal Packaging
Pesticides	2 x 1000 mL amber glass bottle	Iced, 4 ± 2° C	7 days from sample collection to extraction; 40 days from extraction to completion of analysis	Fill to neck of bottle	Overnight	Bubble-wrap
Solid/Soil						
PFAS	One 4-ounce high density polyethylene jar per analysis	Iced, 4 ± 2° C	14 days for extraction; 28 days after extraction for analysis	Fill to shoulder of jar	Overnight	Bubble-wrap
TOP Assay	One 4-ounce glass jar per analysis	Iced, 4 ± 2° C	14 days for extraction; 28 days after extraction for analysis	Fill to shoulder of jar	Overnight	Bubble-wrap
TOC/FOC	One 4-ounce glass jar	Iced, 4 ± 2° C	28 days for analysis	Fill to shoulder of jar	Overnight	Bubble-wrap
Bulk Density	One 4-ounce glass jar	Iced, 4 ± 2° C	Not applicable	Fill to shoulder of jar	Overnight	Bubble-wrap

Notes:

- FOC
- PCBs
- PFAS
- SVOCs
- TOC
- TOP
- TSS
- TCDD
- VOCs
- Fractional Organic Carbon
- Polychlorinated Biphenyl Compounds
- Per- and Polyfluoroalkyl Substances.
- Semi-volatile Organic Compounds
- Total Organic Carbon
- Total Oxidizable Precursor
- Total Suspended Solids
- Tetrachlorodibenzodioxin
- Volatile Organic Compounds

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

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

Appendix A

Analytical Laboratory List

Appendix A Analytical Laboratory List

Eurofins TestAmerica Laboratory- North Canton	
Denise Heckler	Project Manager
Chris Williams	Laboratory Operations Manager
Mark Loeb	Laboratory QA Officer
Laboratory Address 1	4101 Shuffel Street NW, North Canton, Ohio
Phone	(330) 966-9477
Eurofins TestAmerica Laboratory- West Sacramento	
Denise Heckler	Project Manager
Crystal Pollock	Laboratory Operations Manager
Lisa Stafford	Laboratory QA Officer
Laboratory Address	880 Riverside Parkway West Sacramento, California 95605
Phone	(916) 373-5600

Appendix B

Laboratory Standard Operating Procedures

Appendix B Laboratory SOPs

<i>Item No.</i>	<i>Title</i>	<i>SOP No.</i>
01	Density in Soils by Drive Cylinder Method	BR-GT-018, Rev. 8.0
02	Moisture, Ash, and Organic Matter of Peat & Other Organic Soils	BR-GT-019, Rev. 8.0
03	Total Organic Carbon	BR-WC-008, Rev. 16.0
04	Analysis of Pesticides and PCBs	NC-GC-046, Rev. 0
05	Acid Digestion for Aqueous Samples	NC-IP-011, Rev. 8.0
06	GC/MS Semivolatile Organic Compounds	NC-MS-003, Rev. 12.0
07	Dioxin Screen	NC-MS-005, Rev. 3.0
08	GC/MS Volatile Organic Compounds	NC-MS-006, Rev. 8.0
09	Determination of Volatile Organics By Gc/Ms	NC-MS-019, Rev. 6.0
10	Inductively Coupled Plasma	NC-MT-012, Rev. 8.0
11	Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Absorption Spectroscopy	NC-MT-014, Rev. 8.0
12	Total Organic Carbon	NC-WC-017, Rev. 8.0
13	Chromium, Hexavalent	NC-WC-024, Rev. 8.0
14	Total Hardness, Titrimetric	NC-WC-036, Rev. 9.0
15	Sulfide	NC-WC-060, Rev. 12.0
16	Determination of Inorganic Anions by Ion Chromatography	NC-WC-084, Rev. 16.0
17	HEM/SGT-HEM By Solid Phase Extraction	NC-WC-091, Rev. 11.0
18	Determination of Solids in Waters and Wastes	NC-WC-092, Rev. 8.0
19	Total, Carbonate, Bicarbonate, and Hydroxide Alkalinity	NC-WC-093, Rev. 6.0
20	Soil Leaching Procedure for PFAs	Laboratory Standard Operating Procedures, Doc. No. 1, Rev. 0
21	Per- and Polyfluorinated Substances in Water, Soils, Sediments and Tissue	WS-LC-0025, Rev. 3.5

**Title: Density in Soils by Drive Cylinder Method
(ASTM D2937-04)**

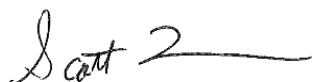
Approval Signatures:



Don Dawicki
Laboratory Director



Matthew Kirk
Operations Mgr/EHS Coordinator



Scott Lavigne
Department Supervisor



Luke Orchard
Quality Assurance Manager

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1.0 Scope and Application

This standard operating procedure (SOP) describes the laboratory procedure for the determination of in-place density of natural, inorganic soil by the drive cylinder method.

This procedure is not suitable for organic soils that can compress upon sampling, very hard natural soils, heavily compacted soils, soils with low plasticity or soils with large amounts of gravel. The procedure is not recommended for friable soils or soft, highly plastic, non-cohesive, saturated or other soils which are not easily deformed.

2.0 Summary of Method

A representative portion of sample is removed from the sample collection tube and dried in an oven maintained at a temperature of 110°C for 16 hours. The moisture content of the sample is determined and expressed as a percent of the oven-dried mass. Density is subsequently calculated by dividing the value obtained for oven-dried mass by the determined volume of the drive cylinder.

This procedure is based on the following reference method:

- ASTM Standard D D2937-04 "Standard Test Method for Density of Soil in Place by the Drive-Cylinder Method. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org

If the laboratory has modified the procedure from the reference method(s) a list of modifications will be provided in Section 16.0.

3.0 Definitions

Not Applicable

4.0 Interferences

This method is not appropriate for samples that can be "altered" during sampling, shipping and/or processing.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-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.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Not applicable.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Oven, 110°C (+/-5°C), Barnstead LC Oven Model# 3513 or equivalent.
- Top loading balance, Mettler Model# PB3002 or equivalent.
- Aluminum measuring pans, Fisher Scientific or equivalent.
- Stainless steel spatulas and spoons, Fisher Scientific or equivalent.
- Ruler/meter stick with millimeter increments
- Heat shield gloves / Oven Tongs, Fisher Scientific or equivalent.

7.0 Reagents and Standards

Not Applicable

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection. Sample collection procedures are provided in this SOP for guidance only. The laboratory recommends that all samples be collected in accordance with a client field and sampling plan. Immediately after collection the sample(s) should be cooled and stabilized with packing material or wax to prevent shifting during transport.

Holding times are not applicable. Unless otherwise specified by client or regulatory program, after analysis samples are held for a minimum of 30 days and then disposed of in accordance with applicable regulations.

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Calibration and Standardization

Check the calibration of the balance on each day of use prior to use using at least 2 Class S weights that bracket the range of use. Record in the logbook designated for this purpose.

Check the temperature of the drying oven(s) each day of use, prior to use. Record in the logbook designated for this purpose.

10.2 Sample Preparation/Analysis

Clean the outside of the sample collection tube then remove the end caps, wax any other protective material from each end of the sample collection tube. Remove any loose material from the collection tube. If the sample extends beyond the tube, trim the end of the sample so that it is equal to the length of the tube.

Note: If a sample is received in a container other than a collection tube, the lab must create an NCM. The lab will then pack a clean, empty, and appropriately sized collection tube with the sample and proceed with the test method.

1. Weigh the tube and sample. Enter value into the TALS Batch Worksheet under "Cyl &+ Samp Wt."
2. Label a clean aluminum pan with the sample ID, and weigh the pan. Record the weight in the TALS Worksheet under "Pan Wt 1."
3. If the sample fills the entire tube, measure the length of the tube. Enter the value in the TALS Worksheet under "Cylinderlength." If the sample does not fill the entire tube, measure the length of empty space in the tube and subtract it from the total length. Then enter that value into the TALS Worksheet.
4. Measure the diameter of the sample tube, and enter the value in the TALS Worksheet under "Cyl Diameter."
5. Empty the sample into the weighed pan with the sample ID. Weigh the pan and sample, and enter the value into the TALS Worksheet under "PanSampWet1." If the entire sample weight cannot be used, thoroughly mix the sample with a spatula to homogenize. Once homogenized measure at least 100g of the sample into the pre-weighed pan, and enter the weight measurement into the TALS Worksheet.
6. Weigh the clean empty tube and enter the weight in the TALS worksheet under "Cylinder Wt."
7. Place the sample into an oven maintained at 110C and allow the sample to dry for a minimum of 16 hours. After this time period has elapsed, remove the pan from the oven and re-weigh. Enter this weight measurement into the TALS Worksheet under "PanSampDry1."

The TALS method calculates the moisture content, sample length, sample volume and in-place density using the equations give in Section 11.0.

11.0 Calculations / Data Reduction

11.1 Calculations

Percent Moisture Content

$$\text{Moisture Content, \%} = [(A-B) * 100]/B$$

Where:

A = pan + wet sample, g

B = pan + dry sample, g

Sample length:

$$L = L_1 - (L_2 + L_3) \text{ mm}$$

Where:

L = sample length

L₁ = length of sample tube

L₂ = average recovery, top

L₃ = average recovery, bottom

Sample volume:

$$V = [(\pi(D/2)^2)L]$$

Where:

V = sample volume (calculated)

D = sample tube diameter

L = sample length

In-place Density:

$$= m_1/V \text{ g/cm}^3 \text{ (dry)}$$

$$= m_2/V \text{ g/cm}^3 \text{ (wet)}$$

Where:

= calculated dry density

m₁ = mass of sample, dry

m₂ = mass of sample, wet

m₃ = mass of sample tube

V = sample volume

11.2 Data Review

Primary Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Enter the batch information into LIMS and complete the batch editor and worksheet for each extraction and cleanup batch performed. Initiate NCMs for any anomalies observed during the process. Set the status of each batch to 1st level review.

Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of each batch to second level review.

Run the QC Checker, review the deliverable and set the job to lab complete.

12.0 Method Performance

12.1 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

- Four aliquots of QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The QC check sample should be prepared using a material that is similar to samples and will provide a measurable (non-zero) result.
- Calculate the average recovery, standard deviation, and relative percent difference of the recovery for each analyte of interest.
- The relative % difference must be within +/- 30%.
- If any analyte does not meet the acceptance criteria, the test must be repeated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.
- Until the IDOC is approved by the QA Manager (or designee); the trainer and trainee must be identified in the batch record.
- Further details concerning demonstrations of proficiency are described in SOP BR-QA-011.

13.0 Pollution Control

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 Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

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 BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste- Satellite Container: 5 Gallon Plastic Bucket.

15.0 References / Cross-References

- ASTM Standard D D2937-04 "Standard Test Method for Density of Soil in Place by the Drive-Cylinder Method. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

16.0 Method Modifications

None

17.0 Attachments

None

18.0 Revision History

Revision 8.0:

- Title Page: Updated Approval signatures and copyright information to include Eurofins
- Headers: removed TestAmerica logo and added Eurofins logo
- Added section 12.2 to detail IDOC procedures

Previous Revisions retained by QA department

Appendix B: Porosity Calculation

Porosity is calculated using the sample's determined Specific Gravity and In Place Density. The calculation is as follows:

$$n = 100 [1 - (pb/pd)]$$

Where:

n = porosity in %

pb = bulk density of the sediment in g/cm³

pd = particle density in g/cm³

Fetter, C.W. 2001. Applied Hydrogeology. Prentice Hall, Upper Saddle River, NJ. on p. 70. Book has 598 p.

**Title: Moisture, Ash, and Organic Matter of Peat & Other Organic Soils
(ASTM D2974- 07a – Methods A & C)**

Approval Signatures:



Don Dawicki
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Approval Date: April 13, 2018

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1.0 Scope and Application

This SOP describes the laboratory procedure for the measurement of moisture content, ash content, and organic matter in organic soils. This procedure may also be used to determine moisture content in organic clays, silts, and mucks.

2.0 Summary of Method

To determine moisture content, a portion of sample is dried in an oven maintained at a temperature of 105 ± 5 °C for 16 hours. The moisture content of the sample is calculated as the difference between the “wet weight” and the “dried weight” of the sample expressed as a percent of oven dry mass.

To determine ash content, the oven-dried sample is ignited in a muffle furnace at a temperature of 440 ± 22 °C for 16 hours. The substance that remains after ignition is ash. The ash content is determined by dividing the mass of the ash by the mass of the oven-dried sample.

The percent organic matter is calculated by subtracting the percent ash content from one hundred. Fractional organic carbon is calculated by multiplying the total organic matter result by 0.58.

This procedure is based on the following reference method:

- ASTM Standard D 2974-07a “Standard test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils”. ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org
- VA30007.09.024 “Sampling and Analysis of Fraction Organic Carbon (foc) in Soils, August 2003. Retrieved from <http://www.epa.ohio.gov/portals/30/vap/tgc/archived/VA30007-09-024.pdf>.

If the laboratory has modified the procedure from the reference method(s) a list of modifications will be provided in Section 16.0.

3.0 Definitions

Not Applicable

4.0 Interferences

Not Applicable

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-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.

5.1 Specific Safety Concerns or Requirements

The recommended weight for this method is 50 g, however, samples containing a large volume of organic material or are contaminated with hydrocarbon can ignite in the muffle furnace and create smoke. When there is a concern that the sample will ignite and produce smoke a smaller aliquot of 5 to 10 grams can be used for this test.

5.2 Primary Materials Used

There are no materials with a health rating of 3 or 4 used in this procedure. If a chemical material is listed, employees must review the information in the SDS (Safety Data Sheet) for each material before using it for the first time or when there are major changes to the SDS

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Oven, 105°C ($\pm$ 5°C), Barnstead LC Oven Model# 3513 or equivalent.
- Top loading balance, Mettler Model# PB3002 or equivalent.
- Aluminum measuring pans not less than 100 mL capacity, Fisher Scientific or equivalent.
- Stainless steel spatulas and spoons, Fisher Scientific or equivalent.
- Muffle Furnace, 440°C ($\pm$ 22°C), Barnstead Model# 30400 or equivalent.
- Heat shield gloves / Oven Tongs, Fisher Scientific or equivalent.

7.0 Reagents and Standards

Not Applicable

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection. Sample collection procedures are provided in this SOP for guidance only. The laboratory recommends that all samples be collected in accordance with a client specified sampling plan.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time ¹	Reference
Solid	Glass	50g	4°C	NA	D2974-07A

Unless otherwise specified by client or regulatory program, after analysis samples are held for a minimum of 30 days and then disposed of in accordance with applicable regulations.

9.0 Quality Control

Not Applicable

10.0 Procedure

10.1 Calibration and Standardization

Check the calibration of the balance on each day of use prior to use using at least 2 Class S weights that bracket the range of use. Record in the logbook designated for this purpose.

Check the temperature of the drying oven(s) each day of use, prior to use. Record in the logbook designated for this purpose.

10.2 Analysis

Percent Moisture Content

For each sample label a clean aluminum pan with the sample ID.

Measure the weight of an empty aluminum pan to the nearest 0.01g for each sample and enter the weight measurements in the LIMS worksheet.

Homogenize the sample by mixing thoroughly with a spatula.

Place a pre-weighed aluminum pan onto the balance and measure at least 50 g of sample into the aluminum pan. Record the weight measurement in the LIMS worksheet and repeat for each sample.

Place the aluminum pans in an oven maintained at 105 ± 5 °C and let the samples dry for a minimum of 16 hours or until constant mass. Remove the aluminum pans from the oven and re-weigh. Record the weight measurements in the LIMS worksheet.

The LIMS worksheet calculates percent moisture content using the calculations provided in Section 11.0.

Ash Content

Place the oven-dried specimen (from moisture content) into a muffle furnace set to gradually heat to 440 ± 22 °C. Allow the samples to ash for a minimum of 16 hours. Remove the aluminum pans from the oven and let them sit until they are cool to the touch. Reweigh each pan and record the weight measurement in the LIMS worksheet.

The LIMS worksheet calculates ash content, total organic matter, and fractional organic carbon using the calculations provided in Section 11.0.

11.0 Calculations / Data Reduction

11.1 Calculations

- Percent Moisture Content

$$\text{Moisture Content, \%} = [(A-B) * 100]/A$$

Where:

A = as received test specimen, g

B = mass of the oven dried specimen, g

- Percent Ash Content

$$\text{Ash Content, \%} = (C * 100)/B$$

Where:

C = ash, g

B = oven dried test specimen, g

- Percent Organic Matter

$$\text{Organic Matter, \%} = 100.0 - D$$

Where:

D = ash content, %

- Fractional Organic Carbon

$$\text{FOC, \%} = E * 0.58$$

Where:

E = Percent Organic Matter

11.2 Data Review

Primary Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Enter the batch information into LIMS and complete the batch editor and worksheet for each extraction and cleanup batch performed. Initiate NCMs for any anomalies observed during the process. Set the status of each batch to 1st level review.

Secondary Data Review

Review project documents such as the Project Plan (PP), Project Memo or any other document/process used to communicate project requirements and verify those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Check the batch editor and worksheet to verify the batch is complete and any outages are documented with an NCM along with the results of any corrective actions taken. Set the status of each batch to second level review.

Run the QC Checker, review the deliverable and set the job to lab complete.

12.0 Method Performance

12.1 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

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 Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

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 BR-EH-001. The following waste streams are produced when this method is carried out.

- Solid Waste- Satellite Container: 5 Gallon Plastic Bucket.

15.0 References / Cross-References

- ASTM Standard D 2974-07a "Standard test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils". ASTM International, West Conshohocken, PA 2003, DOI: 10.1520/C0033-03, www.astm.org
- VA30007.09.024 "Sampling and Analysis of Fraction Organic Carbon (FOC) in Soils, August 2003. Retrieved from <http://www.epa.ohio.gov/portals/30/vap/tgc/archived/VA30007-09-024.pdf>.
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

16.0 Method Modifications

- The laboratory does not perform the subsampling procedure described in Section 7 (7.1 and 7.2) of the reference method.
- The laboratory allows the use of less than 50g of sample when it is highly impacted with hydrocarbons or contains large amounts of organic content as a safety precaution to minimize fire and smoke during the 440°C burn process.

17.0 Attachments

None

18.0 Revision History

Revision 9.0

- Title Page: Updated approval signatures
- Minor formatting and typographical corrections

Previous revision are retained by QA.

**Title: Total Organic Carbon
Lloyd Kahn Method**

Approval Signatures:



Don Dawicki
Laboratory Director



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Matt Kirk
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Ben Kirchner
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Approval Date: January 17, 2017

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1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of total organic carbon (TOC) in soil and solid materials.

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used to determine total organic carbon in soil and solid materials. This procedure may not be amenable to oily matrices.

The routine reporting limit is 1000 mg/kg based on an initial sample weight of 10 mg.

2.0 Summary of Method

10 mg of dried sample is transferred to a tin capsule, treated with phosphoric acid and dried in an oven at a temperature 105°C for 30-60 minutes to separate the organic carbon from inorganic carbonates and bicarbonates. The sample is analyzed on an instrument where it is pyrolyzed in an inductive type furnace. The carbon is converted to carbon dioxide and measured by a differential thermal conductivity detector.

This procedure is based on the following reference documents:

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1988, authored by Lloyd Kahn, Quality Assurance Specialist.

If the laboratory's SOP has been modified from the above referenced document, a list of modifications is provided in Section 15.0 of this SOP.

3.0 Definitions

A list of general laboratory terms and definitions are provided in Appendix A.

4.0 Interferences

Volatile organics in the sediments may be lost in the de-carbonation step resulting in a low bias.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-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.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Table 1 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the SDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. 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. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 Equipment and Supplies

- Drying Oven: Capable of maintaining a temperature of $105 \pm 2^{\circ}\text{C}$.
- Carlo Erba Elemental Analyzer Model EA1108 and Model NA 1500 or equivalent.
- Costech Elemental Analyzer: Model 4010 or equivalent.
- Analytical Balance: Capable of weighing to the nearest 0.0001g.
- Aluminum Weigh Boats.
- Tweezers
- 5mm X 9mm tin capsules
- Quartz Columns: Costech Analytical or equivalent.
- Quartz wool: for segregating and containing column materials
- Copper Wire, Reduced: Costech Analytical or equivalent.
- Tungsten on Alumina: Costech Analytical or equivalent.
- High Temperature Gloves
- Clear Plastic Sample Trays: Costech Analytical or equivalent.
- 100ul Hamilton syringe or similar

7.0 Reagents and Standards

7.1 Reagents

- Reagent water
- Phosphoric Acid, Concentrated: Reagent Grade, J.T. Baker recommended.

Phosphoric Acid Solution (1:19): Add approximately 100 mL of reagent water to a 200 mL volumetric flask. Add 18.34 g of concentrated phosphoric acid to the volumetric flask then adjust to volume with reagent water. Mix the solution well then transfer the solution to a 250 mL

polyethylene bottle. Assign an expiration date of six months from date made and store the solution at room temperature.

7.2 Standards

- Potassium Hydrogen Phthalate (KHP) (Primary Standard Grade) Used to calibrate the instrument. 47.05% Carbon by weight
- Laboratory Control Samples (LCS) Material, Organic Material of known Carbon percentage: Purchased from LECO Corporation.

1% Carbon KHP Solution (10,000 mg Carbon/L): Add 50 mL of reagent water to a 100 mL volumetric flask. Add 2.128 g of KHP and dissolve completely. Adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration of 6 months from the date prepared and store at room temperature.

0.1% Carbon KHP Solution (1000mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 5 mL of 1 % Carbon KHP solution to the flask and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

0.01% Carbon KHP Solution (100mg Carbon/L): Add approximately 25 mL of reagent water to a 50 mL volumetric flask. Add 0.5 mL of 1% Carbon KHP Solution and adjust to final volume with reagent water. To mix the solution, cap the flask and invert. Allow the air bubble to reach the top of the flask. Repeat 9 times. Assign an expiration date of 6 months from the date prepared so long as the parent solution does not expire sooner, in which case use the earliest expiration date. Store the solution at room temperature.

Note: Alternatively a 10,000mg/L TOC standard may be purchased from a reputable vendor (Spex Certiprep, SCP Science or ERA) and diluted appropriately to prepare the intermediate solutions above.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so sampling procedures are not included in this SOP. Sampling requirements may be found in the published reference method. Listed below are the recommended minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time	Reference
Solids	Amber glass	10 g	Chilled to $\leq 4^{\circ}\text{C}$	14 Days	Lloyd Kahn Method

Holding time is calculated from date of sample collection. Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The following QC samples are analyzed with each batch:

QC Item	Frequency	Acceptance Criteria
Method Blank (MB)	1 in 20 or fewer samples	< RL
Laboratory Control Sample (LCS)	1 in 20 or fewer samples**	%R (75-125) **Quad RSD 18%
Sample Quadruplicate	1 in 20 or fewer samples (Only when site specific P&A has been requested)	SD ($\leq 3 \times$ SD of site specific P&A study)
Matrix Spike	Client request	%R (75-125)
Duplicate/Matrix Spike Duplicate	Client request	RPD 20%

**If a site specific P&A study not requested analyze the LCS in quadruplicate as a measure of method precision.

9.2 Instrument QC

The laboratory analyzes the following instrument check standards:

QC Item	Frequency	Acceptance Criteria
Initial Calibration (ICAL)	Initial Method Set-Up, after combustion chamber is changed (approx. every 200 drops)	Correlation coefficient must be >0.995
Initial Calibration Verification (ICV)	Following Calibration	%R (75-125)
Calibration Verification (CCV)	Every 20 drops and at the end of the analytical sequence	%R (75-125)
Calibration Blank (CCB)	After every CCV	<RL

10.0 Procedure

10.1 Calibration

Analyze a calibration curve each time the combustion column is changed. Change the column after 200 drops or when you experience QC recovery issues, odd peak shapes or baseline issues. The column change procedure is provided in Appendix B.

The recommended formulations for each calibration level are provided in the following table:

Calibration Standards	1.0% C KHP uL	0.1% C KHP uL	0.01% C KHP uL	% Carbon KHP	Carbon (mg)	mg/Kg of Carbon (10mg sample)
Level 1	0	0	0	47.05	0	0
Level 2	0	0	100	47.05	0.010	1000
Level 3	0	40	0	47.05	0.040	4000
Level 4	25	0	0	47.05	0.25	25000
Level 5	50	0	0	47.05	0.500	50000
Level 6	75	0	0	47.05	1.000	75000

Using a volumetric Hamilton or similar syringe, measure the specified volume of standard into a tin capsule. Dry the calibration levels completely by placing in the oven at 105°C for 60 minutes. Fold the capsules. A blank (empty) tin must be dropped for the calibration blank. Proceed to Section 10.6 for analysis instructions.

The instrument software system plots peak area against mg of Carbon and calculates a correlation coefficient using standard linear regression. The correlation coefficient (r) must be ≥ 0.995 for the calibration to be considered acceptable. If it is not, repeat the calibration prior to analysis.

10.2 Troubleshooting

- Calibration passes at > 0.995 correlation, but LCS fails abnormally low: Re-calibrate.
- Large peak before Carbon peak; Indicates leak in system, perform leak test, isolate and repair leak.
- Carbon peak “maxes out” at instrument 1200mv (peak has flat top): Reanalyze sample at lower weight.
- No peaks on any chromatograms, no results: Gases to instrument may be off. Turn on all gasses at valve manifold.
- Autosampler will not work at all: Gasses to instrument may be off. Turn on all gasses at valve manifold.
- Carry over; Clean autosampler slide, if persists reduce sample mass. Note sample carryover in NCM. Oily samples may not be amenable to this test.
- Single chromatogram shows results at bottom of page, but no peak or baseline in chromatogram window: Re-print single chromatogram.
- Some or all chromatograms show carbon peak at same retention time as CCV, but peak is not identified as carbon, or is identified as another element: Retention time shifted. Adjust retention time in calibration window, and reprint chromatograms.
- Upon recalibration, peaks are not being identified as carbon: In calibration window, general tab, adjust retention time to match peaks. Starting at level 1, “Open Standard”, open level 1 curve pt. in calibration directory, click “Add Peak” button, click on peak itself. Increase level #, opening standard for each curve pt and add each peak. Carbon Tab should have all five calibration points on curve, if done correctly.
- Peaks in chromatograms identified as carbon, but all results in summary table below chromatogram are zero: Current calibration not associated with run when started. Open current calibration, copy first two columns for all points (5 rows) in small table in general tab. Then, open calibration that was associated with run (should be empty) and paste into table in calibration tab. Reprint all chromatograms on run.
- Software crashes during analysis: Boot up software normally. Chromatograms already printed/analyzed are ok, but, sample that was analyzing during shutdown is lost. Restart table at next sample by un-checking “run” box for samples already run and sample that was lost.

- Autosampler error causes few samples to remain in autosampler tray after run has finished: Identify samples that got stuck. Create a new run and analyze stuck samples (with initial weights) with bracketing QC. No MB/LCS needed.
- Autosampler error causes many sequential samples to remain in autosampler tray after run has finished (usually end of run): Add rows onto existing table. Identify samples that did not get analyzed and repeat IDs and weights into added rows. Restart table. All analyzed samples' status should be blue (analyzed), added rows should be green (not analyzed yet).

10.3 Sample Preparation

Homogenize the sample using the procedure described in SOP BR-QA-020. Refer to Appendix D for Marine Sediment Processing, and Appendix E for Black Carbon Processing

Dry approximately 5-10 g of sample in at 105 °C for 12-24 hrs. (The sample from the moisture fraction may be used for this step.) Disaggregate the sample to break up clumps to ensure exposure to acidification in next step. Do not grind the sample.

Due to the sample size required by the instrumentation, if the sample matrix contains particles that are too large for analysis, the sample will be sieved using a 200 micron (#35) sieve.

For each field sample prepare a tin for analysis. Using tweezers, and working directly from the box, place a tin capsule on the analytical balance and tare the balance. Using the small sample scoop, add approximately 10 mg (or the project specified sample weight) of sample to a tin capsule. Record the actual sample weight used on sample preparation log. Remove the capsule from the balance and place into one of the aluminum holding trays.

To prepare the method blank, set an empty tin capsule into an aluminum holding tray (this tin must be acidified with the remainder of the samples).

To prepare the LCS, weigh 9 to 11 mg of the LECO LCS material into two tin capsules and set them in sequence in an aluminum holding tray. Prepare the LCS in quadruplicate if site specific P&A study has not been requested in the project.

For the matrix spike, weigh out an additional sample aliquot and record its weight. Add 35 uL of 1% KHP calibration stock.

For the sample duplicate, weigh out an additional sample aliquot.

Add one to two drops of 1:19 phosphoric acid to each tin capsule (enough to sufficiently cover the sample until reaction ceases). Place the aluminum trays into a drying oven set to a temperature of 105 ±2 °C for 30-60 minutes or until all samples appear dry.

Using tweezers pinch the top of each tin capsule closed and compress the capsule around the material inside. Work carefully so as not to tear the capsule, but crush it down to the smallest size. Set the prepared samples in line in a clear plastic sample tray for storage, or place directly into an autosampler tray for analysis. For the latter, leave positions open for the CCV check standards and associated calibration blanks.

Prepare the ICV, CCV standards and blanks as follows:

Prepare an ICV for each sequence. To prepare the ICV, weigh 9 to 11 mg of the LECO LCS material into a tin capsule.

For each CCV, transfer 35 μ L of 1% KHP solution into a tin capsule. Dry the capsules in a drying oven set to a temperature of 105 ± 2 °C for 30-60 minutes or until all samples appear dry. Fold the capsule up and compress down to the smallest size possible. Prepare enough CCVs to ensure a frequency of every 20 drops and the end of the analytical sequence. For each associated calibration blank, leave an empty position in the auto-sampler tray (a tin must be analyzed for calibration blanks).

10.4 Preparation of the ICV, CCV and Blanks

For each ICV weigh ~9-11 mg of the LECO LCS material into a tin capsule.

For each CCV, transfer 35 μ L of 1% KHP to a tin capsule. Dry the capsules in a drying oven at 105 °C for 30-60 minutes or until dry. Fold the capsule and compress down to the smallest size possible. Prepare enough CCVs to ensure a CCV frequency of every 20 drops and at the beginning and end of the analytical sequence. Use a folded empty tin for each calibration blank (not acidified).

10.5 Software Set-up and Analysis of a Curve

If there is not a valid curve or the valid curve is not listed in the software, create a calibration curve in the analytical software. Enter the standard type, level, and mg of KHP used for each calibration level. Enter each sample ID and their respective weights into the instrument software, enter a weight of 10 mg for the method blank and calibration blanks and save the sample table. Enter the weight for the LCS. Add the tin capsules to the autosampler tray in sequence and set the tray into the autosampler carriage.

An example analytical sequence that includes ICAL is as follows:

Initial Calibration (calibration blank and 5 calibration standards)

ICV

ICB(blank tin)

CCV

CCB(blank tin)

MB(acidified tin)

LCS (Routine=4 reps; Dixon=2reps)

Samples (Routine=1 rep; Dixon=2reps)

CCV

CCB(blank tin)

Samples (Routine=1 rep; Dixon=2reps)

CCV

CCB(blank tin)

Click the "start" icon to begin the analysis.

11.0 Calculations / Data Reduction

11.1 Calculations

The instrument software calculates TOC using the area response from the calibration curve and sample mass used. The determination of TOC is performed by the laboratory's LIMS system. See Appendix C for equations for percent recovery and relative percent difference.

11.2 Data Review

11.2.1 Primary Data Review

Enter the results of the quadruplicate analysis into the EXCEL spreadsheet designated for this purpose. Compare the standard deviation derived from the quadruplicate sample or LCS against the standard deviation from the appropriate P&A study. If the SD of the sample quadruplicate is greater than 3 times the SD of the study, initiate a nonconformance memo and notify the PM to determine if further action is necessary.

Upload the instrument data to the laboratory information system (LIMS) "TALS". Evaluate the sequence against the acceptance criteria given in Table 2. Perform the recommended corrective action as necessary. If corrective action is not taken or is not successful, initiate a nonconformance memo (NCM) to document the situation. Set the Batch to 1st level reviewed. For Dixon analysis, an additional 2 reps must be performed if the original reps yielded a RSD greater than 40. Then the four different replicates must be entered into the Dixon Outlier Template (FWC200A for 4 reps or FWC200B for 3 reps) from the lowest to the highest result.

Assemble supporting documents including the quad sample calculation spreadsheet and forward to secondary review staff.

11.2.2 Secondary Data Review

Spot-check the analytical results. Verify that acceptance criteria were met and if the results do not fall within the established limits verify the recommended corrective actions were performed. If corrective action was not taken or is unsuccessful, ensure the situation is documented with a nonconformance memo (NCM) and ensure data is qualified accordingly.

Set the batch to second level review. Scan and attach copies of supporting documentation such as; run logs, raw data and quad sample spreadsheet to the batch. Set the job to lab complete, review the form set, correct any problems then forward supporting documentation to report management.

11.2.3 Data Reporting

The report format, application of data qualifiers and creation of the data deliverable is performed by the LIMS using the formatter set by the project manager during log-in.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 Laboratory Records.

12.0 Method Performance

12.1 Detection Limit (DL), Limit of Detection (LOD) and Limit of Quantitation (LOQ)

Establish a DL, LOD and LOQ for the method. Verify the LOQ at initial method set up following the procedures specified in laboratory SOP BR-QA-005. Verify the LOD and LOQ at the frequency established for the method using the procedures specified in BR-QA-005. The frequency of LOD and LOQ verification depends on the strictest frequency of the regulatory program for which the method supports. The frequency requirement is documented in a spreadsheet maintained by the QA Department.

12.2 Annual Precision and Accuracy Study

It is recommended by the laboratory that a P&A study be performed for each project site. In the absence of a site specific P&A study the laboratory will analyze the LCS in quadruplicate for comparison to an annual P&A study on historical LCS recoveries of at least 15 data points. Perform a precision and accuracy study annually or as directed in project setup by analyzing 15 replicates of a representative sample (LCS). Create a control chart of the results, calculate the standard deviation and generate an upper and lower limit at 3X the standard deviation. Use the results of the appropriate P&A study for evaluation of the quadruplicate LCS or sample included in each batch.

13.0 Pollution Control

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 Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

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 BR-EH-001 *Hazardous Waste*.

The following waste streams are produced when this method is carried out.

- Caustic waste – 2.5 L glass satellite container.
- Acidic Waste - 2.5L glass satellite container

The satellite containers are labeled "Hazardous Waste" along with the type of waste category generated. Authorized personnel routinely transfer the contents of the satellite containers to the hazardous waste storage room for future disposal in accordance with Federal, State and Local regulations.

15.0 References / Cross-References

- EPA Region II Document Determination of Total Organic Carbon in Sediment, July 27, 1998, authored by Lloyd Kahn, Quality Assurance Specialist.
- Corporate SOP CW-E-M-001 Corporate Environmental Health and Safety Manual
- Laboratory SOP BR-QA-005, Procedures for the Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ) and Reporting Limits (RL).
- Laboratory SOP BR-QA-011 Employee Training
- Laboratory SOP BR-EH-011 Hazardous Waste
- Laboratory SOP BR-QA-014 Laboratory Records
- Laboratory Quality Assurance Manual (QAM)

16.0 Method Modifications

The laboratory procedure is modified from the reference method as follows:

Modification Number	Method Reference	Modification
1	TOC by Lloyd Kahn	The Laboratory uses 1:19 (w/w) phosphoric acid to decarbonize the sample (to reduce sample loss from effervescence) and dries the sample in an oven at 105°C.
2	TOC by Lloyd Kahn	Due to the small sample size the laboratory dries and disaggregates the sample prior to analysis. This step improves precision associated with high moisture or clay type matrices.
3	TOC by Lloyd Kahn	P&A studies are not performed per the reference method due to variability in project sites. See section 12.2 for the P&A procedure that the laboratory uses.

17.0 Attachments

- Table 1: Primary Materials Used
- Table 2: QC Summary & Recommended Corrective Action
- Appendix A: Terms and Definitions
- Appendix B: Column change procedure
- Appendix C: Equations

18.0 Revision History

BR-WC-008, Revision 16.0

- Added Appendix D for Marine Sediment Process.
- Added Appendix E for Black Carbon Process.
- Combined BR-ME-008 and BR-ME-024 .
- Section 2: Added 30-60 minute requirement
- Section 10.1: Clarified a blank tin must be analyzed for calibration blank.
- Section 10.3: Clarified acidification-added verbiage “until reaction ceases.”; Added sample size requirement is due to instrumentation
- Section 10.3: Clarified MB is an acidified tin, and calibration blanks must analyze a blank tin.
- Section 10.4: Clarified calibration blanks must analyze a blank tin.

- Section 10.5: added sequence clarification for Routine & Dixon analysis, as well as clarification for blank analysis.
- Section 11.12.1: Added when to perform additional reps for Dixon analysis and to fill out Dixon Outlier Template FWC200.

Previous revisions are retained by the QA Department.

UNCONTROLLED

Table 1: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Phosphoric Acid	Corrosive	1 Mg/M3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action (TOC Lloyd Kahn)

QC Item	Frequency	Acceptance Criteria	Recommended Corrective Action ¹
ICAL	Following each column change and when CCV failure indicates calibration may no longer be valid.	correlation coefficient ≥ 0.995	Standards check, re-calibration
CCV	Every 20 drops and at the end of the analytical run	%R (75-125)	Re-prepare and reanalyze samples not bracketed by passing standard. If CCV fails high, and TOC is not detected in any of the bracketed samples, the samples without TOC may be reported without reanalysis.
CCB	Following each CCV	< RL	Re-prepare and reanalyze batch.
Method Blank (MB)	Once per batch of 20 samples	< RL	Re-prepare and reanalyze batch.
LCS	Once per batch of 20 samples. Prepared in quadruplicate unless site P&A study is performed, then analyze as single injection.	%R (75-125)	Re-prepare and reanalyze batch.
Sample Quadruplicate	When site specific P&A study is specified. If no quad specified for any jobs included in the batch analyze the LCS in quadruplicate.	SD $\leq 3X$ annual P&A SD	If sample quad, notify PM. If LCS quad, reanalyze the entire batch.

¹The recommended corrective action may include some or all of the items listed in this column. The corrective action taken may be dependent on project data quality objectives and/or analyst judgment but must be sufficient to ensure that results will be valid. If corrective action is not taken or is not successful, data must be flagged with appropriate qualifiers.

Appendix A: Terms and Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Appendix B: Column Change Procedure:

Turn off the helium and oxygen supplies to the instrument.

Dial the left furnace temperature to a reading of 052 (this equates to 520°C). Wait until the temperature drops below 600°C to remove the column.

Remove the panel covering the furnace and unscrew the autosampler connection from the top of the column.

Unscrew the fitting at the bottom of the column and remove.

Lift the column up and out of the furnace using high temperature gloves.

CAUTION: The column will still be 500-600°C. Do not touch the center portion of the column. Place the spent column in the metal can designated for this purpose.

Lay a new quartz column on the bench top, measure and mark off for the following:

- One inch up from the bottom and add a ½ inch plug of quartz wool. Note: pack the quartz wool tightly enough for it to stay in place.
- Pour in 2 ½ inches of copper wire
- Pack another ½ inch quartz wool plug on top of the copper
- Pour in 3 inches of tungsten
- Pack a final ½ inch quartz wool plug on top of the tungsten

Place the new column into the furnace and reconnect the top and bottom fittings. Snug these up, but don't over tighten.

Replace the panel covering the furnace, dial the furnace temperature back to 102 (this equates to 1020°C), and turn the helium and oxygen supplies back on.

When the instrument comes up to operating temperature, it is ready to calibrate.

Appendix C: Equations

Percent Recovery (%R) LCS and CCVs

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

Where:

SR= Sample Result

SA=Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

Where:

D1 = Sample result

D2 = Duplicate Result

Appendix D: Marine Sediments High in Inorganic Carbon

Sample Preparation

Transfer approximately 10 g of a thoroughly mixed sample to an aluminum weigh dish, and dry in the 105°C oven. Grind the sample with the pink mortar and pestle to a fine powder. Record the weight of a 250 mL Teflon beaker then transfer ~ 5 g of the ground sample to this beaker.

If the sample is to be spiked, weigh the beaker to the nearest 0.1mg and record the weight. Likewise determine and record the weight of the added sample. Add 0.1g of NIST 1632b Trace Elements in Coal (80.11% Carbon) to the sample. Record the weight added. Evenly distribute the spike over the sample and use a glass stir rod to mix the spike with the sample. Do not use that stir rod with any other sample.

Use Talc-free latex gloves from this point on to minimize the risk of acid burns. Add several drops of 1:1 HCL to each sample and stir each sample with its own glass stir rod. Carefully rinse the stir rod and beaker walls with DI water using a fine-tipped squirt bottle. Use only what is needed to bring the entire sample to the bottom of the beaker. **When adding water to acid use necessary precautions to avoid splashing!** Samples with high concentrations of inorganic carbon may effervesce to the point of overflowing the beaker, so take care to add the acid in small aliquots and stir vigorously. If the sample “boils over” it must be re-prepared. Continue to add 1:1 HCL in small aliquots until there is no further reaction, taking sample to dryness after each addition of acid in a 105-degree oven.

Dry the treated samples in the oven after each acid/water addition. Do not add more than a total of 200 mL of 1:1 HCL to any sample.

NOTE: *Samples are hygroscopic and will absorb water if they are exposed to air for too long.*

Weigh beaker with residue and record the residue weight measurement. After the sample is thoroughly dry, scrape the sample residue from the beaker and grind to a powder using the pink mortar and pestle. Transfer the ground sample to a clean, dry 40-mL vial reserved for this analysis.

NOTE: *Depending on the nature of the sample, it may be difficult to completely remove the dried residue from the beaker or to grind it to a homogenous powder. Where difficulties are encountered, make a note on the preparation worksheet.*

Analysis

Perform TOC analysis on processed sample material as outlined in section 10.0 of this SOP.

Appendix E: Determination of Black Carbon in Sediment Procedure

1. Obtain a representative subsample of the sediment. Weight 10 grams of sample into a clean pre-tared aluminum drying pan or equivalent.
2. Dry the sample at 105°C for at least 12 hours.
3. Grind the sample using a mortar and pestle.
4. Sieve the sample using a number 35 sieve (500 μ m).
5. Treat the sample with phosphoric acid. Add acid drop wise until effervescence is no longer observed.
6. Dry the sample at 105°C for 1 hour.
7. Set aside an aliquot of the sample at this stage for direct TOC analysis, reported without correction for the IN623 percent solids. Continue with the sample for Black Carbon.
8. Place the dried sample into a clean crucible and cover the sample.
9. Bake the samples at 375°C in a muffle for 24 hours or until the LCS is +/- 50% of the true value.
10. Allow the samples to cool and transfer approximately 10.0 mg into each of two tin capsules.
11. Transfer the sample (in the tin capsules) to the TOC analyzer for analysis by the Lloyd Kahn Method.
12. The sample is pyrolyzed in an inductive type furnace, where the carbon is converted to carbon dioxide, which is measured using a differential thermal conductivity detector.
13. The results will be reported as mg/Kg Black Carbon.

Note: Black carbon LCS material: NIST Standard Reference Material 1944 New York-New Jersey Waterways Sediment.

References:

Orjan Gustafsson, Thomas D. Bucherli, Zofia Kukulska, Mette Andersson, Claude Largeau, Jean-Noel Rouzaud, Christopher M. Reddy and Timothy I. Eglinton (December 2001) Evaluation of a Protocol for the Quantification of Black Carbon in Sediments, Global Biogeochemical Cycles, Volume 15, pages 881-890.

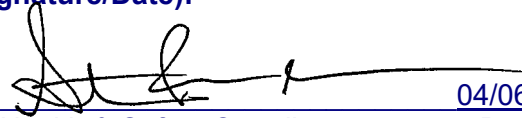
Orjan Gustafsson, Farnaz Haghseta, Charmaine Chan, John MacFarlane & Philip M. Gschwend (1997) Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability, Environmental Science & Technology, Volume 31, pages 203-209.

Title: ANALYSIS OF PESTICIDES AND PCBs

[Method: EPA Method 608.3]

Approvals (Signature/Date):


Technology Specialist 04/05/18
Date


Health & Safety Coordinator 04/06/18
Date


Quality Assurance Manager 04/17/18
Date


Technical Director 04/06/18
Date

This is a new SOP

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of concentrations of pesticides and PCBs in wastewater. It is based on EPA Method 608.3. The working linear range is highly instrument, column, and compound dependent. A list of analytes and CAS numbers are listed in Table 1. Additional analytes that may be analyzed are listed in Table 2 with CAS numbers. Reporting limits are available in TALS.
- 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.
- 4.4. The DDT analogs (DDT, DDD, and DDE) may cause substantial interference with the last major peak of Aroclor 1254. A standard of the DDT analogs is analyzed daily to help monitor for such interference.

- 4.5. Phthalate esters may cause major interferences in the determination of analytes. Phthalate esters are common in plastic materials; therefore, plastic must be avoided in all processes.

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 EH&S Director 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: ChemStation data system or equivalent
 - 6.1.3. Gas chromatographic columns are shown in Table 3.
 - 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. All 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 standards 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 (five or more recommended) working standards is prepared in hexane at concentrations that cover the linear range of the instrument. The lowest level must be at, or below, the method reporting limit. These solutions are stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$, for up to six months. They are replaced sooner if comparisons with laboratory control samples indicate a problem.
- 7.2.5. A performance evaluation mix (PEM) is prepared in hexane and contains the components shown in Table 4. 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 $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$, until the time of extraction.
- 8.2. Sample extracts and dilutions are stored in test tubes and vials at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ 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 August 2017, Table 2).
- 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. Laboratory Control Sample (LCS)

- 9.2.1. 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. An LCS must be analyzed and meet criteria prior to analyzing samples. The PCB LCS will contain Aroclors 1016 and 1260. The pesticide LCS will contain all analytes found in Table 1. If Toxaphene is an analyte of interest, and is found in a sample; the sample will be re-extracted with a Toxaphene LCS and re-analyzed.
- 9.2.2. Corrective Action for LCS
 - 9.2.2.1. If an analyte of interest is outside established control limits the system is out of control and corrective action must occur.
 - 9.2.2.2. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.
 - 9.2.2.3. The only exception is that if the LCS recoveries are biased high and the analyte(s) of interest are not detected above the RL in the associated sample(s), the batch is acceptable. This must be addressed in the project narrative

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 and 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. The MB must be analyzed immediately following the LCS and meet criteria prior to analyzing samples.
- 9.3.2. Corrective Action for MBs
 - 9.3.2.1. 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.

- 9.3.2.2. 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.

9.4. Matrix Spike and Matrix Spike Duplicate (MS/MSD)

- 9.4.1. The matrix spike (MS) and matrix spike duplicate (MSD) are replicates of 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/MSD. 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 have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.
- 9.4.2. An MS/MSD sample pair will be extracted for every batch of up to 20 samples.
- 9.4.3. Corrective Action for MS/MSD
 - 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 is necessary if either DCB or TCMX are outside of acceptance limits in a sample:
 - 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 sample.
 - 9.5.5.2.1. If re-analysis does not confirm original results and recoveries are within QC acceptance criteria, then the problem was within the analyst's control and only the re-analyzed data should be reported.
 - 9.5.5.2.2. If the re-analysis confirms the original result, corrective action is re-extraction and re-analysis of the sample.
 - 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.
 - 9.5.5.4. Samples may be reported when there is obvious matrix interference present; however, such action must be included in the case narrative.
 - 9.5.5.5. No corrective action for surrogate failures will be taken when samples are diluted by a factor of 5 or greater.
- 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.
 - 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. When 4,4'-DDT, endrin, or any of their breakdown products (4,4'-DDE, 4,4'-DDD, endrin ketone, and endrin aldehyde) are analytes of interest the system must be checked for degradation problems by injecting an appropriate volume of the PEM solution (Section 7.2.5). If degradation of either DDT or endrin exceeds 20% replace the glass injection insert and seal. 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:

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

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

10.1.2. Prior to initial calibration, Aroclor 1016 is analyzed separately for pattern recognition purposes. This run is not part of the calibration.

10.1.3. Analyze calibration standards at a minimum of three concentration levels (a minimum of 5 is recommended) utilizing the GC conditions in Section 11.5. One of the standards is analyzed at, or below, the concentration which corresponds to the reporting limit.

- 10.1.4. Each calibration standard is injected into the GC with the same technique used to inject the samples.
 - 10.1.5. Calculations for the different calibration fits can be found in section 12.
 - 10.1.6. Linearity through the origin and over the working range can be assumed when the %RSD is less than 15% for an internal standard calibration, or less than 20% for an external standard calibration. In this instance an average response factor or 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 correspond 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
 - 10.1.10. The initial calibration verification (ICV) standard must be analyzed immediately following the initial calibration. The ICV standard is a second source standard prepared at the mid-level concentration used to verify the accuracy of the calibration. The ICV must meet the same criteria as a CCV. These limits are available in TALS.
- 10.2. Continuing Calibration
- 10.2.1. Mid-level standards are used for the continuing calibration verifications (CCV).
 - 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. The CCV solution is analyzed at the beginning of each day. Samples must be bracketed by a CCV that meets the criteria listed in section 10.2.6.1. The bracketing CCV must be analyzed within 24 hours; however, it is recommended that a CCV is analyzed after every 20 injections, or sooner.
 - 10.2.4. It is not necessary to run a CCV 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) and corresponding %D for each pesticide and PCB is calculated using the equations in Section 12.

10.2.6.1. %D limits for all analytes in the continuing calibration are available in the LIMS. 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. Continued failure to meet criteria is an indicator that a new calibration curve may need to be prepared.

10.2.7. Corrective Action for Samples

10.2.7.1. If a CCV exceeds the continuing calibration criteria, all samples bracketed by that CCV must be re-injected, unless the CCV fails high and no analytes in the samples are detected above the reporting limit. The ND samples may be reported with proper narration.

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, Aroclors and Toxaphene, the maximum deviation must be evaluated for each of the 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.
- 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.
- 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. Instrumentation
 - 11.4.1. Recommended instrument conditions can be found in Table 3, but may vary by instrument or column.
 - 11.4.2. Two columns of dissimilar phase are required.
 - 11.4.3. The injection volume may vary between instruments, but must be consistently applied from calibration through all subsequent runs. Changes in injection volume will require recalibration.

11.5. Sample Analysis

- 11.5.1. 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.
- 11.5.2. 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. Alternative volumes may be used, as long as IS concentrations remain constant in all calibration samples, field samples, and QC samples.
- 11.5.3. For samples analyzed by external calibration models, transfer an adequate amount of extract into an autosampler vial and load the vials onto the instrument.

11.6. 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 analytes of interest are confirmed in the sample.

11.7. Dual Column Quantitation

- 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 lower result is reported unless the RPD between columns is greater than 50%. When the RPD between columns is greater than 50%, this may be evidence of chromatographic interference. If the interfering peak is evident on the column with the lower result, report the lower result and narrate the high RPD. If the interfering peak is not evident on the column with the lower result, the result must be reported as non-detect (ND) at the concentration of the lower result. 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.

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.

- 11.8.2. 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.

11.9. Quantitation of Multi-Response Analytes

- 11.9.1. Select several major peaks from the analyte pattern. Use 3-5 peaks for PCBs and 4-6 peaks for Toxaphene. Calculate the response of each of the major 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.

11.10. 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.

11.11. 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 and associated QC information directly into the LIMS. Level I and Level II review is 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

$$CF = \frac{A_s}{C_s}$$

Where A_s = Peak area (or height) in standard

C_s = Concentration of standard injected ($\mu\text{g/L}$)

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

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 ($\mu\text{g/L}$)

C_{is} = Concentration of the internal standard ($\mu\text{g/L}$)

12.1.2. Evaluating the linearity of the initial calibration using an Average Calibration fit:

$$\text{Mean CF} = \overline{CF} = \frac{\sum_{i=1}^n CF_i}{n} \quad (\text{external calibration})$$

$$\text{Mean RF} = \overline{RF} = \frac{\sum_{i=1}^n RF_i}{n} \quad (\text{internal standard calibration})$$

Where n = the number of calibration standards

$$\text{Standard Deviation (SD)} = \sqrt{\frac{\sum_{i=1}^n (CF_i - \overline{CF})^2}{n-1}} \quad (\text{external calibration})$$

$$SD = \sqrt{\frac{\sum_{i=1}^n (RF_i - \overline{RF})^2}{n-1}} \quad (\text{internal standard calibration})$$

$$\%RSD = \frac{SD}{\overline{CF}} \times 100 \quad (\text{external})$$

$$\%RSD = \frac{SD}{\overline{RF}} \times 100 \quad (\text{internal standard})$$

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

a = Slope of the line

x = Concentration of the calibration standard

b = The intercept

12.2.1. For internal standard the equation for 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 (%D)

$$\% Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3. Quadratic calibration regression (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)

$$COD = \frac{\sum_{i=1}^n (y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p} \right) \sum_{i=1}^n (y_{obs} - y_i)^2}{\sum_{i=1}^n (y_{obs} - \bar{y})^2}$$

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. Curve weighting is required for regression curve fits (linear and quadratic). 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/concentration to determine the regression instead of the concentration.
- 12.5. Calculation of the concentration of an aqueous sample

$$\text{Concentration, } \mu\text{g/L} = \frac{C_{ex} V_t}{V_o}$$

Where: C_{ex} = Concentration in ng on column

V_t = Volume of total extract in μL

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. Vials containing sample extracts: These vials are placed in waste containers located in the GC/MS laboratory and identified as "PCB Vial Waste".

15.2.2. 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 placed 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 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 608.3

16.1.2. Method Update Rule 40CFR136 Table 2, 2017

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

16.1.10 Revision History

Historical File:				

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
- 16.2.7. CA-Q-S-006
- 16.2.8. Standards and Reagents, NC-QA-017
- 16.2.9. Cleanup Procedure for Organic Extractable Samples, NC-OP-025
- 16.2.10. Corporate Policy CA-Q-P-004, Reporting Results for Methods that Require Dual-Column Confirmation
- 16.2.11. Policy for Determining RT Windows for GC/ECD Tests, CA-T-P-005

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

- 17.1.1. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method deviations

- 17.2.1. The laboratory uses vials that are clear and the caps for PCBs are not Teflon® lined.
- 17.2.2. A rinse/equipment blank is analyzed at the beginning of the analytical sequence to demonstrate cleanliness of the analytical system.
- 17.2.3. Method 608.3 does not allow for reporting of data when QC fails to meet criteria. The lab will report data when no analytes are detected above the reporting limit and QC exceed criteria with a high bias.
- 17.2.4. Method 608.3 requires cleanliness to the MDL in method blanks. The lab will monitor cleanliness to the RL.
- 17.2.5. Method 608.3 states the minimum RT window allowed is 0.02 minutes. The lab will utilize 0.01 minutes as directed by corporate policy CA-T-P-005, current revision.

- 17.2.6. Method 608.3 describes the TBA cleanup process as adding a portion of solid sodium sulfite directly to the extract prior to adding the TBA solution. The lab does not add solid sodium sulfite to the extract, but does verify the presence of a precipitate after shaking the samples.
- 17.2.7. Method 608.3 describes re-extraction as the corrective action for surrogate failure. Furthermore, a re-extraction at 1/10th of the initial volume shall be the corrective action for a second surrogate failure. The lab will re-extract and reanalyze a sample one time, without dilution, as the corrective action for surrogate failure. Repeated failure will be included in the narrative.
- 17.2.8. Method 608.3 describes re-extraction at 1/10th of the initial volume as the corrective action for failure of any MS/MSD analytes. The lab will report the data and include the failure in the narrative as long as the LCS meets criteria. If the LCS also fails to meet criteria and re-extraction is performed, the MS/MSD re-extraction will not be at 1/10th of the initial volume.

17.3. Tables

Table 1: Analytes and CAS Numbers

Common Name	CAS Nubmer
Aldrin	309-00-2
α -BHC	319-84-6
β -BHC	319-84-7
δ -BHC	319-86-8
γ -BHC (Lindane)	58-89-9
α -Chlordane	5103-71-9
γ -Chlordane	5103-74-2
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan Sulfate	1031-07-8
Endrin	72-20-8
Endrin Aldehyde	7421-93-4
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3

Table 2: Additional Analytes and CAS Numbers

Common Name	CAS Nubmer
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
Aroclor-1268	11100-14-4
Chlorobenzilate	510-15-6
Diallate	2303-16-4
Endrin Ketone	53494-70-5
Hexachlorobenzene	118-74-1
Isodrin	465-73-6
Kepone	143-50-0
Methoxychlor	72-43-5
Mirex	2385-85-5
Toxaphene	8001-35-2
Technical Chlordane ¹	12789-03-6

¹ Technical Chlordane is not part of Method 608.3, but may be used for comparison to historical reporting

Table 3: Suggested Instrument Columns and 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 volume	1 or 2 µL
Carrier gas	Hydrogen: flow rate of 5-6 mL/minute
Make up gas	Nitrogen: flow rate of 30-35 mL/minute
Y splitter	Restek or J&W or Supelco glass tee

Table 4: Performance Evaluation Mix

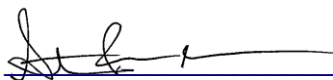
Compound
4,4'DDT
Endrin
TCMX (Surrogate)*
DCB (Surrogate)*

**Both surrogates are in the PEM, but only 4,4'DDT and Endrin are evaluated for breakdown.*

Title: ACID DIGESTION FOR AQUEOUS SAMPLES
[Methods: SW846 3005A, 3010A, and MCAWW 200 Series]
Approvals (Signature/Date):


 Technology Specialist

08/30/18
 Date


 Health & Safety Coordinator

09/05/18
 Date


 Quality Assurance Manager

10/19/18
 Date


 Technical Director

10/05/18
 Date

This SOP was previously identified as SOP No. NC-IP-011, Rev 7, dated 8/4/17

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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 elements 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.

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 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 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 90-95° C
Calibrated thermometer: range 0-110° C
Beakers, assorted sizes: Griffin, calibrated digestion beakers, or equivalent
Vapor recovery Device (Watch glasses, ribbed, or other device)
Whatman #41 filters, or equivalent
Funnels
Graduated cylinder: Various
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 elements 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

Reagents
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. Final concentrations are available in the LIMS. The working spike must be prepared in a matrix of 5% HNO₃. This acid (5 mL of concentrated HNO₃ 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. The expiration date of the working ICP LCS/MS solution is the shorter of six months, the expiration date of the corresponding stock standard or when verification from an independent source indicates a problem.
- 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. Final digestate spike concentrations are available in the LIMS.
- 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 element(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.

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.
- 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 element 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 elements 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 elements 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.

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 elements outside of the RCRA list are requested, 1 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 SOP 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.
- 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 element 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, vapor recovery device, 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 element 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, vapor recovery device, 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 element. 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. Acidic waste containing nitric acid generated by the extraction: This waste is disposed of in the designated container labeled "Acid Waste".

15.2.2. 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 2: 05/17/11		
(as CORP-IP-0003NC)		Revision 3-A: 06/28/12		
Revision 1.2: 03/20/00		Revision 4: 06/28/14		
Revision 1.3: 09/25/01		Revision 5: 08/06/14		
Revision 1.4: 02/19/03		Revision 6: 02/26/16		
Revision 1.5: 12/07/04		Revision 7: 08/04/17		
Revision 1.6: 02/07/07				
(as NC-IP-011)				
Revision 0: 01/07/09				
Revision 1: 01/28/10				

**4/17/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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 Detection and Quantitation Limits, 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 elements 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).

17.2. Appendices

APPENDIX A - TABLES

TABLE 1: Approved Preparation Method Elements - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A
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 Elements – 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: TCLP Reporting Limits and Regulatory Limits for ICP

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)
Arsenic	500	5000
Barium	10000	100000
Cadmium	100	1000
Chromium	500	5000
Lead	500	5000
Selenium	250	1000
Silver	500	5000

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 clean.

Powdered Latex Gloves must not be used in the metals laboratory since the powder contains zinc, as well as other metallic elements. 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 elements.

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.

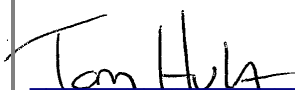
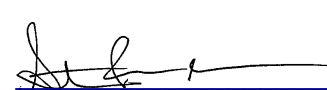
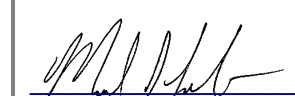
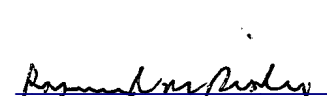
Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

Title: GC/MS Semivolatile Organic Compounds Capillary Column Technique

[Method: EPA Method 625 and 625.1]

Approvals (Signature/Date):

	<u>02/21/19</u>		<u>02/22/19</u>
Technology Specialist	Date	Health & Safety Coordinator	Date
	<u>03/07/19</u>		<u>02/25/19</u>
Quality Assurance Manager	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-MS-003, Rev 11, dated 3/13/18

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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.
- 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 degrades 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'-dichlorobenzidine, 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- μ m 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 μ L 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 µg/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 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 MeC1₂. 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 µL 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:

$$\frac{(A_x)(C_{is})}{(A_{is})(C_x)} = Rf$$

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 ($\mu\text{g/L}$)
 C_{is} = Concentration of the specific internal standard ($\mu\text{g/L}$)

- 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, A_x/A_{is} 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.
- 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 $\pm 20\%$ 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 μ L (5 μ L 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 μ L (5 μ L 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 $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ 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 $\pm 20\%$ 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 $\pm 20\%$ 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 $\pm 20\%$. (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.

$$\frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)} = \text{concentration, ug / L}$$

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 $V_t = 10,000 \mu\text{L}$. 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

$$\%RSD = \frac{SD}{RF} \times 100$$

RF = Mean of RFs from initial calibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\frac{\sum_{i=1}^N (RF_i - \overline{RF})^2}{N - 1}}$$

RF_i = 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:

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."

12.3. 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. **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		Revision 11: 03/13/18

**4/17/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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. Quantitation and Detection Limits, 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
Acenaphthylene	208-96-8	10

Analytes	CAS Number	Water, µg/L
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

Analytes	CAS Number	Water, µg/L
Pyridine	110-86-1	10
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

Analytes	CAS Number	Water, µg/L
p-Chlorobenzilate	510-15-6	10
Pentachlorobenzene	608-93-5	10
Pentachloroethane	76-01-7	10
Pentachloronitrobenzene	82-68-8	10
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-Fluorobiphenyl
Acenaphthene-d ₁₀	p-Terphenyl-d ₁₄
Chrysene-d ₁₂	2-Fluorophenol
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-d ₅	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-d ₅		4-Nitroaniline
		Fluorene
		2-Fluorobiphenyl (Surr)
		Phenyl Ether

1,4-Dichlorobenzene-d ₄	Naphthalene-d ₈	Acenaphthene-d ₁₀
		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-d₅ (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-d₄ (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	43	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d₅ (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-d₈ (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

Analyte	Primary	Secondary	Tertiary
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-d₁₀ (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-d₁₀ (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-d₁₄ (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d₁₂ (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279

Analyte	Primary	Secondary	Tertiary
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-d₁₂ (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
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

Analyte	Primary	Secondary	Tertiary
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

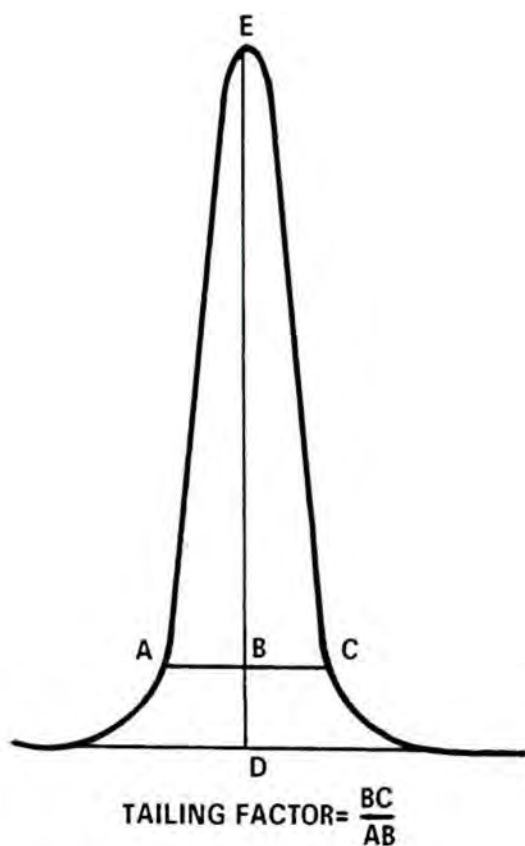
Table 6 – Method 625 LCS and MS/MSD Compounds and Spike Concentrations

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

LCS Compounds	Spiking Level, ng/ μ L in extract	Spiking Level, ng/ μ L in extract LVI Samples
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
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

LCS Compounds	Spiking Level, ng/ μ L in extract	Spiking Level, ng/ μ L in extract LVI Samples
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



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
Therefore: Tailing Factor = $\frac{12}{11} \approx 1.1$

Figure 13. Tailing factor calculation.

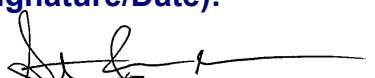
Title: DIOXIN SCREEN

[Method: EPA Method 625]

Approvals (Signature/Date):


Technology Specialist

08/14/18
Date


Health & Safety Coordinator

08/15/18
Date


Quality Assurance Manager

08/15/18
Date


Technical Director

08/31/18
Date

This SOP was previously identified as SOP No. NC-MS-0005, Rev 2, dated 6/7/16

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1. SCOPE AND APPLICATION

- 1.1. This screening procedure is used to determine the presence of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in waters and waste waters. It is based on the Dioxin screening procedure in EPA Method 625. Results are reported as positive or negative.
- 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. An extract prepared for GC/MS Semivolatile compound analysis is injected into the GC/MS. The extract is analyzed by selected ion monitoring (SIM) GC/MS techniques.

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. False positives of this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

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 Corporation 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. Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. Nitrile or similar gloves must be used.
- 5.4. The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohol.
- 5.5. 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.
- 5.6. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
- 5.7. 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.
- 5.8. 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 will be removed and discarded; other gloves will be cleaned immediately.
- 5.9. 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.
- 5.10. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

- 5.11. 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 Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Gas Chromatograph/Mass Spectrometer System

- 6.1.1. 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.
- 6.1.2. Column: 30 m x 0.25 mm I.D. 0.50 micron film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5 or equivalent).
- 6.1.3. Mass Spectrometer: Capable of scanning from 35 to 450 amu every seven seconds or less using 70 volts (nominal) electron energy in the electron impact ionization mode.
- 6.1.4. 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.
- 6.1.5. Syringe: 5 μ L

7. REAGENTS AND STANDARDS

- 7.1. Standards: 0.5 μ L of a 2 ug/mL 2,3,7,8-TCDD Standard is injected for retention time and ion reference.

Note: The standard is not used for quantitation, only for retention time information. Results are reported as positive or negative.

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 $\pm$ 2°C.

- 8.3. The holding time for waters is seven days from sampling to the completion of extraction and 40 days from the completion of extraction to the completion of analysis.
- 8.4. The holding time for solids is 14 days from sampling to the completion of extraction and 40 days from the completion of extraction to the 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, 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.

9.2.2. Corrective Action for MB

- 9.2.2.1. If a positive hit for 2,3,7,8-TCDD is found in the MB, all associated samples are re-prepared and re-analyzed.

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 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. Samples are prepared using SOPs NC-OP-037 or NC-OP-038.

11.4. Sample Analysis

11.4.1. An extract prepared for GC/MS Semivolatile compound analysis is injected into the GC/MS. The extract is analyzed by selected ion monitoring (SIM) GC/MS techniques.

11.4.2. Sample Analysis Procedure

11.4.2.1. If possible, concentrate the base/neutral extract by a factor of 5 (example: 2 mL to 0.4 mL).

11.4.2.2. Recommended GC instrument conditions

Initial:	200°C for one minute
Temperature program:	20°C/minute
Final Temperature:	320° C for 3 minutes

11.4.2.3. Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320, and 322, and Chrysene d₁₂ at 240 and 120 m/z and a dwell time no greater than 333 milliseconds per mass.

11.4.2.4. Add 5 uL of 80 ug/mL internal standard solution to 100 uL sample.

11.4.2.5. Inject 0.5 µL of the base/neutral extract. Collect SIM data for a total of ten minutes.

11.4.2.6. The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

11.4.2.7. Evaluate the internal standard recovery. Chrysene d₁₂ recovery is 50% - 200%.

11.4.2.8. For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, print the signals of each of the three masses.

11.4.3. Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures. Results from this test are reported as either positive or negative.

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 information and associated QC 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. Training Qualifications

13.1.1. 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. Waste Streams Produced by the Method

15.2.1. The following waste streams are produced by this method.

15.2.1.1. **Vials containing sample extracts:** These vials are placed in a container labeled "Vial Waste" located in the GC/MS laboratory.

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 an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. Federal Register – Environmental Protection Agency, 40 CFR, Part 136, Volume 49, No. 209, October 26, 1984, Method 625

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. Reference History

Historical File:		Revision 0: 05/17/95		Revision 1.3: 08/02/07
		Revision 1.0: 05/02/02		Revision 1.4: 08/17/09
		Revision 1.1: 11/15/04		Revision 2: 06/07/18
		Revision 1.2: 03/09/06		

**4/17/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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, NC-OP-037

16.2.2. Separatory funnel Extraction of Organic Compounds from Waters Based on Method SW846 3510C and 600 Series, NC-OP-038

16.2.3. QA Policy, QA-003

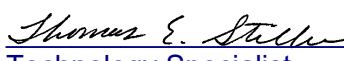
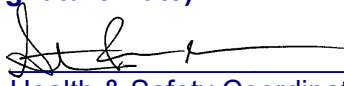
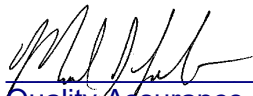
16.2.4. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.5. Standards and Reagents, NC-QA-017

Title: GC/MS VOLATILE ORGANIC COMPOUNDS

[Method 624 and 624.1]

Approvals (Signature/Date):

	<u>08/22/18</u>		<u>08/22/18</u>
Technology Specialist	Date	Health & Safety Coordinator	Date
	<u>08/23/18</u>		<u>08/24/18</u>
Quality Assurance Manager	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-MS-006, Rev 7, dated 9/28/17

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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 Methods 624 and 624.1, a purge-and-trap gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L. Current reporting limits are available in the LIMS.
- 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 Analytical Model 4760 sample concentrator, OI Model 4552 Autosampler, OI Analytical Model 4100 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, OI Analytical Model 4660, 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 $< -10^{\circ}\text{C}$. 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 $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and monitored for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

Gases

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.

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/ μ L 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 is a compound of interest, as this compound cannot be reliably recovered from a preserved sample.

8.2. Samples are stored in glass containers with Teflon®-lined caps at 4° C $\pm$ 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 for method 624 is seven days unless aromatic volatiles (notably benzene, toluene, and ethyl benzene) are not requested, in which case the holding time is 14 days.

8.5. The holding time for an unpreserved sample for method 624.1 is 7 days for all compounds.

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/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 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. Note: for method 624.1, the LCS is used as calibration verification. See section 10.5 for requirements.

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.

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 / Matrix spike duplicate (MS/MSD)

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 / matrix spike duplicate 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/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. 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.

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 SOP 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 for method 624 and 14 hour time period for 624.1. The 24-hour / 14 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-d₅, 1,4-Dichlorobenzene-d₄. 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.

$$RF = \frac{A}{B} \times \frac{C}{E}$$

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.

$$\%RSD = \frac{A}{B} \times 100$$

Where:

RSD = Relative Standard Deviation

A = Standard deviation of average RFs for a compound

B = Average of the five initial RFs for a compound

$$A = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}}$$

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 ratios, 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.

- 10.4.9. The initial calibration verification for method 624.1 is performed using the laboratory control sample (LCS). See section 10.5 for LCS requirements.
- 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 for method 624.
- 10.5.2. An LCS verification standard is analyzed at the beginning of each 12 hour shift. The LCS must be from a source different from the source used for the initial calibration.
- 10.5.3. For method 624 for each parameter, compare the response with the corresponding calibration acceptance criteria found in the LIMS. 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. For method 624.1 requirements see the method.

Note: The large number of parameters 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.

Internal standard Responses method 624.1

LCS verification – The area response of the internal standards in the LCS verification standard must be within 50% to 200% of the respective responses in the mid-point initial calibration standard. If they are not, repeat the LCS using a fresh LCS, or perform and document system repair. Subsequent to repair, repeat the LCS verification test. If the internal standard areas are still outside of 50% to 200%, recalibration of the instrument may be necessary.

Samples, blanks, and MS/MSDs – The area response of each internal standard in each blank, sample, and MS/MSD must be within 50% to 200% of the respective area response in the mid-point initial calibration standard. Failure of an internal standard will require reanalysis unless no analytes are detected in the sample, in which case ignore the failure or report if required by the regulatory authority

- 10.5.4. 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. The mass spectrum of the compound in the sample must correspond with the mass spectrum of the compound in the standard.

11.4.6.3.1. The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

11.4.6.3.2. The retention time must fall within ± 30 seconds of the retention time of the authentic compound.

11.4.6.3.3. The relative peak heights of the three characteristic masses in the EICPS must fall within $\pm 20\%$ 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.)

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.

$$12.1.1. \text{Concentration, } \mu\text{g} / \text{L} = \frac{A \times B}{C \times E \times RF} \times D$$

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 =
$$\frac{\text{Final Dilution Volume, mL}}{\text{Initial Volume Used for Dilution, mL}}$$

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)

$$RPD = \frac{|MSR - MSDR|}{\frac{1}{2}(MSR + MSDR)} \times 100$$

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. Used samples: Samples are collected in boxes and removed from the Lab to storage. The Waste Coordinator handles crushing the vials and proper disposal.

15.2.2. 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".

- 15.2.3. 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".
- 15.2.4. 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. Federal Register - Environmental Protection Agency, 40 CFR, Part 136, August 28, 2017, Purgeables by GC/MS, Method 624.1

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 0: 09/12/96		
		Revision 1: 06/19/03		
		Revision 2: 11/16/04		
		Revision 3: 05/15/08		
		Revision 4: 06/30/10		
		Revision 5: 11/25/14		
		Revision 6: 03/11/16		
		Revision 7: 09/28/17		

**4/17/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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. Detection and Quantitation Limits, 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.

17.1.8. Method 624.1 requires that the blank results be lower than the MDL for the analyte, or lower than 1/3 of the compliance limit, whichever is greater. The

laboratory checks the blanks for cleanliness to the RL. See section 9.2 for more details.

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

Table 2: Internal Standards With Corresponding Analytes

Fluorobenzene	Chlorobenzene-d₅	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-d ₄		
1,2-Dichloroethane		
Benzene		
Trichloroethene		
1,2-Dichloropropane		
Bromodichloromethane		
2-Chloroethylvinyl ether		
Cis-1,3-Dichloropropene		
MTBE		

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-d ₄ (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

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: Additional Purgeables Method 624.1

Compound	CAS Number
1,1,1,2-Tetrachloroethane	630-20-6
1,1-Dichloropropene	563-58-6
1,2,3-Trichlorobenzene	87-61-6
1,2,3-Trichloropropane	96-18-4
1,2,4-Trichlorobenzene	120-82-1
1,2,4-Trimethylbenzene	95-63-6
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
1,2-Dichloroethene (Total)	540-59-0
1,3,5-Trimethylbenzene	108-67-8
1,3-Dichloropropane	142-28-9
1,3-Dichloropropene, Total	542-75-6
1-Chlorohexane	544-10-5
2,2-Dichloropropane	590-20-7
2-Butanone	78-93-3
2-Chlorotoluene	95-49-8
2-Hexanone	591-78-6
3-Chloro-1-propene	107-05-1
4-Chlorotoluene	106-43-4
4-Isopropyltoluene	99-87-6
4-Methyl-2-pentanone	108-10-1
Acetone	67-64-1
Acrolein	107-02-8

Compound	CAS Number
Acrylonitrile	107-13-1
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Butadiene	106-99-0
Carbon disulfide	75-15-0
cis-1,2-Dichloroethene	156-59-2
Cyclohexane	110-82-7
Dibromomethane	74-95-3
Dichlorodifluoromethane	75-71-8
Dichlorofluoromethane	75-43-4
Ethyl acrylate	140-88-5
Ethyl ether	60-29-7
Ethylmethacrylate	97-63-2
Hexachlorobutadiene	87-68-3
Hexane	110-54-3
Iodomethane	74-88-4
Isobutanol	78-83-1
Isopropylbenzene	98-82-8
m and p Xylenes	
Methyl Acetate	79-20-9
Methyl cyclohexane	108-87-2
Methyl <i>tert</i> -butyl ether (MTBE)	1634-04-4
Napthalene	91-20-3
n-Butyl acrylate	123-86-4
n-Butylbenzene	104-51-8
n-Heptane	142-82-5
n-Propylbenzene	103-65-1
o-xylene	95-47-6
Sec-butylbenzene	135-98-8
Styrene	100-42-5
t-1,4-Dichloro-2-butene	110-57-6
tert-Butyl alcohol	75-65-0
Tert-Butylbenzene	98-06-6
Tetrahydrofuran	109-99-9
Total xylenes	1330-20-7
Trichlorotrifluoroethane	76-13-1
Trihalomethanes, Total	
Vinyl acetate	108-05-4

Title: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED ON METHODS 8260C, 8260B, AND 8260A

[Method: EPA Methods 8260A, 8260B, and 8260C]

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07/23/18
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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 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 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 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	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.			

- 5.4. 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 hazardous 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.
- 6.11. Chlorine Test Paper: 0 ppm to 10 ppm
- 6.12. Gases
 - 6.12.1. Helium: UHP, gr. 5, 99.999%.
 - 6.12.2. Nitrogen: UHP from cylinders or gas generators may be used as an alternative to helium for purge gas.
- 6.13. Purge and Trap Device: The purge and trap device consists of the sparger, trap, and desorber.
 - 6.13.1. 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.
 - 6.13.2. Trap: A variety of traps may be used, depending on the target analytes required. Vocab 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).
 - 6.13.3. Desorber: The desorber must be capable of rapidly heating the trap to at least 180°C.
 - 6.13.4. Sample Heater: A heater capable of maintaining the purge device at 40°C is necessary for low-level soil analysis.
- 6.14. GC/MS System – HP (Agilent) GC/MSD 5973/5975 or equivalent
 - 6.14.1. Autosampler – Archon or OI
 - 6.14.2. The GC system must be capable of temperature programming.
 - 6.14.3. GC Columns: Capillary Column: 20m x 0.18 ID DB-624 or equivalent, with 1 µm film thickness.

- 6.14.4. 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.
- 6.14.5. 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.
- 6.14.6. 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.
- 6.14.7. Chemstation software is used in Canton MS VOA laboratory for data acquisition.
- 6.14.8. 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.
- 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 3 for internal standard components.
- 7.3.3. Surrogate Standards: Refer to Table 4 for surrogate standard components and spiking levels.
- 7.3.4. Laboratory Control Sample Spiking Solutions: Refer to Table 5 for LCS components. Spiking levels are available via the LIMS. 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 5. 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-Bromofluorobenzene 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 $\text{pH} \leq 2$ 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 ($< 50 \mu\text{g/kg}$ 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 $\mu\text{g/mL}$ 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 μ L 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 μ L of 50 μ g/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 μ L 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 μ g/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 $<-10^{\circ}\text{C}$ 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. Methanol Preserved - Field Preservation for ISM (Incremental Sampling Method) Samples

- 8.9.1. Prior to sample collection for ISM samples, the client must contact the laboratory PM and notify them of the number of increments that will be sampled. The laboratory supplies the sample bottle containing the appropriate amount of Methanol needed to preserve the sample. The ratio of Methanol to sample is normally 1:1. Approximately 5 g of sample are collected per increment.

Note: Each bottle supplied by the lab has a "Contains Methanol" label affixed. After the appropriate volume of Methanol has been added, the bottle with the Methanol gets weighed. The tare weight must be recorded on the label.

- 8.9.2. The sampler places approximately 5 g per increment into the bottles supplied by the lab. The samples must be stored at $4 \pm 2^{\circ}\text{C}$.
- 8.9.3. The ISM preserved samples have a 14 day holding time from sampling completion to analysis.
- 8.9.4. Matrix spike compounds and surrogate compounds are spiked into sample aliquots and batch QC prior to analysis.

- 8.10. Aqueous samples are stored in glass containers with Teflon®-lined septa at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ with no headspace.

- 8.11. 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.

- 8.12. 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 two weeks.

Note: An unpreserved sample must be analyzed when 2-Chloroethyl vinyl ether (2-CLEVE) is a compound of interest, as it cannot be reliably recovered from a preserved sample. If an unpreserved sample is received with 2-CLEVE requested as a target analyte, the sample must be analyzed within 7 days of collection. If 2-CLEVE 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-CLEVE 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 4. 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 re-preparation 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 5), 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, (c) the failing compound(s) is a poor performing compound, or (d) 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 are given in Table 5. 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. Recommended Instrument settings
- | | |
|-----------------------|---|
| 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 6 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 the BFB injection.

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. See the LIMS for details on calibration levels. 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 3. 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 10 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 9 for the CCCs. These criteria 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 7 for the SPCC compounds for Method 8260B and required minimum response factors. Refer to Table 8 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. $1/\text{Concentration}^2$ 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 ≥ 0.99 . For Method 8260C, % RSD is $\pm 20\%$ 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 40°C 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 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C 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.

10.5. Initial Calibration Verification (ICV)

10.5.1. 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 $\leq 20\%$. The recovery for non-CCC compounds must be $\leq 50\%$ with an allowance of up to six compounds $> 50\%$.

10.5.1.1. 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%:

10.6. Continuing Calibration

10.6.1. The calibration must be verified every 12 hours.

10.6.2. 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.

10.6.3. 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.

10.6.4. For Method 8260B, the % difference or % drift of the CCCs must be $\leq 20\%$ for the continuing calibration to be valid. The exception to this is if the CCC fails criteria on the high side and the samples are ND, the results may be reported with proper narration. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 7. In addition, the percent drift of all analytes must be $\leq 50\%$ with allowance for up to six target analytes to have percent drift $> 50\%$.

10.6.4.1. 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%.

10.6.5. If the CCCs and/or the SPCCs do not meet the criteria in Section 10.5.3 and Table 7, 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.

- 10.6.6. 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.)

10.7. Secondary Calibration Testing

- 10.7.1. In order to be in compliance with NELAC and SW-846 the method 8260C non-average curve types need to be evaluated both by COD and by a secondary test. The secondary test used for method 8260C is the %RSE test. RSE (Relative Standard Error) is calculated for the curve. If the curve fails the RSE limit, the calibration curve may not provide accurate quantitation. RSE uses the ICVRSE limit type.
- 10.7.2. The RSE acceptance limit criterion (expressed as %) for the calibration model is the same as the RSD limit for individual RF or Avg. of Individual in the determinative method. The RSE limit for method 8260C is set at =20% for good performing compounds and =30% for poor performing compounds.

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.
- 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.

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 1 μL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1 μL 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 5 μ L of a 2500 μ g/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, 5 μ L of a 2500 μ g/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 μ L for a 5 mL purge) methanolic extract (from Sections 8.5 or 8.6) to the syringe. If less than 5 μ L of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1 μ L 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 $\geq 5 \mu\text{L}$. 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 $\mu\text{g/L}$ 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 35°C).
- 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°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.

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 10 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 $\pm 30\%$ 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

$$SD = \sqrt{\sum_{i=1}^N \frac{(X_i - \bar{X})^2}{N - 1}}$$

Where:

X_i = Value of X at i through N

N = Number of points

$\bar{X}$ = 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

$$\% \text{ Drift} = \frac{C_{\text{expecte}} - C_{\text{found}}}{C_{\text{expecte}}} \times 100$$

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 $\leq 15\%$ ($\leq 20\%$ for method 8260C).

12.3.5.2. Calculation of Concentration Using Average Response Factors

Equation 5

$$\text{Concentration } \mu\text{g} / \text{L} = \frac{x}{\overline{RF}}$$

12.3.5.3. Calculation of Concentration using Linear Fit

Equation 6

$$\text{Concentration } \mu\text{g} / \text{L} = A + Bx$$

12.3.5.4. Calculation of Concentration Using Quadratic Fit

Equation 7

$$\text{Concentration } \mu\text{g} / \text{L} = A + Bx + Cx^2$$

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

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, μ L

W_s = Weight of sample extracted, g

$$D = \frac{100 - \% \text{moisture}}{100}$$

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 V_t 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 V_t . The total solvent/water volume is calculated as follows:

Equation 11

$$\mu\text{L solvent/water } V_t = [\text{mL of solvent} + ((\% \text{moisture}/100) \times \text{g of sample})] \times 1000 \mu\text{L/mL}$$

V_t solvent/water is then used in the formula in section 12.3.5.6.

- 12.3.7. MS/MSD Recovery

Equation 12

$$\text{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample result

SR = Sample Result

SA = Spiked amount

- 12.3.8. Relative % Difference (RPD) calculation for the MS/MSD:

Equation 13

$$\text{RPD} = \frac{|\text{MSR} - \text{MSDR}|}{\frac{1}{2}(\text{MSR} + \text{MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

12.3.9. Relative Standard Error (%RSE) for Secondary Calibration Testing

Equation 14

$$\%RSE = 100 \times \sqrt{\sum_{i=1}^n \left[\frac{x'_i - x_i}{x_i} \right]^2 / (n - p)}$$

X_i = True value of the calibration level i

X'_i = Measured concentration of calibration level i

P = Number of terms in the fitting equation (average = 1, linear = 2, quadratic = 3)

N = Number of calibration points

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.

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: 02/17/12		
(formerly CORP-MS-0002NC)		Revision 3: 06/29/12		
Revision 2.0: 12/15/97		Revision 4: 05/21/14		
Revision 2.1: 03/06/00		Revision 5: 03/11/16		
Revision 2.2: 11/28/00				
Revision 2.3: 05/23/01				
Revision 2.4: 09/27/04				
Revision 2.5: 04/03/07				
Revision 0: 06/30/08 (NC-MS-019)				
Revision 1: 01/07/09				

**4/17/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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. Detection and Quantitation Limits, 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.
- 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 calculated results and recoveries.

ICV/CCV Poor Performer list

Acetone
4-Methyl-2-pentanone
1,2-Dibromo-3-chloropropane
1,4-Dioxane
2-Butanone
Hexachlorobutadiene
Methylene Chloride
Naphthalene
1,2,4-Trichlorobenzene
Methyl acetate
2-Hexanone
cis-1,3-Dichloropropene

Table 1: Compound List with CAS Numbers

Compound	CAS Number
Dichlorodifluoromethane	75-71-8
Chloromethane	74-87-3
Bromomethane	74-83-9
Vinyl chloride	75-01-4
Chloroethane	75-00-3
Trichlorofluoromethane	75-69-4
Acrolein	107-02-8
Acetone	67-64-1
Trichlorotrifluoroethane	76-13-1
Iodomethane	74-88-4
Carbon disulfide	75-15-0
Methylene chloride	75-09-2
tert-Butyl alcohol	75-65-0
1,1-Dichloroethene	75-35-4
1,1-Dichloroethane	75-34-3
Trans-1,2-Dichloroethene	156-60-5
Acrylonitrile	107-13-1
Methyl tert-butyl ether (MTBE)	1634-04-4
Hexane	110-54-3
cis-1,2-Dichloroethene	156-59-2
1,2-Dichloroethene (Total)	540-59-0
Tetrahydrofuran	109-99-9
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
Dibromomethane	74-95-3
2-Butanone	78-93-3
1,4-Dioxane	123-91-1
1,1,1-Trichloroethane	71-55-6
Carbon tetrachloride	56-23-5
Bromodichloromethane	75-27-4
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
Trichloroethene	79-01-6
1,2-Dibromoethane	106-93-4
1,2,3-Trichloropropane	96-18-4
1,1,2-Trichloroethane	79-00-5
Benzene	71-43-2
Ethylmethacrylate	97-63-2

Compound	CAS Number
Trans-1,3-Dichloropropene	10061-02-6
Bromoform	75-25-2
4-Methyl-2-pentanone	108-10-1
2-Hexanone	591-78-6
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,2,2-Tetrachloroethane	79-34-5
2-Chloroethyl vinyl ether	110-75-8
Vinyl acetate	108-05-4
Chlorobenzene	108-90-7
Ethylbenzene	100-41-4
Styrene	100-42-5
t-1,4-Dichloro-2-butene	110-57-6
m and p Xylenes	
o-xylene	95-47-6
Total xylenes	1330-20-7
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
1,2-Dichlorobenzene	95-50-1
2,2-Dichloropropane	590-20-7
Bromochloromethane	74-97-5
1,1-Dichloropropene	563-58-6
Bromodichloromethane	75-27-4
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
Isopropylbenzene	98-82-8
Bromobenzene	108-86-1
n-Propylbenzene	103-65-1
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
1,3,5-Trimethylbenzene	108-67-8
Tert-Butylbenzene	98-06-6
1,2,4-Trimethylbenzene	95-63-6
Sec-butylbenzene	135-98-8
4-Isopropyltoluene	99-87-6
n-Butylbenzene	104-51-8
1,2,4-Trichlorobenzene	120-82-1
Napthalene	91-20-3
Hexachlorobutadiene	87-68-3
1,2,3-Trichlorobenzene	87-61-6

Compound	CAS Number
Cyclohexane	110-82-7
Methyl Acetate	79-20-9
Methyl cyclohexane	108-87-2
Epichlorohydrin	106-89-8
Propylene Oxide	75-56-9
2-Ethyltoluene	611-14-3
3-Ethyltoluene	620-14-4
1-Chlorohexane	544-10-5
Ethylene Oxide	75-21-8
1,1,1,2-Tetrachloroethane	630-20-6
1,2-Dibromo-3-chloropropane	96-12-8
3-Chloro-1-propene	107-05-1
Dichlorofluoromethane	75-43-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
n-Heptane	142-82-5
1,3-Dichloropropene, Total	542-75-6
Butadiene	106-99-0
Ethyl acrylate	140-88-5
n-Butyl acrylate	123-86-4
Trihalomethanes, Total	

Table 2: Appendix IX Compounds with CAS Numbers

Compound	CAS Number
Acetonitrile	75-05-8
Isopropyl ether	108-20-3
Chloroprene	126-99-8
n-Butanol	71-36-3
Propionitrile	107-12-0
Methacrylonitrile	126-98-7
Methyl methacrylate	80-62-6
Ethyl Acetate	141-78-6
2-Nitropropane	79-46-9
Cyclohexanone	108-94-1

Compound	CAS Number
Isopropylbenzene	98-82-8
1,2,3-Trimethylbenzene	526-73-8
1,3,5-Trichlorobenzene	108-70-3
Benzyl chloride	100-44-7
Pentachloroethane	76-01-7
Tert-Amyl methyl ether	994-05-8
Tert-Butyl ethyl ether	637-92-3
2-Methylnaphthalene (Michigan only)	91-57-6

Table 3 - 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 4 - 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 generated from historical data and are maintained by the QA Dept.
- 3) There is no corrective action for Dibromofluoromethane for Method 8260C.

Table 5: Matrix Spike / LCS Compounds

Compound
1,1,1,2-Tetrachloroethane
1,1,1-Trichloroethane
1,1,2,2-Tetrachloroethane
1,1,2-Trichloro-1,2,2-trifluoroethane
1,1,2-Trichloroethane
1,1-Dichloroethane
1,1-Dichloroethene
1,1-Dichloropropene
1,2,3-Trichlorobenzene
1,2,3-Trichloropropane
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,2-Dichlorobenzene
1,2-Dichloroethane
1,2-Dichloroethene (total)
1,2-Dichloropropane
1,3,5-Trimethylbenzene
1,3-Dichlorobenzene
1,3-Dichloropropane
1,4-Dichlorobenzene
1,4-Dioxane
2,2-Dichloropropane
2-Butanone
2-Chloroethyl Vinyl Ether
2-Chlorotoluene
2-Methyl-2-propanol
2-Hexanone
3-Chloro-1-propene
4-Chlorotoluene
4-Methyl-2-pentanone
Acetone
Acetonitrile
Acrolein
Acrylonitrile
Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
Carbon disulfide
Carbon tetrachloride
Chlorobenzene
Chloroethane
Chloroform
Chloromethane

Compound
cis-1,2-Dichloroethene
cis-1,3-Dichloropropene
Cyclohexane
Dibromochloromethane
Dibromomethane
Dichlorodifluoromethane
Dichlorofluoromethane
Ethylbenzene
Ethyl ether
Ethyl methacrylate
Hexachlorobutadiene
Iodomethane
Isobutyl alcohol
Isopropylbenzene
Methyl acetate
Methyl tert-butyl ether (MTBE)
Methylcyclohexane
Methylene chloride
Naphthalene
n-Butylbenzene
n-Heptane
n-Hexane (Ohio VAP only)
n-Propylbenzene
p-Isopropyltoluene
sec-Butylbenzene
Styrene
tert-Butylbenzene
Tetrachloroethene
Toluene
trans-1,2-Dichloroethene
Tetrahydrofuran
trans-1,3-Dichloropropene
trans-1,4-Dichloro-2-butene
Trichloroethene
Trichlorofluoromethane
Vinyl Acetate
Vinyl chloride
Xylenes (total)

Note: This list is subject to change without notice

Table 6 - 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 7 - 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 8 - 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	0.05	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

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 9 - 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 10 - 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

Table 10 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Acrylonitrile	53	52	51
Methyl <i>tert</i> 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
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	

Table 10 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
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	
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.

TABLE 11:
Internal Standards with Corresponding Analytes and Surrogates
Assigned for Quantitation

1,4-Dichlorobenzene-d ₄	Fluorobenzene	Fluorobenzene Cont'd
trans-1,4-Dichloro-2-butene	Dichlorodifluoromethane	Methyl methacrylate
1,1,2,2-Tetrachloroethane	Chloromethane	2-Chloroethyl vinyl ether
Bromobenzene	Vinyl chloride	Methylcyclohexane
n-Propylbenzene	Bromomethane	cis-1,3-Dichloropropene
2-Chlorotoluene	Chloroethane	4-Methyl-2-pentanone
4-Chlorotoluene	Trichlorofluoromethane	Butadiene
1,3,5-Trimethylbenzene	Acrolein	Dichlorofluoromethane
Pentachloroethane	Acetone	2-Methyl-2-propanol
Tert-butylbenzene	Ethyl ether	Hexane
1,2,4-Trimethylbenzene	1,1-Dichloroethene	Isobutyl alcohol

sec-Butylbenzene	Iodomethane	n-Heptane
1,3-Dichlorobenzene	Acrylonitrile	Acetonitrile
1,4-Dichlorobenzene	Methylene chloride	Ethyl acetate
4-Isopropyltoluene	1,1,2-Trichloro-1,2,2-trifluoroethane	Propionitrile
1,2-Dichlorobenzene	Methyl acetate	n-Butanol
n-Butylbenzene	3-Chloro-1-propene	Ethyl acrylate
1,2-Dibromo-3-chloropropane	Carbon disulfide	Dibromofluoromethane (Surr)
1,2,4-Trichlorobenzene	trans-1,2-Dichloroethene	1,2-Dichloroethane-d ₄ (Surr)
Naphthalene	Methyl tert-butyl ether	
Hexachlorobutadiene	1,1-Dichloroethane	
1,2,3-Trichlorobenzene	Vinyl acetate	
1,2,3-Trichloropropane	2-Chloro-1,3-butadiene	Chlorobenzene-d₅
Cyclohexanone	2-Butanone	Chlorobenzene
1,2,3-Trimethylbenzene	Isopropyl ether	Ethylbenzene
Benzyl chloride	Methacrylonitrile	Styrene
1,3,5-Trichlorobenzene	cis-1,2-Dichloroethene	1,1,2,2-Tetrachloroethane
2-Methylnaphthalene	Chlorobromomethane	Tetrachloroethene
	Chloroform	1,3-Dichloropropane
	2,2-Dichloropropane	Ethylene dibromide
	tert-Butyl ethyl ether	Xylenes
	Tetrahydrofuran	Ethyl methacrylate
	1,1,1-Trichloroethane	2-Hexanone
	1,1-Dichloropropene	Chlorodibromomethane
	Cyclohexane	1,1,2-Trichloroethane
	Carbon tetrachloride	1-Chlorohexane
	1,2-Dichloroethane	Bromoform
	Benzene	Isopropylbenzene
	tert-Amyl methyl ether	trans-1,3-Dichloropropene
	Dibromomethane	1,1,2-Trichloroethane
	1,2-Dichloropropane	Toluene
	Trichloroethene	n-Butyl acetate
	2-Nitropropane	Toluene-d ₈ (Surr)
	Dichlorobromomethane	4-Bromofluorobenzene (Surr)
	1,4-Dioxane	

*The closest eluting internal standard is used.

Table 12: Poor Performers and Common Lab Contaminants

Compound	Poor Performer	Common Contaminant
1,1,2-Trichloro-1,2,2-trifluoromethane	X	
1,2,4-Trichlorobenzene	X	
1,2-Dibromo-3-chloropropane	X	
1,3-Dichloropropene, Total	X	
1,4-Dioxane	X	
2,2-Dichloropropane	X	
2-Butanone	X	
2-Chloroethyl vinyl ether	X	
2-Hexanone	X	
2-Methyl-2-propanol	X	
2-Nitropropane	X	
3-Chloro-1-propene	X	
4-Methyl-2-pentanone	X	
Acetone	X	X

Compound	Poor Performer	Common Contaminant
Acrolein	X	
Acrylonitrile	X	
Bromoform	X	
Bromomethane	X	
Butadiene	X	
Chlorobromomethane	X	
Chloroethane	X	
Chloromethane	X	
cis-1,3-Dichloropropene	X	
Cyclohexanone	X	
Dibromomethane	X	
Dichlorodifluoromethane	X	
Dichlorofluoromethane	X	
Ethyl methacrylate	X	
Ethylene dibromide	X	
Hexachlorobutadiene	X	
Hexane	X	
Isobutyl alcohol	X	
Methacrylonitrile	X	
Methyl acetate	X	
Methylene chloride	X	X
Naphthalene	X	
n-Heptane	X	
Pentachloroethane	X	
Tetrahydrofuran	X	
trans-1,4-Dichloro-2-butene	X	
Trichlorofluoromethane	X	

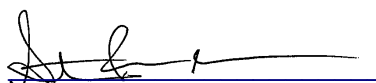
**Title: INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION
SPECTROSCOPY, SPECTROMETRIC METHOD FOR ELEMENT
ANALYSES**

[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

- 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 $4^{\circ}\text{C} \pm 2^{\circ}$ 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 $\pm 35\%$ of the true value and $\pm 30\%$ for 6010C. The % RSD between successive LLOQ's should be $\leq 20\%$. 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 $\pm$ the RL. For elements with a reporting limit of 10 $\mu\text{g/L}$ or less, the signal must be $\pm$ 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 $< \text{RL}$ 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.

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.

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).

- 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 $\pm 5\%$ 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 $\pm 10\%$ 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 $\pm$ the RL from zero for each element.

- 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 $\pm 10\%$ 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 $\pm$ 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.

- 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 ug/L must fall within $\pm$ 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 $\pm 2 \times$ 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 $\pm 2 \times$ 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 $\pm 50\%$ 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 $\pm 50\%$ 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: $\text{Cr}^{+3} = \text{total Cr} - \text{Cr}^{+6}$

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 $\text{CaCO}_3/\text{L} = [2.497 \times (\text{Ca concentration in mg/L})] + [4.118 \times (\text{Mg concentration in mg/L})]$

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

- 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	

**4/17/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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% HNO₃/5% HCl instead of the specified 2% HNO₃/10% 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

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

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.

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

**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:

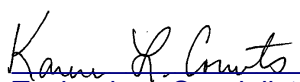
Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

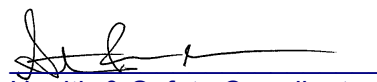
**Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND
SOLID SAMPLES BY COLD VAPOR ATOMIC
ABSORPTION SPECTROSCOPY**

**[Method: MCAWW Method 245.1, SW846 Method 7470A,
SW846 7471A, and 7471B]**

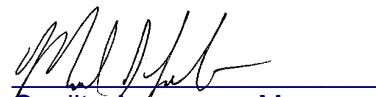
Approvals (Signature/Date):


Technology Specialist

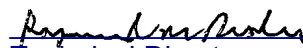
03/13/19
Date


Health & Safety Coordinator

03/08/19
Date


Quality Assurance Manager

03/18/19
Date


Technical Director

03/18/19
Date

This SOP was previously identified as SOP No. NC-MT-014, Rev 7, dated 2/13/18

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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).

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
 - 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% HNO₃. This acid (300 uL of concentrated HNO₃) 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% HNO₃. This acid (150 uL of concentrated HNO₃) 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. The laboratory control sample (LCS) solution is prepared by transferring 5.0 mL (solids) or 2.5 mL (waters) of working standard into sample preparation bottles and proceeding as specified in Section 11. 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.

- 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 $50\text{g} \pm 0.5\text{g}$ 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 $240\text{g} \pm 0.5\text{g}$ of sodium chloride and $240\text{g} \pm 0.5\text{g}$ 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 $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ (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.
- 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 SOP 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.
- 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. 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 $\pm 10\%$. See Section 12 for the CCV calculation.

10.8.3. A CCB is analyzed immediately following each CCV (see Section 11.6.4 for required run sequence). The CCB result must fall within $\pm$ 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 $\pm 50\%$ 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, add 0.6 g of Teflon chips, 5 mL of reagent water and 5 mL of the working mercury standard (0.1 ppm) (see Section 7).
- 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 0.6 g $\pm$ 0.1 g 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.
- 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.

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:

$$\%R = 100 \left(\frac{\text{Found(ICV)}}{\text{True(ICV)}} \right)$$

- 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:

$$mg/kg, dry weight = (C \times V \times D)/(W \times S)$$

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)		Revision 7: 02/13/18		
Revision 1: 01/07/09 (011)				
Revision 0: 01/07/09 (013)				
Revision 0: 09/27/10 (014)				
Revision 1-A: 04/17/12				

*4/17/19: Changed logo and copyright information. No changes made to revision number or effective date.

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. Detection and Quantitation Limits, 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 $\pm$ 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

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.

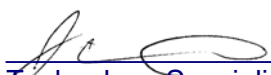
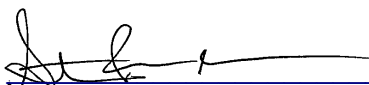
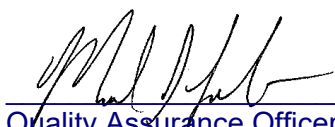
Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

Title: TOTAL ORGANIC CARBON (TOC)

[Method: SW846 Method 9060, 9060A, and SM 5310C]

Approvals (Signature/Date):

	<u>02/27/19</u>		<u>03/01/19</u>
Technology Specialist	Date	Health & Safety Coordinator	Date
	<u>03/08/19</u>		<u>02/28/19</u>
Quality Assurance Officer	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-WC-017, Rev 7, dated 3/15/18

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Total Organic Carbon (TOC) in waters and similar matrices. It is based on SW846 Methods 9060 and 9060A, and SM 5310C. The working linear range is instrument dependent at 1 mg/L to 100 mg/L with a reporting limit of 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. Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO₂) by wet chemical oxidation. The CO₂ formed is then measured by nondispersive infrared (NDIR) detector. The amount of CO₂ in a sample is directly proportional to the concentration of carbonaceous material in the sample.

3. DEFINITIONS

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

4. INTERFERENCES

- 4.1. Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause method interferences. 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. Carbonate and bicarbonate interfere but are eliminated by the acidification and purging steps of the instrument. Note that the removal of carbonate and bicarbonate by acidification and purging with nitrogen, or other inert gas, can result in the loss of volatile organic carbonaceous substances.
- 4.3. This procedure is applicable only to homogeneous samples, which can be injected into the apparatus reproducibly by means of a Microliter-type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particle, which may be included in the sample.
- 4.4. Large organic particles or very large or complex organic molecules such as tannins, lignins, and humic acid may be oxidized slowly because persulfate oxidation is rate-limited.

- 4.5. Persulfate oxidation of organic molecules is slowed in samples containing significant concentrations of chloride above 0.05%. To remove this interference, extend reaction time and/or increase amount of persulfate solution in heated-persulfate instruments.

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 auto-sampler has a probe that is sharp. Use caution not to stick yourself.
- 5.3. The furnace is very hot and can cause severe burns if touched.
- 5.4. Sodium persulfate is a strong oxidizer. Avoid contact with combustible materials, organic materials, strong reducing agents, and excess heat.
- 5.5. 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
Sulfuric Acid	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.
Phosphoric Acid	Corrosive	1 mg/m ³ TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Sodium Persulfate	Oxidizer Corrosive	0.1 mg/m ³ - TWA as Persulfates	Causes irritation to the respiratory tract. Symptoms may include sore throat, shortness of breath, inflammation of nasal passages, coughing, and wheezing. Causes severe irritation or burns to the skin and eyes. Symptoms include redness, itching, pain and burns. May cause allergic skin reactions. Can cause eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 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 will be removed and discarded; other gloves will be cleaned immediately.

- 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 Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. O-I Corporation Model 1030 TOC Analyzer with 1088 vial multi-sampler or equivalent
- 6.2. Nitrogen Gas and Regulator
- 6.3. Volumetric flasks: Various sizes
- 6.4. Volumetric pipettes: Various sizes
- 6.5. Vials: 40 mL glass
- 6.6. Graduated cylinders: Various sizes
- 6.7. 0.45 micron filters (for DOC analysis only)
- 6.8. Whatman filter #4 or equivalent
- 6.9. Top loading balance: Capable of accurately weighing ± 0.01 g
- 6.10. Analytical balance: Capable of accurately weighing ± 0.0001 g

7. REAGENTS AND STANDARDS

- 7.1. All standards and reagents are stored according to manufacturer's specification unless otherwise noted in this SOP.
- 7.2. Reagents
 - 7.2.1. Sodium Persulfate: Reagent Grade

7.2.2. Sodium Persulfate Solution: Add 200 g sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) to a 1 liter volumetric flask and dilute to volume with reagent water. Remake after 6 months or as needed.

7.2.3. Phosphoric Acid, concentrated: Reagent Grade

7.2.4. Phosphoric Acid Solution: Carefully add 59 mL concentrated phosphoric acid (H_2PO_4) to 900 mL of reagent water in a 1 liter volumetric flask. Dilute to volume with reagent water. Remake after 1 year or as needed.

7.2.5. Sulfuric Acid (H_2SO_4), concentrated: Reagent Grade

7.3. Standards

7.3.1. All standards should be prepared in volumetric flasks using volumetric pipettes, and diluted to volume with reagent water.

7.3.2. TOC Stock Standard

7.3.3. Primary and secondary sources are needed.

7.3.3.1. TOC 1000 mg/L

7.3.3.1.1. Dilute 1.06 g potassium acid phthalate (KPH) to volume in a 500 mL volumetric flask. Prepare every six months.

7.3.3.1.2. A commercially prepared solution may also be used.

7.3.4. Inorganic Carbon (TIC) Stock Solution

7.3.4.1. Carbonate-Bicarbonate stock solution: 1000 mg/L carbon: On an analytical balance, weigh 0.3500 g of sodium bicarbonate (NaHCO_3) and 0.4418 g of sodium carbonate (Na_2CO_3) and transfer both to the same 100 mL volumetric flask. Bring to volume with DI. Make each day of use.

7.3.4.2. Carbonate-Bicarbonate standard solution, 50 mg/L: Pipette 5 mL of the 1000 mg/L stock solution into approximately 50 mL of DI in a 100 mL volumetric flask. Dilute to volume with DI. Make each day of use.

7.3.5. TOC Calibration Standards

7.3.6. Prepare the following standards from the primary stock standard described in Section 7.3.3.1.

Standard	Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
Working Standard / High Level Cal 4	100	10	1000	100
High Level Cal 3	50	5	1000	100
High Level Cal 2 / High Level ICV	25	2.5	1000	100
High Level Cal 1 / Low Level Cal 4	10	1	1000	100
Low Level Cal 3 / Low Level ICV	5	0.5	1000	100
Low Level Cal 2	2.5	0.25	1000	100
Low Level Cal 1	0.5	0.05	1000	100

7.3.7. Prepare the following standards from the secondary stock standard described in Section 7.3.3.1.

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
25 (CCV/MS/MSD)	6.25	1000	250
5 (CCVL)	1.25	1000	250

7.3.8. TOC Verification Standard (LCS)

7.3.8.1. A commercially prepared solution is used.

7.3.9. Inorganic Verification Standard

7.3.9.1. After each calibration check efficiency of inorganic carbon removal by analyzing the 50 mg/L inorganic (TIC) standard solution (section 7.2.4.2). The TOC result must be less than the RL.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1. Samples are preserved to a pH <2 with sulfuric acid (H₂SO₄) or hydrochloric acid (HCl) and stored in plastic or glass vials or bottles protected from sunlight and atmospheric oxygen at 4°C±2°C.
- 8.2. The holding time is 28 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 (LCS, MB, 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. For Method 5310C, the MB must be run in duplicate, and the average of the two results reported.
- 9.2.3. Corrective Action for MBs
 - 9.2.3.1. 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 results **must be addressed in the project narrative**.
 - 9.2.3.2. 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. LCSs are well characterized, laboratory generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS 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.
- 9.3.2. A purchased LCS must be analyzed with each batch of samples.
- 9.3.3. For Method 5310C, the LCS must be run in duplicate, and the average of the two results reported.
- 9.3.4. Corrective Action for LCS
 - 9.3.4.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.
 - 9.3.4.2. 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.
 - 9.3.4.3. 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/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. 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 only have immediate bearing on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.
- 9.4.2. An MS/MSD consisting of 20 mL of sample and 20 mL of the 25 mg/L standard will be analyzed with each analytical batch of samples.

NOTE: For Method 9060, one MS/MSD pair is required per 10 samples analyzed.

NOTE: For Method 5310C, the MS/MSD must be run in duplicate, and the average of the two results reported.

9.4.3. Corrective Action for MS/MSDs

- 9.4.3.1. 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.
- 9.4.3.2. If laboratory error is suspected, consultation with the PM and/or 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 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. 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 SOP 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. Recommended Initial Setup

Constant Settings	Low Curve	High Curve
Sample Volume	7.5 mL	2 mL
Acid Volume	1 mL	2 mL
Oxidant Volume	2 mL	2 mL

10.1.1. Adjust the nitrogen to 60 ± 5 psi using the flow valve on the tank.

10.1.2. Remove the reagent bottles and fill with appropriate reagents (phosphoric acid solution and sodium persulfate). Do not fill bottles completely full; leave a small amount of air space. Loosely reconnect caps (and tubing), and replace the bottles into the instrument.

10.1.3. Calibrate the instrument when QC consistently fails to meet acceptance criteria, after major instrument maintenance, or when other problems are encountered.

10.1.3.1. Create a new sequence with both low and high calibration levels containing the correct methods.

10.1.3.2. Two calibrations, a high level range and a low level range, will be used simultaneously. Both calibrations must meet criteria

10.1.3.3. Analyze an ICV/ICB (section 10.2) followed by the TIC check standard (section 7.3.9).

10.1.3.4. Save the file using the current date as the filename.

10.1.3.5. When the analysis is complete, print the run.

10.1.3.6. Evaluate the data. The correlation coefficients of the original curves must be ≥ 0.995 or recalibration is required.

NOTE: If only one curve fails, it is only necessary to re-analyze that curve.

10.2. Initial Calibration Verification/Initial Calibration Blank (ICV/ICB)

10.2.1. The calibrations are verified by using midrange ICVs, one for the high level calibration curve and one for the low level calibration curve. The ICVs must not vary from the associated original curve by more than $\pm 10\%$, or recalibration is required. ICB samples are analyzed after each of the two ICVs. They cannot contain TOC levels above the reporting limit, or recalibration is required.

10.2.2. The calibration curves, ICVs, ICBs, and TIC check standard must meet criteria before samples are analyzed.

10.3. Continuing Calibration Verification (CCV)

10.3.1. The run is checked at the beginning, after every ten samples, and at the end of the run of the same species using a midrange CCV made from a secondary source (Section 7.2.4. or 7.2.7.) to verify continued linearity. A high and low CCV will be alternated throughout the batch. Both a high and low will be run at the end of the sequence. If a run contains only known high or low samples, only the appropriate CCV and LCS needs to be used in the run. A CCV cannot vary from the original curve by more than $\pm 10\%$ or re-analysis of samples bracketed by the failing CCV is required. Recalibration may be necessary if problem persists.

10.3.2. CCVs that bracket samples being analyzed by Method 5310C must be run in replicate.

10.3.3. System cleanliness is checked every ten samples and at the end of the run using Continuing Calibration Blank (CCB). A CCB cannot contain the analyte of interest above the reporting limit, or re-analysis of samples bracketed by the failing CCB is required. Recalibration may be necessary if problem persists.

10.3.3.1. CCBs that bracket samples being analyzed by Method 5310C must be run in replicate.

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 Procedure

11.2.1. If excess particulate matter exists, filter an aliquot of sample through a Whatman #4 filter into a TOC vial or decant. Narrate the data accordingly.

11.2.2. If DOC analysis is requested, and samples are not filtered in the field, an unpreserved sample aliquot will be filtered using a 0.45 micron filter.

11.2.2.1. A filtered blank must be analyzed with DOC samples requiring lab filtration.

11.3. Sample Analysis Procedure

11.3.1. Type a run protocol sequence into the computer. The run template may be used if desired. Update the data file information in the setup/win TOC output.

- 11.3.2. For Method 9060, quadruplicate analysis is required on client samples. If quadruplicate reporting is requested, each of four results is reported. Replicate analysis should be taken from four separate vials, if available. If only one reportable result is requested per sample, the four results should be taken from one vial, and the average of the four results are reported.
- 11.3.3. For Method 5310C, replicate analysis is required for samples **and standards**. Two results should be taken from one vial, and the average of the two results is reported. Both results will be reported upon client request.
- 11.3.4. All samples and standards should be poured into 40 mL vials. Samples received in vials of this type can be run in the original containers, provided there is not an excess of solids.
- 11.3.5. Be sure the samples are loaded on the sampler, the first one positioned under the needle.
- 11.3.6. Click the "Start" button.
- 11.3.7. Samples with results that exceed the linear range of the high level calibration curve (>100 mg/L) must be diluted and reanalyzed.
 - 11.3.7.1. Samples following a high sample should be re-analyzed if carryover is a concern.
- 11.3.8. Print the run.
- 11.3.9. When analysis is complete, properly dispose of or put away samples and standards.

12. DATA ANALYSIS AND CALCULATIONS

- 12.1. Preparation Documentation
 - 12.1.1. Record any sample preparation in LIMS.
- 12.2. Analytical Documentation
 - 12.2.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.
 - 12.2.2. Record the standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

12.2.3. 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.

12.2.4. Record or upload all sample results and associated QC into the LIMS. Level I and Level II review is performed in the LIMS

12.2.5. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12.3. Calculations

$$12.3.1. \text{ LCS \% Recovery} = \frac{\text{Instrument values} * \text{True Value}}{\text{True Value}} \times 100$$

MS/MSD % recovery =

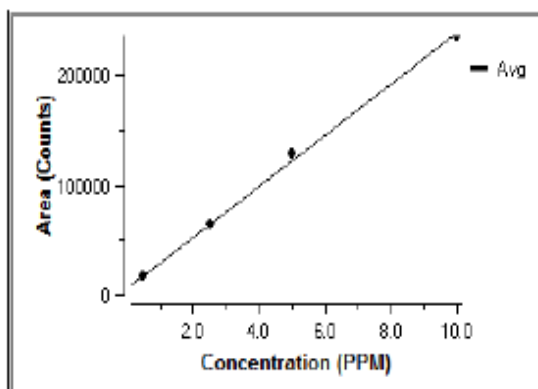
$$\left(\frac{(\text{Instrument values} * \text{MS or MSD}) - (\text{Avg sample instrument value} * \div 2)}{12.5} \right) \times 100$$

12.3.2. Instrument Calculations

Calculations:

$$\text{Concentration} = \frac{\text{RF} \times \text{Area}}{\text{volume}}$$

Samples: $\text{Area} = \text{Area}_{\text{Peak}} - \text{Area}_{\text{Offset}}$ or $\text{Area} = \text{Area}_{\text{Peak}} - \text{Area}_{\text{RB}}$
 CHK Stds: $\text{Area} = \text{Area}_{\text{Peak}} - \text{Area}_{\text{Offset}}$ or $\text{Area} = \text{Area}_{\text{Peak}} - \text{Area}_{\text{RW}}$
 QC Samples: $\text{Area} = \text{Area}_{\text{Peak}} - \text{Area}_{\text{GC.BBlank}}$



$$y = m \times x + b$$

$y \Rightarrow \text{Area}$

$$m \Rightarrow \frac{1000}{\text{RF} \times \text{volume}}$$

$b \Rightarrow 0$

* For 9060 and 9060A analysis, one of the values may be judged erroneous and disregarded if three of the four are consistent. If no consistency can be found in the four values, the sample must be rerun.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file and the laboratory must have corresponding method detection limit information on file.

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 This Method:
 - 15.2.1. Acidic waste from the auto-analyzer: This waste is disposed of in a designated container identified as "Acid Waste."
 - 15.2.2. 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.

16. REFERENCES

- 16.1. References
 - 16.1.1. SW846, Test Methods for Evaluating Waters, Third Edition, Total Organic Carbon, Method 9060.
 - 16.1.2. SW846, Test Methods for Evaluating Waters, Total Organic Carbon Method 9060A, Rev. 1, November 2004.
 - 16.1.3. Standard Methods for the Examination of Water and Wastewater, Method 5310C, 2000
 - 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: 11/20/96		Revision 4: 11/07/14
		Revision 2: 06/01/99		Revision 5: 12/14/15
		Revision 2.1: 08/17/00		Revision 6: 04/28/17
		Revision 2.2: 01/24/03		Revision 7: 03/15/18
		Revision 2.3: 12/16/04		4/2/19: Changed logo. No changes
		Revision 2.4: 08/01/07		made to revision # or date.
		Revision 2.5: 04/30/08		
		Revision 2.6: 12/16/09		
		Revision 2.7: 10/22/10		
		Revision 3: 07/25/13		

**4/18/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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. 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 lower reporting limit is 1 mg/L

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Troubleshooting Guide

17.2.1. See the manufacturer's instructions for an instrument troubleshooting guide and maintenance requirements.

17.3. Method Deviations

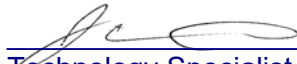
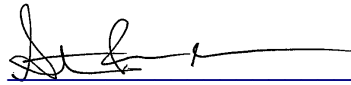
17.3.1. A blender is not used to homogenize samples.

17.3.2. Methods 9060 and 9060A state that samples should have a 10 minute nitrogen purge time. The instrument purges with nitrogen for approximately 2 to 3 minutes prior to analysis.

Title: CHROMIUM, HEXAVALENT (COLORIMETRIC)

[Method: SW846 Method 7196A and SM 3500-CR-B]

Approvals (Signature/Date):

	<u>12/04/18</u>		<u>12/05/18</u>
Technology Specialist	Date	Health & Safety Coordinator	Date
	<u>12/10/18</u>		<u>12/14/18</u>
Quality Assurance Manager	Date	Technical Director	Date

This SOP was previously identified as SOP NC-WC-024, Rev 7, dated 11/7/17

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1. SCOPE AND APPLICATION

- 1.1. This method is used to determine the concentration of Hexavalent Chromium (Cr[VI]) in solids, groundwaters and waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present. It is based on SW846 Methods 7196A and Standard Methods 3500-CR-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. Hexavalent chromium in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, is determined colorimetrically by reaction with diphenylcarbazide in acid solution and measurement of the resulting red-violet color at 540 nm.

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. The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to ten times that of chromium will not cause trouble.
- 4.3. Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong; and no difficulty is encountered normally if the absorbance is measured photometrically at the appropriate wavelength.

- 4.4. Interfering amounts of molybdenum, vanadium, iron, and copper can be removed by extraction of the cupferates of these metals into chloroform using cupferron solution.

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. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.4. 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
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.
Phosphoric Acid	Corrosive	1mg/m ³ TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Acetone	Flammable	1000 ppm- TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.

Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 mg/m ³ TWA as CrO ₃	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. Solvent and waste containers must be kept closed unless transfers are being made. 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 must 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 a Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Spectrophotometer for use at 540 nm
- 6.2. 1 cm Spectrophotometer Cell – disposable cuvettes
- 6.3. Beakers: 150 mL, Class A glass, or calibrated plastic disposable
- 6.4. Volumetric flasks: 1 L
- 6.5. Autopipettor with disposable tips
- 6.6. Funnels: various
- 6.7. Calibrated SnapSeal® containers
- 6.8. Glass culture tubes
- 6.9. Whatman #4 Filter Paper

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Sulfuric Acid (H_2SO_4): concentrated

7.1.2. Phosphoric Acid (H_3PO_4): concentrated

7.1.3. Acetone: reagent grade: Avoid material that comes in containers with metal or metal-lined caps.

7.1.4. 1,5-Diphenylcarbazide: Reagent grade

7.1.5. Diphenylcarbazide Solution: Dissolve 0.25 g of 1,5-Diphenylcarbazide in 50 mL of acetone. **The solution must be stored in an amber bottle.** Prepare the solution weekly. If a marked color change is noted, a new solution must be prepared. This solution is commercially available.

7.1.6. Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$): Primary standard grade

7.2. Standards

7.2.1. Primary Chromium Stock Solution, 50 mg/L: Dissolve 0.1414 g of dried potassium dichromate in 800 mL of reagent water. Dilute to 1 liter in a volumetric flask with reagent water. Stable for up to six months. Additional information can be found in SOP NC-QA-017.

7.2.1.1. Water Calibration Standards: Add the indicated volume of the appropriate standard and dilute to volume with reagent water. Note: the low standard must be at or below the reporting limit.

Conc., mg/L	MLs	Source, mg/L	Final Vol., mL
0.5	0.5	50	50
0.25	0.25	50	50
0.1	0.10	50	50
0.01	0.01	50	50
0.005	0.005	50	50

7.2.1.2. Secondary Chromium Stock Solution, 50 mg/L: Dissolve 0.1414 g of dried potassium dichromate (secondary source) in 800 mL of reagent water. Dilute to 1 liter in a volumetric flask with reagent water. Stable for up to six months.

7.2.1.3. Verification Standards: Add the indicated volume of the appropriate standard and dilute to volume with reagent water.

Use	Conc., mg/L	mLs	Source, mg/L	Final Vol., mL
MS/MSD (waters)	0.25	0.25	50	50
CCV	0.25	0.25	50	50
LCS (waters)	0.25	0.25	50	50

7.2.1.4. Solid Calibration Standards: The solid calibration standards are prepared according to SOP NC-WC-086 Alkaline Digestion for Hexavalent Chromium.

Conc.				
mg/L	mg/kg *	mLs	Source, mg/L	Final Vol., mL (after complete sample prep)
1.0	40	2.0	50	100
0.5	20	1.0	50	100
0.25	10	0.5	50	100
0.10	4.0	0.2	50	100
0.02	0.8	0.04	50	100
0.01	0.4	0.02	50	100

*Assuming 2.5 g solid to 100mL final volume

7.2.1.5. Verification Standards: The solid verification standards are prepared according to SOP NC-WC-086 Alkaline Digestion for Hexavalent Chromium.

Use	Conc. mg/kg	mLs	Source, mg/L	Final Vol., mL (after complete sample prep)
CCV/LCS	20	1.0	50	100

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1. To retard the chemical activity of hexavalent chromium, the samples and extracts must be stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until analyzed.
- 8.2. For aqueous samples, the maximum holding time prior to analysis of the samples or extracts is 24 hours from sampling to analysis.
- 8.3. The holding time for solid samples is 30 days from sampling to digestion and 168 hours after digestion 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 50mL 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 hexavalent chromium concentrations or false positive data. The MB must not contain any hexavalent chromium at or above the reporting limit. For Ohio VAP projects, the MB must not contain hexavalent chromium above the reporting limit.

9.2.2. Corrective Action for MBs

- 9.2.2.1. If the hexavalent chromium level in the MB exceeds the reporting limit for 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 hexavalent chromium 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. Acceptance limits are listed in LIMS.
- 9.3.2. An LCS for waters, consisting of 0.25 mg/L standard, is analyzed with each analytical batch of samples.
- 9.3.3. For solids, two LCSs must be digested 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.
 - 9.3.3.1. An insoluble LCS for solids is analyzed with each analytical batch of samples. Weigh approximately 0.01g of PbCrO_4 (diluted to 50 mL with digestion solution). Record the actual amount added and use in the %R calculation (Section 12.5). Acceptance criterion is 75-125%.
 - 9.3.3.2. A soluble LCS for solids, consisting of 1.0 mL of the 50 mg/L secondary standard diluted to 50 mL with digestion solution is prepared and analyzed with each analytical batch of samples. This LCS is also used as the ICV. Acceptance criterion is 80-120%.
- 9.3.4. Corrective Action for LCSs
 - 9.3.4.1. If hexavalent chromium recovery is outside established control limits, the system is out of control and corrective action must occur.
 - 9.3.4.2. 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 projects, re-preparation of the batch is required unless criteria in Section 9.4.6.3 are met.
 - 9.3.4.3. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for hexavalent chromium, the batch is acceptable. **This must be addressed in the project narrative.**

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD) (Water Samples only)

9.4.1. One MS/MSD pair must be processed for every 10 samples (water matrix). A matrix spike (MS) is a field sample to which known concentrations of hexavalent chromium 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/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. An MS/MSD consisting of 50 mL of sample and 0.25 mL of 50 mg/L secondary standard must be prepared and analyzed with every batch of samples.

9.4.3. Corrective action for MS/MSDs

9.4.3.1. 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 failure.

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 hexavalent chromium concentration in the MS/MSD exceeds four times the spike level for that analyte, the MS/MSD results are flagged with a "4".

9.4.3.5. If the client program requirements specify to confirm matrix interferences, re-preparation, and re-analysis of the MS/MSD may be necessary.

9.5. Additional information of 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.

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 SOP 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. This is not applicable for Ohio VAP.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

10.1.1. A calibration curve is prepared monthly prior to the analysis of water samples, and a calibration curve is digested with each batch of solid samples.

10.2. Initial Calibration

10.2.1. Zero the instrument using a blank. Analyze initial calibration standards for both water and solid matrices as needed and record all absorbances on the analytical logsheet. Derive the correlation coefficient (r), slope (a), and y-intercept (b). The correlation coefficient must be ≥ 0.995 to continue. If the criteria are not met, re-analysis or re-calibration is required.

10.2.2. See Section 7.2.1 for preparation of calibration standards.

10.2.2.1. For water samples, add 1mL diphenylcarbazide solution to each container and swirl to mix. For solid samples, add 0.1 mL diphenylcarbazide solution to each container and swirl to mix.

10.2.2.2. Add concentrated sulfuric acid (drop by drop) to each flask until the pH is 2.0 ± 0.5 . Measure the pH by placing a drop of sample or digestate on narrow range pH paper ($0 - 3 \pm 0.25$). Solid digests may take approximately 1 mL, and all other samples (standards and waters) may take approximately 5 - 10 drops.

NOTE: For samples that may cause color interferences, a second

acidified aliquot must be analyzed without the diphenylcarbazide solution. Record the absorbance on the analytical logsheet.

10.2.2.3. Allow five to ten minutes for color development.

10.3. Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB)

10.3.1. The calibration is verified at the beginning, 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 $\pm 10\%$. For aqueous samples, recalibration is required. The previous ten samples must be re-analyzed and bracketed by a CCV that passes criteria. For solid samples, re-digestion of the sample batch is required.

10.3.2. The system cleanliness is verified at the beginning, every ten samples, and at the end of the run using a CCB. The CCB is 50 mL of reagent water, which is processed through all corresponding preparation and analysis steps like a method blank. It cannot contain the analyte of interest at or above the reporting limit for aqueous samples, or recalibration is required. The previous ten samples must be re-analyzed and bracketed by a CCB that passes criteria. For solid samples, re-digestion of the sample batch is required.

10.4. All supportive laboratory equipment is calibrated as specified in 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.

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 Ohio VAP.

11.3. Recommended Instrument Conditions

11.3.1. Turn on the spectrophotometer and adjust the wavelength to 540 nm. Set the instrument to the absorbance mode. Allow the spectrophotometer to warm up for at least 10 minutes before use.

11.4. Sample Preparation

11.4.1. Water samples require minimal sample preparation. Solid samples require an alkaline digestion procedure after which the sample can be treated as a water sample throughout the remainder of the analysis.

11.4.1.1. Solids: Refer to SOP NC-WC-086, Alkaline Digestion for Hexavalent Chromium.

11.4.1.2. Water Samples

11.4.1.2.1. No preparation is necessary.

11.5. Sample Analysis

11.5.1. Preliminary Evaluation

11.5.1.1. Preliminary evaluation can consist of visual determination by comparison to the standards to determine if dilutions are required.

11.5.1.2. Transfer 50 mL, or aliquot diluted to 50 mL with reagent water, of calibration standards, CCV, CCB, LCS, MBs, and water samples to suitable containers. For solids, pipette 5 mL of filtered sample into a culture tube.

11.5.1.3. Method SM3500 Cr-B (not applicable for solids)

11.5.1.3.1. Add 0.25 mL (approximately 5 drops) of concentrated phosphoric acid to each sample.

11.5.1.3.2. Add concentrated sulfuric acid (drop by drop) to each flask until the pH is 1.0 ± 0.3 . Measure the pH by placing a drop of sample on narrow range pH paper ($0 - 3 \pm 0.25$). Standards and waters may take approximately 5 - 10 drops.

NOTE: Samples may cause color interferences, therefore a second acidified aliquot must be analyzed without the diphenylcarbazide solution. Record the absorbances in the LIMS.

11.5.1.3.3. For water samples, add 1mL diphenylcarbazide solution to each container and swirl to mix.

11.5.1.4. Method 7196A

11.5.1.4.1. For water samples, add 1mL diphenylcarbazide solution to each container and swirl to mix. For solid samples and MSA standards, add 0.1 mL diphenylcarbazide solution to each container and swirl to mix.

11.5.1.4.2. Add concentrated sulfuric acid (drop by drop) to each container until the pH is 2.0 ± 0.5 . Measure the pH by placing a drop of sample or digestate on narrow range pH paper ($0 - 3 \pm 0.25$). Solid digests may take approximately 1 mL, and all other samples (standards and waters) may take approximately 5 - 10 drops.

NOTE: Samples may cause color interferences, therefore a second acidified aliquot must be analyzed without the diphenylcarbazide solution. Record the absorbances in the LIMS.

11.5.1.5. Allow five to ten minutes for color development.

11.5.1.6. Analyze each sample and MSA standard for absorbance, and record the value in the LIMS.

11.5.1.7. A CCV and CCB are analyzed at the beginning and end of the run and every ten samples to verify linearity. The CCV must be $\pm 10\%$ or recalibration is required. The CCB must be less than the reporting limit. All samples after the invalid CCV/CCB must be re-analyzed.

11.5.1.8. Any sample with absorbance values greater than the highest calibration standard must be diluted and re-analyzed.

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. 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.

11.6.4. Record all sample results and associated QC into the LIMS. Level I and Level II review is performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Use linear regression or the following equation to calculate sample results.

$$\frac{\text{Absorbance} - a}{b} = \text{mg/L Cr}^{6+}$$

Where:

a = y-intercept

b = slope

12.2. **Waters, mg/L Cr⁺⁶ = (A - B) x C**

Solids, mg/kg Cr⁺⁶ = (A - B) x C x D

Where:

A = mg/L of sample colorized

B = mg/L of non-colorized sample

C = Dilution Factor = $\frac{\text{Final Volume}}{\text{Initial Volume}}$

D = Weight/Volume Factor = $\frac{\text{Final Volume}}{\text{Sample Weight}}$

12.3. **Water(Laboratory Control Sample) LCS Recovery = $\frac{\text{mg/L}}{0.25 \text{ (true)}} \times 100$**

12.4. **Water CCV Recovery = $\frac{\text{mg/L}}{0.25 \text{ (true)}} \times 100$**

12.5. **Water or Solid –Matrix Spike/Matrix Spike Duplicate**

$$(MS/MSD \text{ Recovery}) = \frac{E - F}{0.25 (\text{true})} \times 100$$

Where:

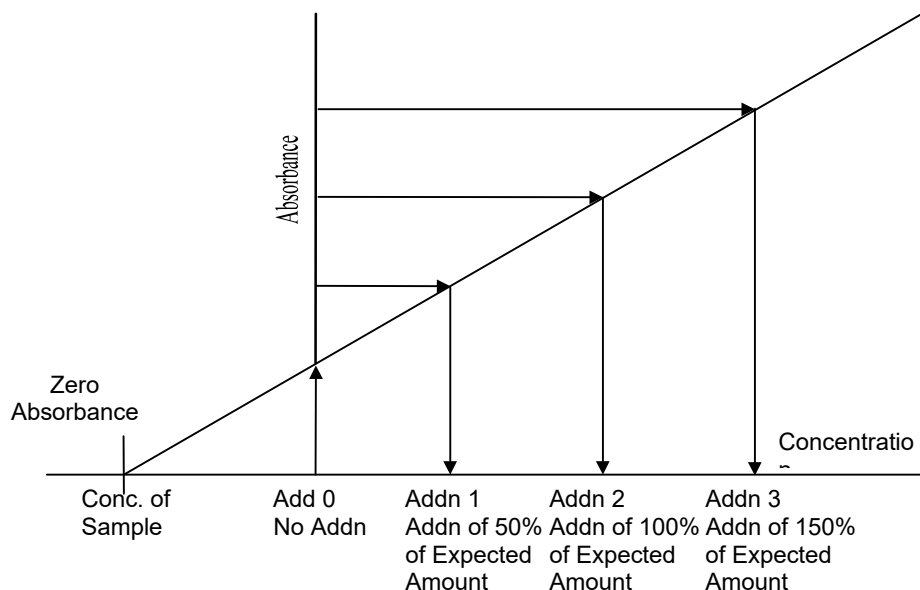
E = Matrix Spike/Matrix Spike Duplicate (MS/MSD), mg/L

F = Sample, mg/L

12.6. **Method of Standard Addition – Solid Extracts only**

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbency, the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should reflect the aqueous standard curve.
- The correlation coefficient of the MSA curve must be 0.995 or greater. If the criteria is not met, the corrected ABS of the unspiked sample will be calculated against the calibration curve to obtain a more accurate result.

12.7. The correlation coefficient (r) for solids is determined by the Pearson product moment correlation coefficient formula:

$$r = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

12.8. Solid Laboratory Control Sample (LCS) Recovery = $\frac{\text{mg/kg}}{20(\text{true})} \times 100 = \% \text{ Recovery}$

12.9. Solid CCV Recovery = $\frac{\text{mg/kg}}{20 (\text{true})} \times 100 = \% \text{ Recovery}$

12.10. Solid Soluble Laboratory Control Sample (LCS) Recovery = $\frac{\text{mg/kg}}{20 (\text{true})} \times 100 = \% \text{ Recovery}$

12.11. Solid Insoluble Laboratory Control Sample (LCS) Recovery =

$$\frac{\text{mg/kg}}{G \bullet H/I} \times 100 = \% \text{ Recovery}$$

Where:

G = mg of PbCrO₄ spiked

H = 0.16 (fraction of Cr in PbCrO₄)

I = kg of sample spiked

12.12. 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. The laboratory must have 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. Acidic or basic waste generated by the analysis. This waste is disposed of in designated acid waste containers located in the lab.
- 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, Third Edition, Chromium, Hexavalent (Colorimetric), Method 7196A

16.1.2. Standard Methods For the Examination of Water and Wastewater, Method 3500-CR-B, 2009

16.1.3. TestAmerica Canton Quality Assurance Manual (QAM), current version

16.1.4. SW846 Test Method for Evaluating Solid Waste, Third Edition, Method 7000A, Section 8.7 Method of Standard Additions.

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 4: 10/31/13		
Revision 1.1: 06/03/97		Revision 5: 08/19/15		
Revision 3.0: 03/08/99		Revision 6: 10/12/16		
Revision 3.1: 10/24/01		Revision 7: 11/07/17		
Revision 3.2: 06/12/02				
Revision 3.3: 10/08/04				
Revision 3.4: 03/07/08				
Revision 3.5: 03/07/08				
Revision 3.6: 07/12/10				
Revision 3.7-A: 04/13/12				

**4/18/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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. Detection and Quantitation Limits, CA-Q-S-006

16.2.5. Standards and Reagents, NC-QA-017

16.2.6. Alkaline Digestion for Hexavalent Chromium, NC-WC-086

16.2.7. Selection of Calibration Points, CA-T-P-002

16.2.8. Calibration Curves (General), CA-Q-S-005

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting Limits

17.1.1. The lower reporting limit (RL) is 0.02 mg/L for waters and 0.8 mg/kg for solids.

Note: Some programs may require lower reporting limits. The laboratory's calibration curve can compensate for RLs down to 0.005 mg/L.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

Title: TOTAL HARDNESS (mg/L CaCO₃), TITRIMETRIC

[Method: Standard Method 2340C]

Approvals (Signature/Date):



01/28/19
Date



01/29/19
Date



01/28/19
Date



02/05/19
Date

This SOP was previously identified as SOP NC-WC-036, Rev 8, dated 12/28/17

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Hardness in waters and wastewaters. It is based on Standard Method 2340C. The approximate working range is 2 to 400 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. Calcium and magnesium ions in the sample are sequestered upon the addition of magnesium ethylenediamine tetraacetate (MgEDTA). The end point of the reaction is detected using Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

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. Some metal ions interfere by causing color fading and indistinct endpoints for the titration. If this is observed, the sample will be analyzed by Method 2340B Hardness by Calculation.

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
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns 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.
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 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 to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Stir plate and stir bars
- 6.2. Erlenmeyer flasks: various
- 6.3. Graduated cylinders: various
- 6.4. Autopipettor and disposable tips
- 6.5. Class A Microburette: 10 mL
- 6.6. Volumetric flasks: various
- 6.7. Plastic bottles: various
- 6.8. Analytical balance: Capable of accurately weighing ± 0.1 mg

7. REAGENTS AND STANDARDS

- 7.1. Reagents
 - 7.1.1. Ammonium Chloride (NH_4Cl): reagent grade
 - 7.1.2. Ammonium Hydroxide (NH_4OH): reagent grade
 - 7.1.3. Magnesium EDTA: reagent grade
 - 7.1.4. EDTA Buffer Solution: Dissolve 16.9 g of NH_4Cl in 143 mL of NH_4OH . Add 1.25 g of magnesium salt of EDTA and dilute to 250 mL with reagent water. Mix well and store in a plastic bottle. This solution is stable for one month. Alternatively, use purchased hardness buffer. Buffer must be kept at room temperature.
 - 7.1.5. Buffer for Water Hardness: Ammonium Chloride-Hydroxide Buffer with Magnesium EDTA. Buffer must be kept at room temperature
 - 7.1.6. Eriochrome Black T Indicator: reagent grade
 - 7.1.7. Sodium Chloride (NaCl): reagent grade
 - 7.1.8. Indicator: Mix together 0.5 g of Eriochrome Black T and 100 g of NaCl . Alternatively, use purchased indicator (such as Calamagite). Indicator must be kept at room temperature.

7.1.9. 1 N Ammonium Hydroxide: Dilute 7 mL of NH_4OH to 100 mL with reagent water and mix well. This solution must be kept at room temperature.

7.1.10. Disodium EDTA Dihydrate: Primary standard grade

7.1.11. 0.02 N EDTA Titrant: Prepare titrant by dissolving 3.723 g of disodium EDTA dihydrate in about 400 mL of reagent water in a 1000 mL volumetric flask. Dilute to 1 liter with reagent water and mix well. This solution is stable for six months. Calibrate weekly against a standard calcium solution by titration. Store the titrant in polyethylene bottle at room temperature.

Note: Purchased EDTA may also be used. Purchased EDTA that is certified does not require weekly standardization unless LCS recovery limits are greater than $\pm 10\%$.

7.1.11.1. Titrant Standardization Procedure: Place 5.0 mL of 1000 ppm standard calcium solution in a vessel containing about 50 mL of reagent water. Add 1 mL of buffer solution. Add about 0.5 - 1 g of dry indicator. Titrate slowly with continuous stirring until the last reddish tinge disappears, adding the last few drops at 3 - 5 second intervals. At the end point, the color is blue. Repeat the standardization procedure two more times and average the values.

$$\text{N of EDTA} = \frac{0.1}{\text{mL of EDTA}}$$

7.2. Standards

7.2.1. Calcium Carbonate Standard Solution, 1000 mg/L: Purchased standard (Hach or other supplier). Alternately, a standard may be made: Place 1.0 g of anhydrous calcium carbonate (primary standard grade) in a 500 mL Erlenmeyer flask. Slowly add 6 N HCl until all the CaCO_3 has dissolved. Add 200 mL of reagent water and boil for five minutes. Cool the solution and add several drops of methyl red indicator. Adjust the solution to an intermediate orange color with 3 N NH_4OH or 6 N HCl as required. Quantitatively transfer the solution to a 1 liter volumetric flask and dilute to volume with reagent water. This solution is stable for six months.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are preserved to a $\text{pH} < 2$ with concentrated nitric acid.

8.2. Samples are stored in plastic or glass containers and may be stored at room temperature, or cold-stored at $4^\circ\text{C} \pm 2^\circ\text{C}$.

8.3. The holding time is six months from sampling to the 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, Method Blank, MS, MSD, 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. 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. A reagent water blank consisting of 50 mL of reagent water and all other reagents added to samples must be analyzed with each analytical batch of samples.

9.2.3. Corrective Action for Blanks

9.2.3.1. 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 holding time considerations, the corresponding sample data **must be addressed in the project narrative**.

9.2.3.2. 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 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 midrange LCS must be analyzed with each analytical batch of samples. The LCS is made of 45 mL reagent water and 5.0 mL 1000 ppm CaCO_3 standard. Alternatively, use 25mL water and 25mL purchased hardness standard.

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.

- 9.3.3.2. The only exception is that if the LCS recovery is 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.**

- 9.3.3.3. 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/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. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. 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. An MS/MSD must be analyzed per analytical batch. The MS/MSD is composed of 20 mL sample, 25 mL reagent water, and 5 mL 1000ppm CaCO_3 .

9.4.3. Corrective Action for MS/MSDs

- 9.4.3.1. 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.

- 9.4.3.2. 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 parent sample used to prepare the MS/MSD exceeds 4x the spike level, the recovery data is reported and flagged with a "4" in the LIMS.

9.4.3.5. If client program requirements specify to confirm matrix interference's, reparation and re-analysis of the MS/MSD may be necessary.

9.5 Sample Duplicate (DU)

9.5.1 Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.6 Control Limits

9.6.1 Control limits are established by the laboratory as described in 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 SOP 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 See section 7.1.11.1 for EDTA titrant standardization procedure.

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. Not applicable

11.4. Sample Analysis Procedure

11.4.1. Samples must be at ambient temperature prior to analysis.

11.4.2. Rinse the burette with reagent water once and with EDTA titrant once. Fill with EDTA titrant and be sure all air bubbles are removed.

11.4.3. Place 25 mL of sample and 25 mL of reagent water in an Erlenmeyer flask. Add approximately 1 to 2 mL of 1N NH_4OH , approximately 1 to 2 mL of EDTA buffer (or add 3-4mL of the purchased buffer) and approximately 0.5 to 1 g of Indicator. Titration should be completed within 5 minutes of the addition of the buffer.

11.4.4. While stirring, slowly titrate with EDTA titrant until the last reddish tint disappears. The end point is blue. Record the volume of titrant used and its true normality on the analytical logsheet.

Note: Samples requiring more than 10 mL of titrant must be diluted. An aliquot is diluted to 25 mL with reagent water and treated as a sample.

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

$$12.1. \quad \text{Hardness, mg/L CaCO}_3 = \frac{(A - B) \times N \times 50,000}{C} \times D$$

Where:

A = Volume of EDTA titrant used for sample, mL
 B = Volume of EDTA titrant used for blank, mL
 C = Volume of sample used, mL (not total volume after addition of DI water)

$$D = \text{Dilution Factor} = \frac{\text{Final Dilution Volume, mL}}{\text{Initial Sample Volume Used For Dilution, mL}}$$

N = Normality of EDTA titrant
 50,000 = 50 (Equivalent weight of Calcium) x 1000 mg/g

12.1.1. LCS Recovery

$$\text{LCS \% Recovery} = \frac{\text{mL titrant} \times N \times 50,000}{(25) \text{ LCS TV}} \times 100$$

Where:

N = Normality of EDTA titrant
 LCS TV = value of purchased hardness standard

12.1.2. MS/MSD Calculation

$$\text{MS / MSD \% Recovery} = \frac{(A - B)}{200} \times 100$$

Where:

A = MS/MSD concentration (from 12.1)
 B = Sample concentration (from 12.1)

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

15.2.1.1. **Aqueous 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 acid waste drum labeled as "Acid 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 Method for EDTA Titrimetric Method, Method 2340C, 1997.

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: 12/23/98		Revision 3.4: 11/18/10
		Revision 3: 04/19/99		Revision 4: 12/26/13
		Revision 3.1: 11/06/04		Revision 5: 6/11/15
		Revision 3.2: 03/21/08		Revision 6: 6/7/16
		Revision 3.3: 04/28/10		Revision 7: 02/27/17

**4/18/19: Changed logo and copyright information. No changes made to revision number or effective date.*

16.2. Associated SOPs and Policies, current version

16.2.1. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.2. QA Policy, QA-003

16.2.3. Glassware Washing, NC-QA-014

16.2.4. Method Detection Limits and Instrument Detection Limits, NC-QA-021 and CA-Q-S-006

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting Limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 5 mg/L CaCO₃.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Deviation from Standard Method 2340C:

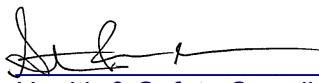
17.2.1. Wastewater samples are not digested.

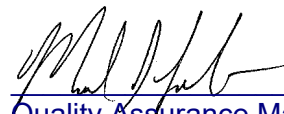
Title: SULFIDE

**[Methods: SW846 Methods 9030B and 9034,
and SM4500 S2-F]**

Approvals (Signature/Date):

 02/17/18
Technology Specialist Date

 02/19/18
Health & Safety Coordinator Date

 02/15/18
Quality Assurance Manager Date

 03/01/18
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°C and the hydrogen sulfide (H₂S), 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.)

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 ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) 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 $\text{KH}(\text{IO}_3)_2$ 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:

$$\text{Na}_2\text{S}_2\text{O}_3 \text{ Normality} = \frac{(a)(b)}{c}$$

Where:

- a = mLs Biodate (20 mL)
- b = Normality Biodate (0.025N)
- c = mLs of $\text{Na}_2\text{S}_2\text{O}_3$ 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:

$$\text{Normality Iodine} = \frac{(\text{Normality Na}_2\text{S}_2\text{O}_3)(\text{mL of titrant Na}_2\text{S}_2\text{O}_3)}{20 \text{ mL Iodine}}$$

- 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.

- 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 $5\text{g} \pm 0.1\text{ g}$ 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 0.025 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

$$\text{Sulfide, mg / L or mg / kg} = \frac{[(A \times B) - (C \times D)] \times 16,000}{\text{mL or g of sample used}}$$

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

$$\text{LCS \% Recovery} = \frac{\text{mg/L (from 12.1.1)}}{20 \text{ (true)}} \times 100$$

Note: The true value of the standard is determined daily.

12.1.2. MS/MSD Recovery

$$\text{MS/MSD \% Recovery} = \frac{A - B}{20 \text{ (waters) or } 1000 \text{ (solids)}} \times 100$$

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		

**4/19/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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.

17.2. Method Deviations

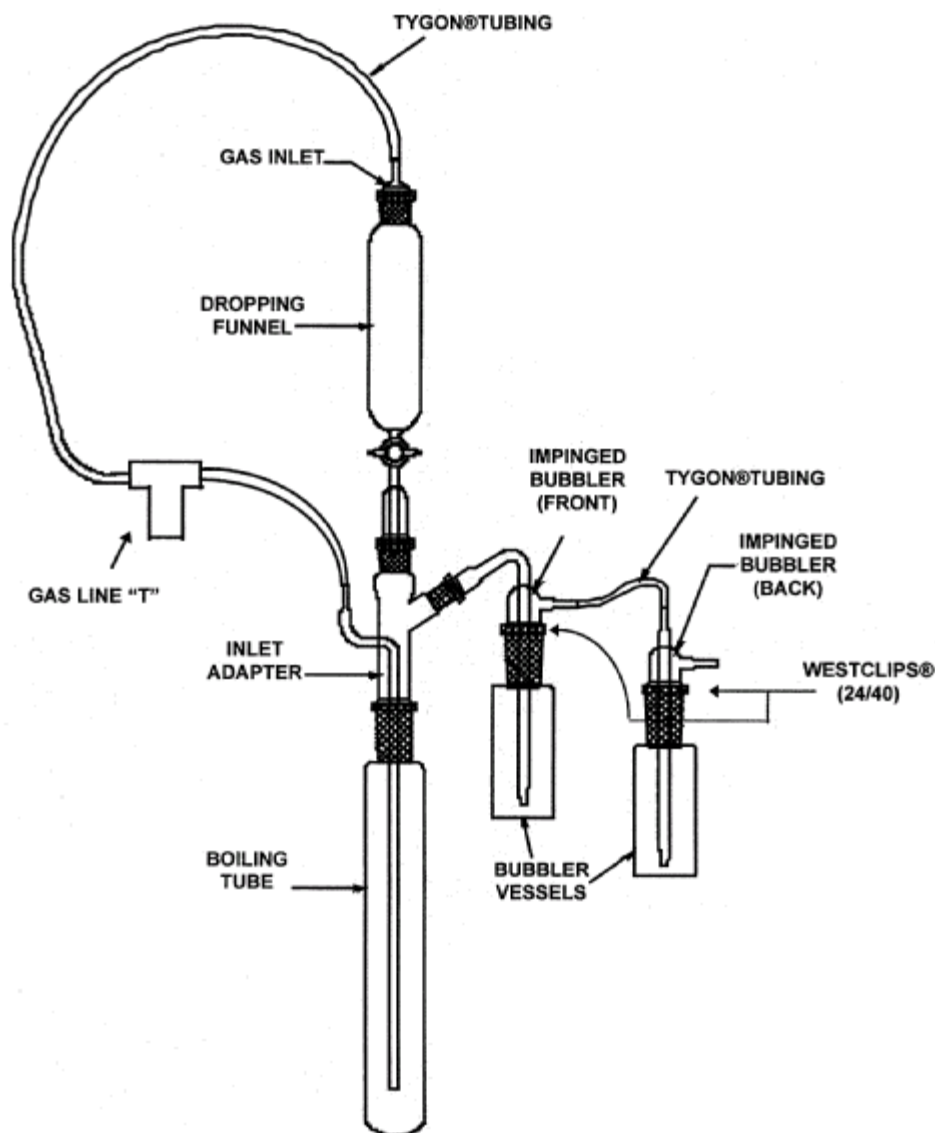
17.2.1. The laboratory does not add formaldehyde due to interferences with the analysis.

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.

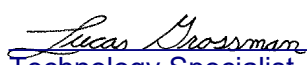
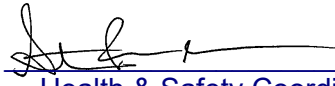
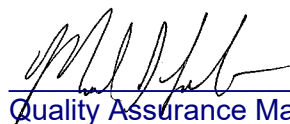
FIGURE 1
ACID-SOLUBLE SULFIDE DISTILLATION APPARATUS



Title: DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

[Method: EPA Method 300.0A and SW846 Method 9056A]

Approvals (Signature/Date):

 _____ Technology Specialist	<u>03/08/18</u> Date	 _____ Health & Safety Coordinator	<u>03/12/18</u> Date
 _____ Quality Assurance Manager	<u>03/16/18</u> Date	 _____ Technical Director	<u>03/12/18</u> 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.

- 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 μ L of calibration standard #9, and add 4.975 mL of DI.
- 7.5.1.2. Calibration Standard #2: Take 125 μ L of calibration standard #9, and add 4.875 mL of DI.
- 7.5.1.3. Calibration Standard #3: Take 250 μ L 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.

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 $\pm 10\%$, 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 $\pm 10\%$ 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 $\pm 20\%$.
- 10.4. Initial Calibration Verification (ICV) – The Initial Calibration is verified immediately following calibration, prior to sample analysis. The acceptance criterion is $\pm 10\%$ 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/Integriion 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:

$$\frac{\text{Conductivity}}{400} = \text{DILUTION FACTOR}$$

- 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.

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

$$CF = \frac{\text{Peak Area (or height) of the compound in the standard}}{\text{Mass of the compound injected}}$$

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

$$RSD = \frac{SD}{\overline{CF}} \times 100$$

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 calculate 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

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		

**4/19/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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

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

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.

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

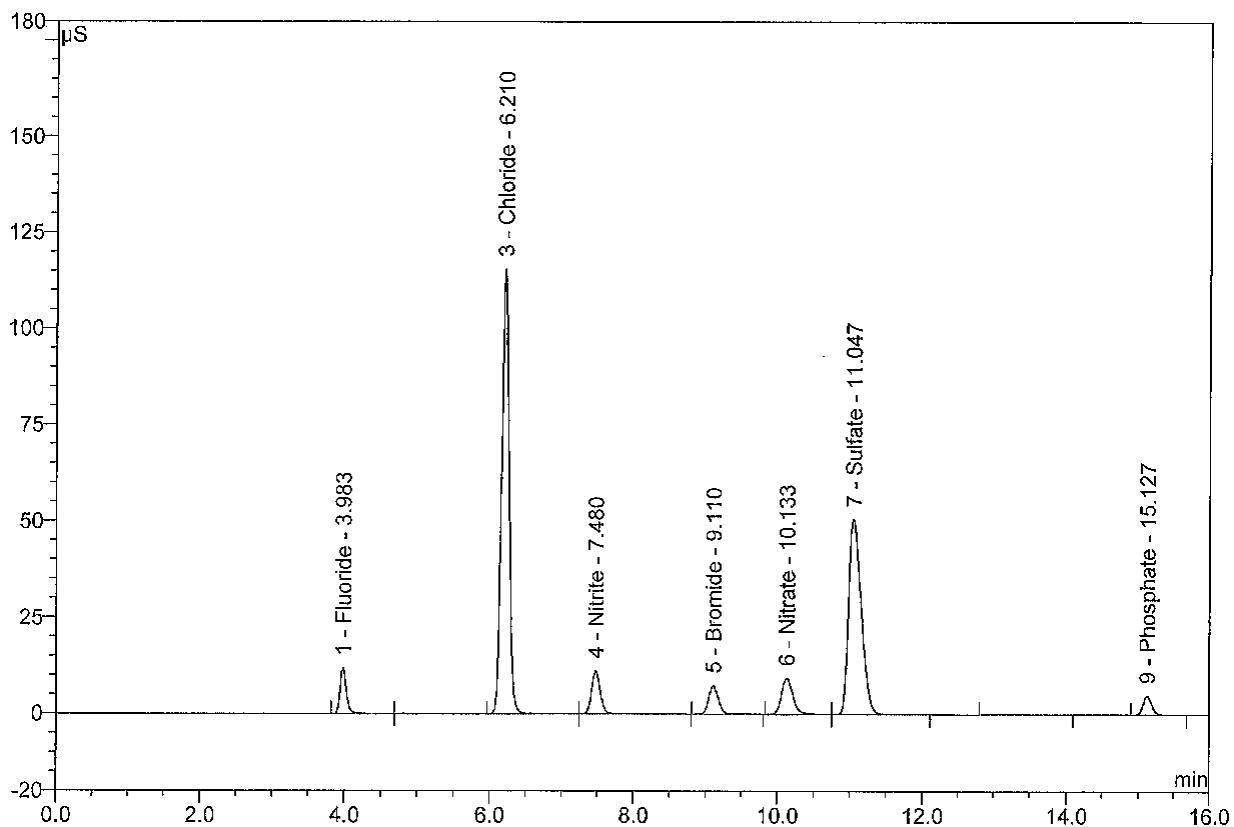
TABLE 2
Standard Run Retention Time Matrix (minutes)*

ICS-2100 / Integrion

<u>Analyte</u>	<u>Concentration (mg/L)</u>												
	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
NO₂⁻	7.49		7.50			7.49	7.48	7.47					
Br⁻		9.14			9.14			9.12	9.10	9.08			
NO₃⁻	10.18		10.17			10.15	10.12	10.07					
SO₄²⁻				11.20				11.19			11.08	11.00	10.86

FIGURE 1
EXAMPLE ION CHROMATOGRAM

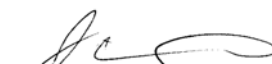
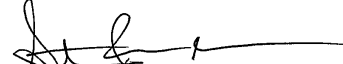
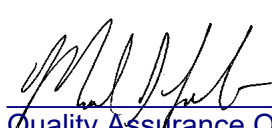
ICS-2100 and Integrion



Title: HEM / SGT-HEM BY SOLID PHASE EXTRACTION (SPE)

[Method: 1664A and 1664B]

Approvals (Signature/Date):

	<u>02/19/19</u>		<u>02/19/19</u>
Technology Specialist	Date	Health & Safety Coordinator	Date
	<u>02/20/19</u>		<u>02/25/19</u>
Quality Assurance Officer	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-WC-091, Rev. 10, dated 11/28/18

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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.
- 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.

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.

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 -23°C (-9°F), 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 H₂O, **slowly** add 250 mL of concentrated hydrochloric acid. Bring to mark with DI H₂O. (Other volumes may be prepared as is convenient).
- 7.4. n-Hexane, 85% purity, 99.0 % min. saturated C₆ 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 $\pm$ 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.

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 H₂SO₄ 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 $\pm$ 2°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 $\pm 10\%$ (i.e., 0.2 mg) at 2mg and $\pm 0.5\%$ (i.e., 5 mg) at 1000 mg. If values are not within these limits, see section

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.
 - 11.2.2. Glassware is cleaned by washing in hot water containing detergent, then rinsing with tap and distilled water. Heavily soiled glassware may require additional washing procedures as deemed necessary by the analyst.
- 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 ($\pm$ 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.
- 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.

Note: If there is a water layer present in the collection vessel, drain this off into the hexane waste container prior to pouring the hexane into the evaporating/weighing pan.

- 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.

Note: Crystals of stearic acid are routinely observed for the OPR/LCS and matrix spikes.

- 11.6.4. 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.

11.6.4.1. 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.

11.6.4.2. 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:

$$V_a = \frac{1000V_t}{W_h}$$

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:

$$\text{HEM}(mg/L) = \frac{W_{\text{HEM}}(mg)}{V_s(L)}$$

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:

$$W_c(mg) = \frac{V_t}{V_a} W_d(mg)$$

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:

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n-1}}$$

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. Acidic waste generated by the analysis. This waste is collected in the laboratory in a designated container identified as "Acid Waste".
- 15.2.2. Solvent waste: This waste is disposed of in a flammable liquid solvent container identified as "Flammable Solvent Waste".

15.2.3. 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. Method 1664B, 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, February 2010

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 4: 04/13/12		
Revision 1.0: 11/15/99		Revision 5: 03/29/13		
Revision 1.1: 08/28/01		Revision 6: 11/07/14		
Revision 1.2: 11/05/04		Revision 7: 12/10/15		
Revision 1.3: 07/16/07		Revision 8: 02/16/17		
Revision 0: 09/30/08		Revision 9: 03/01/18		
Revision 1: 11/07/08		Revision 10: 11/28/18		
Revision 2: 12/18/09				
Revision 3: 01/26/11				

*4/19/19: changed logo and copyright information. No changes made to revision number or effective date.

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. Detection and Quantitation Limits, CA-Q-S-006

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.

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.

17.1.4. The reference method uses sodium sulfate to remove possible water from the hexane. The laboratory runs the analysis by Solid Phase Extraction which does not require the use of sodium sulfate.

17.2. Tables and Appendices

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

Appendix A: Preprogrammed Methods For The Horizon SPE-DEX 3000XL

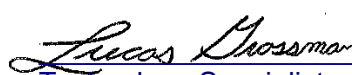
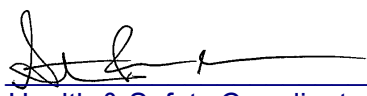
	Method 26	Method 27	Method 28	Method 29	Method 30
<u>Disk Setup Size / Prefilter</u>	<u>Pacific Premium 47 mm / None</u>	<u>Pacific Premium 47 mm / Prefilter</u>	<u>Pacific Premium 100 mm / None</u>	<u>Pacific Premium 100 mm / Prefilter</u>	<u>None / None</u>
<u>PW Hexane</u>					
Dispense	6 s	6 s	10 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
<u>PW Methanol</u>					
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
<u>Process Sample</u>					
<u>Air Dry</u>	3 min.	5 min.	3 min.	8 min.	0 s
<u>Hexane Rinse</u>					
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	
<u>Hexane Rinse</u>					
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	
<u>Hexane Rinse</u>					
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	
<u>MeOH Discard</u>					
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

	Method 26	Method 27	Method 28	Method 29	Method 30
<u>Hexane Rinse</u>					
Rinse	2 s	2 s	4 s	4 s	<u>3 s</u>
Soak	45 s	45 s	45 s	45 s	<u>0 s</u>
Elute	45 s	45 s	45 s	45 s	<u>15 s</u>
<u>Hexane Rinse</u>					
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	
<u>Hexane Rinse</u>					
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	
<u>Hexane Rinse</u>					
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):

	<u>07/18/18</u>		<u>07/20/18</u>
Technology Specialist	Date	Health & Safety Coordinator	Date
	<u>07/30/18</u>		<u>07/23/18</u>
Quality Assurance Manager	Date	Technical Director	Date

This SOP was previously identified as SOP No. NC-WC-092, Rev 7, dated 7/27/17

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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.
- 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.
- 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 $4\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ 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.
- 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.
 - 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. **Note:** Do not place TDS samples into an oven that contains active TSS samples.

- 11.9.3.8. If filtrate volume exceeds dish capacity, add successive portions to the same dish after evaporation.
- 11.9.3.9. Dry the evaporated sample in an oven for at least one hour at 180 ± 2 °C.
- 11.9.3.10. 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.
- 11.9.3.11. Using tongs remove the weighing dish from the oven and place in a desiccator and cool to room temperature.
- 11.9.3.12. 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.
- 11.9.3.13. 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.
- 11.9.3.14. 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.
- 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. Acidic sample waste generated by the analysis. This waste is disposed of in designated acid waste containers located in the laboratory.

15.2.2. 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		Revision 7: 07/27/17

**4/19/19: Changed logo and copyright information. No changes made to revision number or effective date.*

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. Detection and Quantitation Limits, CA-Q-S-006

16.2.5. Volumetric Dispenser Calibrations, NC-QA-004

16.2.6. Standards and Reagents, NC-QA-017

16.2.7. Support Equipment Calibration and Verification, 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

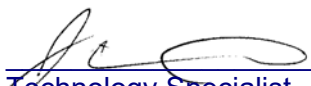
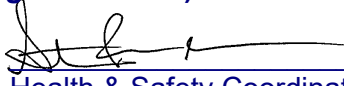
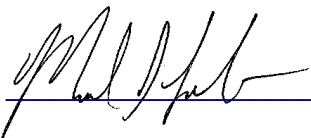
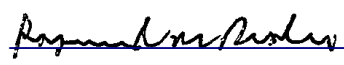
QC Samples	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	1 per batch of up to 20 samples	$< \pm \text{RL}$	Re-analyze all samples associated with unacceptable MB. If the MB fails high, associated samples that are below the reporting limit may be reported with narration.
Laboratory 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	$\leq 20\%$ RPD when results $> 5x \text{RL}$. For TSS, RPD must be $\leq 10\%$.	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

**Title: TOTAL, CARBONATE, BICARBONATE, AND HYDROXIDE
ALKALINITY**

[Method: SM2320B]

Approvals (Signature/Date):			
	<u>11/01/18</u>		<u>10/23/18</u>
Technology Specialist	Date	Health & Safety Coordinator	Date
	<u>10/22/18</u>		<u>11/05/18</u>
Quality Assurance Manager	Date	Technical Director	Date

This SOP was previously identified as SOP NC-WC-093, Rev 5 dated 3/12/18

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable for the determination of total, carbonate, bicarbonate, and hydroxide alkalinity in surface, saline, domestic, and industrial waters and wastewaters. It is based on Standard Method 2320B. The working linear range is 5 to 2500 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. An unaltered sample is titrated to an electrometric endpoint of pH 4.5. **The sample must not be filtered, concentrated, or altered in any way.** The sample is tested for alkalinity, and calculations are performed to determine carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), and/or hydroxide (OH^-).

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica Canton Laboratory QA 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 with salts of weak organic or inorganic acids and greases or oils will interfere with pH measurements.
- 4.3. The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titrant volume greater than 25 mL.
- 4.4. Suspended solids or precipitates may coat the electrode and cause a sluggish response.

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
Sulfuric Acid	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.
Note: Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3. Eye protection, 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. 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. Alkalinity – Manual (Appendix A)
 - 6.1.1. Stir plate and stir bars
 - 6.1.2. Class A graduated cylinders: various
 - 6.1.3. Class B calibrated beakers: various

6.1.4. Buret: Class A 25 mL or 50 mL (preferred)

6.2. Alkalinity - Automated

6.2.1. Autotitrator

6.2.2. 15 mL centrifuge tubes

6.3. Alkalinity – Manual and Automated

6.3.1. pH meter and electrode(s) with temperature compensation

6.3.2. Volumetric pipettes: various

6.3.3. Autopipettor and disposable tips

6.3.4. Top loading balance: Capable of accurately weighing ± 0.01 g

6.3.5. Class A volumetric flasks: various

6.3.6. Oven

6.3.7. Desiccator

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. 0.02 N Sulfuric Acid: reagent grade, purchased. If a certified reagent is purchased standardization is not necessary.

Note: If the 0.02 N sulfuric acid titrant is made by the laboratory group, it will require standardization monthly. See Appendix B for recipe and standardization process.

7.1.2. Sodium Carbonate (Na_2CO_3): reagent grade, dry overnight in 180°C oven and cool in a desiccator, or purchased primary standard.

7.1.3. Sodium Carbonate Solution: Add 0.20g of Na_2CO_3 (record exact weight of Na_2CO_3 used) to a 250mL volumetric flask and dilute to volume with reagent water. Mix well.

7.2. Standards

7.2.1. Target Calibration Standard

7.2.1.1. pH Buffers: 4, 7, 10, and 12 (purchased)

7.2.2. Laboratory Control Sample

- 7.2.2.1. Alkalinity Standard, 25,000 mg/L CaCO₃, purchased or other commercially available reference solutions

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 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 (LCS, Method Blank, or 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. 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 form of Alkalinity at or above the reporting limit.
- 9.2.2. An MB consisting of 15 mL of reagent water and all other reagents added to samples within the analytical batch is analyzed with each analytical batch of samples.
- 9.2.3. Corrective Action for MBs
- 9.2.3.1. If the level in the MB exceeds the reporting limit for Alkalinity 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**.

- 9.2.3.2. If there is no Alkalinity 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) for Total Alkalinity Only

- 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.
- 9.3.2. An LCS consisting of 0.25mL of the 25,000 mg/L alkalinity standard and 15 mL reagent water or other commercially available reference solution is analyzed with each analytical batch of samples.
- 9.3.3. Corrective Action for LCS
 - 9.3.3.1. If the Alkalinity level is outside established control limits the system is out of control and corrective action must occur.
 - 9.3.3.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for Alkalinity, the batch is acceptable. **This must be addressed in the project narrative.**
 - 9.3.3.3. Corrective action will be re-preparation and re-analysis of the batch, unless the client agrees that other corrective action is acceptable.

9.4. Sample Duplicates (DU) for Total Alkalinity Method 2320B, Carbonate, Bicarbonate, and Hydroxide Alkalinity

- 9.4.1. DUs are performed at a minimum frequency of one per 10 analytical samples and must meet laboratory-specific limits for precision.

9.5. QC Acceptance Criteria

- 9.5.1. Control limits are established by the laboratory as described in NC-QA-018.
- 9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are listed in the TestAmerica Canton Quality Assurance Manual (QAM) and the latest version is 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 SOP 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. Instrument Directions

10.1.1. Calibrate the pH meter according to the manufacturer's specifications. See pH Electrode Method SOP NC-WC-010 if measuring for alkalinity manually.

10.2. Initial Calibration

10.2.1. The pH meter is calibrated everyday with the 4, 7, 10 and 12 calibration buffers and is verified at the beginning of the run by using the 7 buffer. The pH buffers must bracket the sample concentration.

10.2.2. To verify proper operation of the pH electrode, verify that the pH 7 buffer solution reads within the range of -30 to +30 mV.

10.3. Continuing Calibration

10.3.1. The pH meter is checked every ten readings with a midrange (pH 7) buffer to ensure the calibration remains linear. The acceptance range for the calibration check is 7 ± 0.10 pH units or recalibration is necessary.

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 root cause and corrective action described.

11.3. Sample Preparation

11.3.1. No preparation is necessary for water samples.

11.4. Sample Analysis – Manual

11.4.1. See Appendix A for the manual sample analysis procedure.

11.5. Sample Analysis – Automated – Summary

11.5.1. The samples are analyzed on the autotitrator for Alkalinity.

11.5.2. Do not shake sample.

11.5.3. Samples should be analyzed at room temperature

11.5.4. Place 15 mL of sample or an aliquot diluted to 15 mL with reagent water, in a 15 mL centrifuge tube. See Manufacturer's information for operating instructions.

11.5.5. If a dilution of the sample was done, change the volume on the schedule to reflect the dilution (based on a 10 mL sample inject). For alkalinity, the dilution factor will be taken into account in the final calculation. Do not manually multiply the dilution unless it was not typed into the schedule.

11.5.6. After the results have been gathered from the instrument make sure to check the pH of all samples. If a sample has an initial pH >4.5 and the Total Alkalinity is zero, the sample must be diluted and re-analyzed.

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. 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.

11.6.4. 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. Calculations

$$12.1.1. \text{Total Alkalinity, mg/L CaCO}_3 \text{ to pH 4.5} = \frac{A \times N \times 50,000}{\text{mL of sample}}$$

$$12.1.2. \text{LCS \%} = \frac{\text{mg/L}}{500 (\text{true})} \times 100$$

Where:

A = mL of titrant
N = Normality of titrant
B = MS/MSD, mg/L
C = Sample, mg/L

12.1.3. Phenolphthalein alkalinity is calculated when titrating to an endpoint of 8.3, and is performed by the instrument.

12.1.4. Calculate the following alkalinities using the total alkalinity value.

ALKALINITY RELATIONSHIPS

Result of Titration	Hydroxide Alkalinity as CaCO_3	Carbonate Alkalinity as CaCO_3	Bicarbonate Concentration as CaCO_3
$P = 0$	0	0	T
$P < \frac{1}{2} T$	0	2P	$T - 2P$
$P = \frac{1}{2} T$	0	2P	0
$P > \frac{1}{2} T$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

P = Phenolphthalein alkalinity

T = Total alkalinity

12.1.5. Calculation of alkalinity relationships: see the referenced method for these calculations.

13. METHOD PERFORMANCE

13.1. Each analyst must have initial demonstration of performance data on file and the laboratory must have applicable method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure an associate who has been properly trained in its use and has the required experience performs this procedure.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the analyst 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
 - 15.2.1. This waste is drained from the titration cell into the aqueous waste stream since the pH range 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".
- 15.3. 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. Standard Methods for the Examination of Water and Wastewater, Alkalinity Method, 2320B, 1997.
 - 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: (formerly NC-WC-003 and NC-WC-006)		Revision 3: 02/23/16		
(-003) Rev 1: 05/16/95 (-006) Rev 2: 03/04/98		Revision 4: 04/28/17		
(-003) Rev 2: 03/20/00 (-006) Rev 3: 04/04/00		Revision 5: 03/12/18		
(-003) Rev 2.1: 02/08/01 (-006) Rev 4: 02/06/01				
(-003) Rev 2.2: 12/07/04 (-006) Rev 5: 10/25/04				
(-003) Rev 2.3: 11/09/07 (-006) Rev 6: 01/30/06				

(-006) Rev 7: 03/01/08				
Revision 0: 05/27/11				
Revision. 1: 09/19/13				
Revision 2: 02/10/15				

*4/19/19: Changed logo and copyright information. No changes made to revision number or effective date.

16.2. Associated SOPs

16.2.1. pH Electrode Method for Wet Chemistry Parameters, NC-WC-010

16.2.2. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.3. QA Policy, QA-003

16.2.4. Glassware Washing, NC-QA-014

16.2.5. Detection and Quantitation Limits, CA-Q-S-006

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The lower reporting limit (RL) for undiluted samples is 5 mg/L CaCO_3 .

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. A fixed endpoint of 4.5 is used for all samples since the sample concentration is often unknown.

17.2.2. The Sodium Carbonate (Na_2CO_3) is dried at 180°C overnight instead of at 250° C for 4 hours.

17.2.3. The standard acid solution is not boiled for 3-5 minutes under a watch glass cover.

17.2.4. A sample dilution will be needed if the 4.5 endpoint cannot be reached after adding the maximum amount of acid.

17.2.5. Low alkalinity samples will also be determined by the method above, and not by the low-alkalinity method.

17.2.6. All Alkalinity samples will be titrated with 0.02 N sulfuric acid.

Appendix A: Manual procedure for determining Alkalinity

Note: The manual procedure is to be used only when absolutely required in order to meet sample hold times. For the manual procedure, an RL of 20 mg/L is required. Alternately, Project Managers may send samples out to an appropriately certified facility for analysis if holding time permits.

- Sample Analysis – Manual
 - Do not shake sample.
 - Record the initial pH prior to sample analysis.
 - Use a sufficiently large volume of titrant (>20 mL in a 50 mL burette) to obtain good precision while keeping the volume low enough to permit a sharp end point
 - Place 50 mL of sample or an aliquot diluted to 50 mL with reagent water, in a beaker. Begin mixing; measure and record initial pH of the sample. Titrate the sample to an endpoint of pH 4.5 with 0.02 N H₂SO₄. Record the volume of the titrant in LIMS. Samples requiring >50 mL titrant (> 75 mL using autotitrator) should be re-analyzed using less sample volume. Record any dilutions in LIMS.

Appendix B: 0.02 N Sulfuric Acid Titrant: Creation and Standardization

- 0.02 N Sulfuric Acid Titrant Solution
 - 1 N H₂SO₄ Solution: Fill a 100 mL volumetric flask approximately half way with reagent water. Carefully pipette 2.75 mL of concentrated Sulfuric Acid into the flask and bring to volume with reagent water.
 - 0.02 N H₂SO₄ Titrant solution: Fill a 1 L volumetric flask approximately half way with reagent water. Carefully add 20 mL of 1 N H₂SO₄ Solution and bring to final volume with reagent water.
 - This titrant must be standardized monthly.
- Standardization
 - To standardize 0.02 N sulfuric acid, titrate 50 mL (15 mL on the autotitrator) of the sodium carbonate solution with 0.02 N H₂SO₄ to a pH of 4.5. This should be performed monthly or on a new lot of acid (whichever is more frequent). Calculate as follows:

$$N = \frac{A \times 1000}{53.00 \times B} \quad (\text{Manual Method})$$

$$N = \frac{A \times 1000}{53.00 \times B} \times \frac{10}{15} \quad (\text{Autotitrator})$$

Where: A = g of Na₂CO₃

B = mL of 0.02 N H₂SO₄ titrant

- Repeat standardization two or three more times. Record the standardization as an intermediate reagent for the Sulfuric acid in the LIMS Reagents module. The standardization must be 0.018 – 0.022 or re-standardization and/or re-preparation is required.

PFAS Leaching Procedure



Table of Contents

1.	Identification of the Method	2
2.	Applicable Matrix or Matrices	2
3.	Scope and Application.....	2
4.	Summary of Method	2
5.	Safety:	2
6.	Equipment and Supplies:	3
6.1	Personal Protective Equipment	3
6.2	Test Equipment and Supplies	3
7.	Reagents and Standards	3
8.	Sample Collection, Preservation, Shipment, and Storage.....	3
9.	Procedure.....	4
10.	Pollution Prevention	4
11.	References	4



1. Identification of the Method

This method is used to leach soils and sediments for per- and polyfluoroalkyl substances (PFAS) using groundwater that is either from the site or based on site groundwater chemistry. The procedure is performed in-house by GHD's Innovative Technology Group (ITG).

2. Applicable Matrix or Matrices

Soil, sediment, sand, or clay and drinking, ground, surface, or saline water.

3. Scope and Application

This method is used to generate a leachate from soil and sediment samples for PFAS analyses.

4. Summary of Method

This method describes the required steps to generate a leachate from soil and sediment samples for PFAS analyses using water with chemistry similar to that at the site in order to assess the potential for mobilization of PFAS compounds that are bound to soil.

5. Safety

Lab staff are required to implement the GHD Safety Means Responsibility Awareness Teamwork (SMART) program as follows:

- A Job Safety Analysis (JSA) for each task has been reviewed, modified for the specific site conditions, and communicated to all appropriate personnel.
- Incorporate Stop Work Authority; Stop, Think, Act, Review (STAR) process; Safe Task Evaluation Process (STEP); Observations process; Near Loss and incident Management process in the day-to-day operations of the job.
- Review and implement applicable sections of the GHD Safety and Health Policy Manual.
- Be prepared for emergency situations, locating safety showers, fire protection equipment, evacuation route, rally point, and first aid equipment before being working, and make sure that the equipment is in good working order.
- Each staff member should review the Laboratory Chemical Hygiene Plan and take the Laboratory Safety Training annually.
- Be prepared to call the GHD Incident Hotline at 1-866-529-4886 for all involving injury/illness, property damage, vehicle incident, and/or significant Near Loss.



- It is the responsibility of the Project Manager to ensure that all GHD personnel have received the appropriate health and safety and laboratory training and are qualified to complete the work.

6. Equipment and Supplies

6.1 Personal Protective Equipment

- Safety Glasses
- Closed toed shoes
- Nitrile gloves
- Lab coat

6.2 Test Equipment and Supplies

- Pipettes
- Pipette bulb
- Tumbler
- 2 liter HDPE bottles for tumbler
- 0.7 micron glass fiber filter paper
- Vacuum filtration apparatus

7. Reagents and Standards

- Sodium Sulfide (site-specific)
- Sodium Dithionite (site-specific)
- Certified-PFAS free water

8. Sample Collection, Preservation, Shipment, and Storage

Soil samples can be collected in glass jars. If groundwater samples are being used, they should be collected in HDPE bottles. Samples should be stored at 4°C and leaching should be performed immediately upon arrival.



9. Procedure

Soil Leaching Procedure

1. Measure out 25 g of soil into a 1.0 liter HDPE bottle
2. Add 500 mL of the certified-PFAS free water or site groundwater and add sodium sulfide/sodium dithionite mixture to the bottle to replicate site conditions
3. Place the bottle on the Tumbler for 15-18 hours
4. After the tumble, filter the sample through the filter paper
5. Pour the filtrate into appropriate sample containers for PFAS analyses.
6. The sample is then ready for analysis
7. Repeat for each sample

Note that for saturated soil samples, the soil will be placed on a vacuum filtration apparatus with a 0.7 micron glass fiber filter to remove water from the sample prior to placing the soil in the HDPE bottle.

10. Pollution Prevention

Any leftover samples will be disposed of into the correct waste container. All lab ware will be rinsed into the correct waste container. The waste containers will be disposed of by a waste disposal company upon completion of the project.

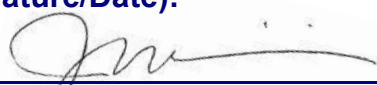
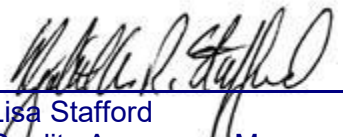
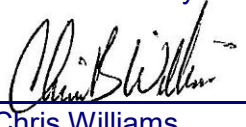
11. References

- United States Environmental Protection Agency (USEPA) Method 1311. Toxicity Characteristic Leaching Procedure. Revision 0 dated July 1992.
- USEPA Method 1312. Synthetic Precipitation Leaching Procedure. Revision 0 dated September 1994.

**Title: Per- and Polyfluorinated Substances (PFAS) in Water, Soils,
Sediments and Tissue**

**[Method 537 (Modified), Method PFAS by LCMSMS Compliant with QSM
5.1 Table B-15]**

Approvals (Signature/Date):

 Robert Hrabak Technical Manager	<u>02/22/2019</u> Date	 Joe Schairer Health & Safety Manager / Coordinator	<u>02/25/2019</u> Date
 Lisa Stafford Quality Assurance Manager	<u>02/25/2019</u> Date	 Chris Williams Laboratory Manager	<u>02/26/2019</u> Date

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1. SCOPE AND APPLICATION

- 1.1. This procedure describes the analysis of water, soil, sediment, and tissue samples for the following compounds using liquid chromatography / tandem mass spectrometry (LC/MS/MS).

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUdA (PFUnA)	2058-94-8
Perfluoro-n-dodecanoic acid	PFDaA	307-55-1
Perfluoro-n-tridecanoic acid	PFTTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA (PFTA)	376-06-7
Perfluoro-n-hexadecanoic acid (non-routine analyte)	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid (non-routine analyte)	PFODA	16517-11-6
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanedisulfonic acid	PFBS	375-73-5
Perfluoro-1-pentadisulfonic acid	PFPeS	2706-91-1
Perfluoro-1-hexadisulfonic acid	PFHxS	355-46-4
Perfluoro-1-heptadisulfonic acid	PFHpS	375-92-8
Perfluoro-1-octadisulfonic acid	PFOS	1763-23-1
Perfluoro-nonadisulfonic acid	PFNS	8789-57-2
Perfluoro-1-decadisulfonic acid	PFDS	335-77-3
Perfluoro-1-dodecadisulfonic acid	PFDoS	79780-39-5
Perfluorinated sulfonamides (FOSA)		
Perfluoro-1-octanesulfonamide	FOSA	754-91-6
Perfluorinated sulfonamidoacetic acids (FOSAA)		
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9
Fluorotelomer sulfonates (FTS)		
1H,1H,2H,2H-perfluorohexane sulfonate (4:2)	4:2 FTS	757124-72-4

Compound Name	Abbreviation	CAS #
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2 FTS	27619-97-2
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2 FTS	39108-34-4
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2 FTS	120226-60-0

Abbreviations in parenthesis are the abbreviations listed in Method 537, where they differ from the abbreviation used by the laboratory's LIMS.

- 1.2. Additional analytes supported by this method: The following analytes can be supported by this method under special request.

Compound Name	Abbreviation	CAS #
Fluorinated Replacement Chemicals		
Dona (Donic acid)	Dona	919005-14-4
Perfluoro(2-propoxypropanoic) acid	HFPO-DA or GenX	13252-13-6
F53B (reported as the summation of the following)	F53B	NA
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate	F53B major	73606-19-6
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate	F5B minor	83329-89-9

- 1.3. The working range of the method is listed below. The linear range can be extended by diluting the extracts.

Matrix	Nominal Sample Size	Reporting Limit	Working Range
Water	250 mL	2.0 ng/L – 20 ng/L	2.0 ng/L - 400 ng/L
Soil/Sediment	5 g	0.2 ug/kg – 2.0 ug/kg	0.2 ug/kg - 40 ug/kg
Tissue	1 g	1.0 ug/kg – 10 ug/kg	1.0 ug/kg – 200 ug/kg

- 1.4. The procedure for the analysis of water samples via in line solid phase extraction (SPE) for a subset of the list in Section 1.1 using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a SCIEX 5500 is described in Attachment 1 of this SOP.
- 1.5. This procedure also includes direction for preparing and analyzing samples to determine “Total Oxidizable Precursors”, which may assist in improving understanding of potential PFAS environmental risk.
- 1.6. When undertaking projects for the Department of Defense (DoD) and/or the Department of Energy (DOE) the relevant criteria in QA Policy WS-PQA-021, “Federal Program Requirements” must be checked and incorporated.

2. SUMMARY OF METHOD

- 2.1. Water samples are extracted using a solid phase extraction (SPE) cartridge. PFAS are eluted from the cartridge with an ammonium hydroxide/methanol solution.

- 2.2. Soil/sediment/tissue samples are extracted with a KOH/methanol solution using an orbital shaker for 3 hours followed by sonication for 12 hours. The mixture is centrifuged and the solvent filtered.
- 2.3. The final 80:20 methanol:water extracts are analyzed by LC/MS/MS. PFAS are separated from other components on a C18 column with a solvent gradient program using 20 mM ammonium acetate/water and methanol. The mass spectrometer detector is operated in the electrospray (ESI) negative ion mode for the analysis of PFAS.
- 2.4. An isotope dilution technique is employed with this method for the compounds of interest. The isotope dilution analytes (IDA) consist of carbon-13 labeled analogs, oxygen-18 labeled analogs, or deuterated analogs of the compounds of interest, and they are spiked into the samples at the time of extraction. This technique allows for the correction for analytical bias encountered when analyzing more chemically complex environmental samples. The isotopically labeled compounds are chemically similar to the compounds of concern and are therefore affected by sample-related interferences to the same extent as the compounds of concern. Compounds that do not have an identically labeled analog are quantitated by the IDA method using a closely related labeled analog.
- 2.5. Quantitation by the internal standard method is employed for the IDA analytes/recoveries. Peak response is measured as the area of the peak.
- 2.6. Samples for the "Total Oxidizable Precursor" assay (TOP) are analyzed in two phases – an aliquot is prepared and analyzed as a normal sample, and a second aliquot is subjected to oxidation with potassium persulfate and sodium hydroxide prior to solid phase extraction and analysis. The total perfluorocarboxylic acid value is determined for each aliquot, and the difference calculated.

3. DEFINITIONS

- 3.1. PFCAs: Perfluorocarboxylic acids
- 3.2. PFSA: Perfluorinated sulfonic acids
- 3.3. FOSA: Perfluorinated sulfonamide
- 3.4. PFOA: Perfluorooctanoic acid
- 3.5. PFOS: Perfluorooctane sulfonic acid
- 3.6. PTFE: Polytetrafluoroethylene (e.g., Teflon®)
- 3.7. SPE: Solid phase extraction

- 3.8. PP: Polypropylene
- 3.9. PE: Polyethylene
- 3.10. HDPE: High density polyethylene
- 3.11. AFFF: Aqueous Film Forming Foam
- 3.12. IDA: Isotope dilution analyte
- 3.13. Further definitions of terms used in this SOP may be found in the glossary of the Laboratory Quality Assurance Manual (QAM).

4. INTERFERENCES

- 4.1. PFAS have been used in a wide variety of manufacturing processes, and laboratory supplies should be considered potentially contaminated until they have been tested and shown to be otherwise. The materials and supplies used during the method validation process have been tested and shown to be clean. These items are listed below in Section 6.
- 4.2. To avoid contamination of samples, standards are prepared in a ventilation hood in an area separate from where samples are extracted.
- 4.3. PTFE products can be a source of PFOA contamination. The use of PTFE in the procedure should be avoided or at least thoroughly tested before use. Polypropylene (PP) or polyethylene (PE, HDPE) products may be used in place of PTFE products to minimize PFOA contamination.
 - 4.3.1. Standards and samples are injected from polypropylene autosampler vials with polypropylene screw caps once. Multiple injections may be performed on Primers when conditioning the instrument for analysis.
 - 4.3.2. Random evaporation losses have been observed with the polypropylene caps causing high IDA recovery after the vial was punctured and sample re-injected. For this reason, it is best to inject standards and samples once in the analytical sequence.
 - 4.3.3. Teflon-lined screw caps have detected PFAS at low concentrations. Repeated injection from the same teflon-lined screw cap have detected PFNA at increasing concentration as each repeated injection was performed, therefore, it is best to use polypropylene screw caps.
- 4.4. Volumetric glassware and syringes are difficult to clean after being used for solutions containing high levels of PFOA. These items should be labeled for use only with

similarly concentrated solutions or verified clean prior to re-use. To the extent possible, disposable labware is used.

- 4.5. Both branched and linear PFAS isomers can potentially be found in the environment. Linear and branched isomers are known to exist for PFOS, PFOA, PFHxS, PFBS, EtFOSAA, and MeFOSAA based upon the scientific literature. If multiple isomers are present for one of these PFAS they might be adjacent peaks that completely resolve or not, but usually with a deflection point resolved during peak integration. The later of these peaks matches the retention time of its labeled linear analog. In general, earlier peaks are the branched isomers and are not the result of peak splitting.
- As of this writing, only PFOS, PFOA, and PFHxS are commercially available as technical mixtures. These reference standards of the technical mixtures for these specific PFAS are used to ensure that all appropriate peaks are included during peak integration.
- 4.6. In an attempt to reduce PFOS bias, it is required that m/z 499>80 transition be used as the quantitation transition.
- 4.7. Per the Certificate of Analysis for labeled perfluorohexadecanoic acid ($^{13}\text{C}_2$ -PFHxDA) produced by Wellington Laboratories, the stock standard contains roughly 0.3% of native perfluorohexadecanoic acid. This equates to roughly 0.30 ng/L or 0.015 ug/kg of perfluorohexadecanoic acid expected in all samples and blanks.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Sacramento Supplement to the CSM, and this document. All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported **immediately** to a supervisor, the EH&S Staff, or a senior manager.

5.1. Specific Safety Concerns

- 5.1.1. Preliminary toxicity studies indicate that PFAS could have significant toxic effects. In the interest of keeping exposure levels as low as reasonably achievable, PFAS and PFAS samples must be handled in the laboratory as hazardous and toxic chemicals.
- 5.1.2. Exercise caution when using syringes with attached filter disc assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.
- 5.1.3. Laboratory procedures such as repetitive use of pipets, repetitive transferring of extracts and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best

position to realize when they are at risk for these types of injuries.

Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

- 5.1.4. Eye protection that satisfies ANSI Z87.1 (as per the TestAmerica Corporate Safety Manual), laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.1.5. Perfluorocarboxylic acids are acids and are not compatible with strong bases.
- 5.1.6. The use of vacuum systems presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed, or marred in any manner must not be used under vacuum. It must be removed from service and replaced.
- 5.1.7. Glass containers are not to be used for “tumbling” soil samples.

5.2. Primary Materials Used

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 ⁽¹⁾	Hazards	Exposure Limit ⁽²⁾	Signs and Symptoms of Exposure
Acetic Acid (3-2-1)	Corrosive Poison Flammable	10 ppm-TWA 15 ppm-STEL	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.

Material ⁽¹⁾	Hazards	Exposure Limit ⁽²⁾	Signs and Symptoms of Exposure
Ammonium Hydroxide (3-0-0)	Corrosive Poison	50 ppm-TWA	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage to the upper respiratory tract. 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 damage, including blindness. Brief exposure to 5000 PPM can be fatal.
Hexane (2-3-0)	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 (3-0-1)	Corrosive Poison	5 ppm (Ceiling)	Can cause pain and severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause deep ulcerations to skin, permanent eye damage, circulatory failure and swallowing may be fatal.
Methanol (2-3-0)	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.
Potassium Hydroxide (3-0-1)	Corrosive Poison		Severe irritant. Can cause severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause severe scarring of tissue, blindness, and may be fatal if swallowed.
Potassium Persulfate (2-0-1-OX)	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.
Sodium Hydroxide (3-0-1)	Corrosive Poison	2 mg/cm ³ (Ceiling)	Severe irritant. Can cause severe burns upon inhalation, ingestion, eye or skin contact. Exposure to concentrated solutions may cause severe scarring of tissue, blindness, and may be fatal if swallowed.

(1) Always add acid to water to prevent violent reactions.

(2) Exposure limit refers to the OSHA regulatory exposure limit.

6. EQUIPMENT AND SUPPLIES

- 6.1. 15 mL polypropylene test tubes with polypropylene screw caps.
- 6.2. 50 mL graduated plastic centrifuge tubes.
- 6.3. 125 mL HDPE bottles with HDPE screw caps.
- 6.4. 250 mL HDPE bottles with HDPE screw caps. The average weight of the HDPE bottles with HDPE screw caps are calibrated once per year. The calibration is performed by weighing 10 bottles with caps and dividing by 10 to get the average weight. The average weight is used in section (11.3.5.1.d).
- 6.5. Analytical balance capable of accurately weighing to the nearest 0.0001g, and checked for accuracy each day it is used in accordance with WS-QA-0041.
- 6.6. Extract concentrator or nitrogen manifold with water bath heating to 50-55°C.
- 6.7. Syringe filter, Millipore Millex-HV 0.45 μ m, or equivalent. Do not use PTFE type filters.
- 6.8. 300 μ L autosampler vials, polypropylene, with polypropylene screw caps, Waters PN 1860004112, or equivalent.
- 6.9. SPE columns
 - 6.9.1. Phenomenex Strata SPE C18, 6 mL, 500 mg, part number 8B-S002-HCH, Waters SepPak C18, 1 to 10g, or equivalent.
 - 6.9.2. Waters Oasis WAX 150 mg/6 cc (PN 186002493) for the cleanup of solids.
 - 6.9.3. Waters Oasis WAX 500 mg/6 cc (PN 186004647) for extraction of PFAS from aqueous sample.
 - 6.9.4. Phenomenex Gemini 3 μ m C18 110Å, 50 X 2 mm, Part No. 00B-4439-B0.
 - 6.9.5. Phenomenex Luna 5 μ m C18(2) 100Å, 30 X 3 mm, Part No. 00A-4252-Y0.
 - 6.9.6. Penomenex Gemini 3 μ m C18 110A, 50 X 3mm, Part No. 00B-4439-Y0.
- 6.10. Graphitized carbon (Envi-CarbTM or equivalent).
- 6.11. Vacuum manifold for Solid Phase Extraction (SPE).

- 6.12. Miscellaneous laboratory apparatus (beakers, test tubes, volumetric flasks, pipettes, etc.). These should be disposable where possible, or marked and segregated for high-level versus low-level use.
- 6.13. Water bath: Heated with concentric ring cover capable of temperature control ($\pm 5^{\circ}\text{C}$) up to 95°C . The bath must be used in a fume hood.
- 6.14. Plastic tub for an ice bath, AKRO-N.S.T. part No. 35-180 or equivalent.
- 6.15. pH indicator paper, wide range.
- 6.16. Bottle rotating apparatus for soil extractions.
- 6.17. Glass fiber filter, Whatman GF/F, catalog number 1825 090 or equivalent.
- 6.18. Liquid Chromatography/Tandem Mass Spectrometer (LC/MS/MS) – Either of the instruments described below, or equivalent, may be used for this method. Both HPLC are equipped with a refrigerated autosampler, an injection valve, and a pump capable of variable flow rate. The use of a column heater is required to maintain a stable temperature throughout the analytical run. Data is processed using Chrom Peak Review, version 2.1 or equivalent.
 - 6.18.1. SCIEX LC/MS/MS

This system consists of a Shimadzu HPLC interfaced with a SCIEX 5500 Triple Quad MS. The instrument control and data acquisition software is SCIEX Analyst, version 1.6.3 or equivalent.

 - 6.18.1.1. Shimadzu CTO-20AC HPLC equipped with 3 LC-20AD pumps and one DGU-20 degassing unit or equivalent.
 - 6.18.1.2. Phenomenex Gemini C_{18} 3 μm , 3.0 mm x 100 mm, Part No. 00D-4439-Y0, or equivalent.
 - 6.18.1.3. PFAS Isolator column, Phenomenex Luna C_{18} 5 μm , 50 mm x 4.6 mm, part no. 00B-4252-E0 or equivalent. This is plumbed between the UPLC pumps and autosampler valve to minimize PFAS background from the UPLC solvent lines and filters.
 - 6.18.2. Waters LC/MS/MS

This consists of a Waters Acquity UPLC system interfaced with a Waters Quattro Premier tandem mass spectrometer. The instrument control and data acquisition software is MassLynx version 4.1, or equivalent.

 - 6.18.2.1. Analytical column: Waters Acquity UPLC BEH C_{18} 1.7 μm , 3.0 mm x 150 mm, Part No. 186004690

- 6.18.2.2. PFAS Isolator column, Waters Acquity UPLC BEH Shield RP-18, 1.7 μ m, 2.1 mm x 50 mm, PN 186004476, or equivalent. This is plumbed between the UPLC pumps and autosampler valve to minimize PFAS background from the UPLC solvent lines and filters.

- 6.19. Preventive and routine maintenance is described in the table below

HPLC/MS/MS Preventative Maintenance	
<u>As Needed:</u> Change pump seals. Change in-line filters in autosampler (HPLC). Check/replace in-line frit if excessive pressure or poor performance. Replace column if no change following in-line frit change. Clean corona needle. Replace sample inlet tube in APCI (10.1 cm). Replace fused silica tube in ESI interface. Clean lenses. Clean skimmer. Ballast rough pump 30 minutes. Create all eluents in Reagent module, label eluent containers with TALS label and place 2nd label into maintenance log when put into use.	<u>Daily (When in use)</u> Check solvent reservoirs for sufficient level of solvent. Verify that pump is primed, operating pulse free. Check needle wash reservoir for sufficient solvent. Verify capillary heater temperature functioning. Verify vaporizer heater temperature. Verify rough pump oil levels. Verify turbo-pump functioning. Verify nitrogen pressure for auxiliary and sheath gasses. Verify that corona and multiplier are functioning.
<u>Semi-Annually</u> Replace rough-pump oil (4-6 months). Replace oil mist and odor elements. Replace activated alumina filter if applicable	<u>Annually</u> Vacuum system components including fans and fan covers. Clean/replace fan filters, if applicable.

7. REAGENTS AND STANDARDS

- 7.1. Reagent grade chemicals shall be used in all tests whenever available. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on the 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.

- 7.1.1. Acetic acid, glacial
- 7.1.2. Ammonium acetate (20 mM in water): Prepared by weighing 1.509g of ammonium acetate and dissolving in 1L of water. The resultant solution is filtered through a 0.22um filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.
- 7.1.3. Ammonium hydroxide (NH₄OH), 0.3% in methanol: Prepared by diluting 12mL of ammonium hydroxide into 4L of methanol.
- 7.1.4. Hexane
- 7.1.5. Hydrochloric acid (HCl), 2.0 M solution in water
- 7.1.6. Hydrochloric acid (HCl), concentrated, reagent grade
- 7.1.7. Methanol
- 7.1.8. Potassium hydroxide (KOH), 0.4% in methanol: Prepared by weighing 16g of potassium hydroxide and dissolving in 4L of methanol.
- 7.1.9. Potassium persulfate, reagent grade
- 7.1.10. Ottawa Sand
- 7.1.11. Sodium hydroxide (NaOH), 0.1N, in water: Prepared by diluting 400mL of 1N NaOH into 3.6L of water for a total volume of 4L.
- 7.1.12. Sodium hydroxide (NaOH), 10N, reagent grade
- 7.1.13. Water, Nanopure or Millipore, must be free of interference and target analytes.
- 7.2. Standards
 - 7.2.1. PFAS are purchased as high purity solids (96% or greater) or as certified solutions. Standard materials are verified compared to a second source material at the time of initial calibration. The solid stock material is stored at room temperature or as specified by the manufacturer or vendor.
 - 7.2.1.1. Per the Certificate of Analysis for labeled perfluorohexadecanoic acid (13C₂-PFHxDA) produced by Wellington Laboratories, the stock standard contains roughly 0.3% of native perfluorohexadecanoic acid. This equates to roughly 0.30 ng/L or 0.015 ug/kg of perfluorohexadecanoic acid expected in all samples and blanks.

7.2.2. If solid material is used for preparing a standard, stock standard solutions are prepared from the solids and are stored at $4 \pm 2^\circ\text{C}$. Stock standard solutions should be brought to room temperature before using. Standards are monitored for signs of degradation or evaporation. Standard solutions must be replaced at least annually from the date of preparation.

7.2.3. PFBS, PFHxS, PFHpS, PFOS, PFDS, and many other PFAS are not available in the acid form, but rather as their corresponding salts, such as sodium or potassium. The standards are prepared and corrected for their salt content according to the equation below.

$$\text{Mass}_{\text{acid}} = \text{Measured Mass}_{\text{salt}} \times \text{MW}_{\text{acid}} / \text{MW}_{\text{salt}}$$

Where: MW_{acid} is the molecular weight of PFAA

MW_{salt} is the molecular weight of the purchased salt.

7.2.4. For example, the molecular weight of PFOS is 500.1295 and the molecular weight of NaPFOS is 523.1193. Therefore, the amount of NaPFOS used must be adjusted by a factor of 0.956.

7.3. Calibration Standards

The calibration stock solution is prepared by diluting the appropriate amounts of stock solutions in 80% methanol/water. The calibration stock solution is diluted with methanol to produce initial calibration standards. These are the normal calibration levels used. A different range can be used if needed to achieve lower reporting limits or a higher linear range.

7.4. Initial Calibration (ICAL) Levels (ng/mL)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Perfluoroalkylcarboxylic acids (PFCAs)							
PFBA	0.5	1.0	5.0	20	50	200	400
PFPeA	0.5	1.0	5.0	20	50	200	400
PFHxA	0.5	1.0	5.0	20	50	200	400
PFHpA	0.5	1.0	5.0	20	50	200	400
PFOA	0.5	1.0	5.0	20	50	200	400
PFNA	0.5	1.0	5.0	20	50	200	400
PFDA	0.5	1.0	5.0	20	50	200	400
PFUdA	0.5	1.0	5.0	20	50	200	400
PFDoA	0.5	1.0	5.0	20	50	200	400
PFTTrDA	0.5	1.0	5.0	20	50	200	400
PFTeDA	0.5	1.0	5.0	20	50	200	400
PFHxDA	0.5	1.0	5.0	20	50	200	400
PFODA	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonic acids (PFSAs)							

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
PFBS	0.5	1.0	5.0	20	50	200	400
PFPeS	0.5	1.0	5.0	20	50	200	400
PFHxS *	0.5	1.0	5.0	20	50	200	400
PFHpS	0.5	1.0	5.0	20	50	200	400
PFOS *	0.5	1.0	5.0	20	50	200	400
PFNS	0.5	1.0	5.0	20	50	200	400
PFDS	0.5	1.0	5.0	20	50	200	400
PFDoS	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonamides (FOSA)							
FOSA	0.5	1.0	5.0	20	50	200	400
Perfluorinated sulfonamidoacetic acids (FOSAA)							
EtFOSAA	0.5	1.0	5.0	20	50	200	400
MeFOSAA	0.5	1.0	5.0	20	50	200	400
Fluorotelomer sulfonates (FTS)							
4:2 FTS	0.5	1.0	2.0	20	50	200	400
6:2 FTS	0.5	1.0	5.0	20	50	200	400
8:2 FTS	0.5	1.0	5.0	20	50	200	400
10:2 FTS	0.5	1.0	5.0	20	50	200	400
Labeled Isotope Dilution Analytes (IDA)							
13C4-PFBA	50	50	50	50	50	50	50
13C5-PFPeA	50	50	50	50	50	50	50
13C2-PFHxA	50	50	50	50	50	50	50
13C4-PFHpA	50	50	50	50	50	50	50
13C4-PFOA	50	50	50	50	50	50	50
13C5-PFNA	50	50	50	50	50	50	50
13C2-PFDA	50	50	50	50	50	50	50
13C2-PFUdA	50	50	50	50	50	50	50
13C2-PFDoS	50	50	50	50	50	50	50
18O2-PFHxS	50	50	50	50	50	50	50
13C4-PFOS	50	50	50	50	50	50	50
13C3-PFBS	50	50	50	50	50	50	50
13C2-PFTeDA	50	50	50	50	50	50	50
13C2-PFHxDA	50	50	50	50	50	50	50
13C8-FOSA	50	50	50	50	50	50	50
d5-EtFOSAA	50	50	50	50	50	50	50
d3-MeFOSAA	50	50	50	50	50	50	50
M2-4:2FTS †	50	50	50	50	50	50	50
M2-6:2FTS	50	50	50	50	50	50	50
M2-8:2FTS	50	50	50	50	50	50	50
Internal Standard (IS)							

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
13C2-PFOA	50	50	50	50	50	50	50

* Both branched and linear isomers are used.

‡ - This compound is used as a reverse surrogate for the TOP analysis.

Note: Sample extracts are in 80% MeOH/H₂O.

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7
Fluorinated Replacement Chemicals							
HFPO-DA	0.5	1.0	5.0	20	50	200	400
9CI-PF3ONS (F53B major)	0.5	1.0	5.0	20	50	200	400
11CI-PF3OUdS (F53B minor)	0.5	1.0	5.0	20	50	200	400
Dona	0.5	1.0	5.0	20	50	200	400
Labeled Isotope Dilution Analytes							
13C3-HFPO-DA	0.5	1.0	5.0	20	50	200	400

Note: Sample extracts are in 80% MeOH/H₂O.

Note: The above calibration limits are provided only as an example. The actual ICAL level used for each analytical batch will depend upon the LOQ requirements of the program. The concentration of the calibration solutions for non-concentrated extracts is 1/20th the levels indicated above.

7.4.1. A technical (qualitative) grade PFOA standard which contains both linear and branched isomers is used as a retention time (RT) marker. This is used to integrate the total response for both linear and branched isomers of PFOA in environmental samples while relying on the initial calibration with the linear isomer quantitative standard. This technical (qualitative) grade PFOA standard is analyzed initially, after every initial calibration or when significant changes are made to the HPLC parameters.

7.4.1.1. Attach this document to the ICV from the associated ICAL by scanning the document and associating it to the file as a document type of High Res MS Tune in TALS. Use the following naming convention: “_ZbatchnumberTPFOA”.

7.5. Initial Calibration Verification Standard (ICV)

A second source solution for PFAS is purchased from the same vendor; the PFC-MXB contains most of the target analytes in this mixture and is used as an ICV. A few compounds are not available in this mixture, may not be available as another lot, and are not available from another vendor. For these analytes only, a second analyst may prepare a second source standard from the same source as the ICAL to produce an ICV. The recommended concentration of the ICV standard should be in the mid-range of the

calibration curve. The concentration may be adjusted if the initial calibration levels are changed or altered. The IDA and IS are added at a fixed concentration of 50 ng/mL.

7.6. LCS/Matrix PFC Spike Solution, 20 ng/mL

The PFC spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at a concentration of 20 ng/mL in methanol.

7.7. PFC Isotope Dilution Analyte Solution, 50 ng/mL

The PFC-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each compound at a concentration of 50 ng/mL in methanol.

7.8. Reverse Surrogate Solution, 1000 ng/mL

The reverse surrogate solution is prepared by diluting M2-4:2 FTS to produce a solution containing this compound at a concentration of 1000 ng/mL in methanol. This is added to all samples for the TOP assay to monitor the efficiency of the oxidation process.

7.9. Internal Standard Solution, 250 ng/mL

The internal standard solution is prepared by diluting $^{13}\text{C}_2$ -PFOA to produce a solution containing this compound at a concentration of 250 ng/mL in methanol. This is added to all extracts prior to analysis. The internal standard solution used for the non-concentrated extracts is at a concentration of 50 ng/mL.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Water samples are collected in pre-cleaned 250 mL HDPE containers. Soil samples are collected in pre-cleaned 8 oz. HDPE containers. Other containers may also be suitable. Samples are chilled to 0 - 6°C for shipment to the laboratory.

8.1.1. Water samples collected from a known chlorinated source should be preserved with Trizma.

8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6°C. Water samples must be extracted within 14 days of collection. Soil samples must also be extracted within 14 days of collection. Tissue samples must be extracted within 1 year of collection if stored at -20°C. Extracts must be refrigerated at 0 - 6°C, and analyzed within 40 days from extraction.

8.2.1. Projects performed for the state of New Jersey have an analytical holding time 28 days from the extraction date.

8.2.2. For projects performed for the state of New Jersey a field reagent blank (FRB) must be collected with each sample set. Acceptance limits are <RL for each analyte.

***Note:** As of this writing, Method 537 provides for a 14 day holding time for water samples preserved with Trizma buffer. The scientific literature indicates that perfluorinated substances are highly persistent in the environment. TestAmerica Sacramento has conducted time stability studies that support a 14 day holding time for aqueous samples with and without Trizma preservation. TestAmerica Denver has conducted stability studies indicating that medium- and low-level solutions of PFOA are stable for at least three months in polystyrene and polypropylene plastics at 0-6°C. The 14/40 day holding times given above are based on the stability study and general EPA convention for the holding time of extractable organic compounds in water and soil.*

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability (IDOC)

The initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2. Batches are defined at the sample preparation step. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC program document (WS-PQA-003) for further details of the batch definition.

9.2.1. The quality control batch is a set of up to 20 samples of the same matrix processed using the same procedure 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. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count toward 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 a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD, an LCSD may be substituted if batch precision is required by the program or client. In the event that multiple MS/MSDs are run with a batch due to client requirements, the additional MS/MSDs do not count toward the maximum 20 samples in a batch.

9.3. One method blank (MB, laboratory reagent blank) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. For aqueous samples, the method blank is an aliquot of laboratory reagent water. For solid samples, the method blank is an aliquot of Ottawa sand. The method blank is processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, and then implemented when target analytes are detected in the method blank above the reporting limit or when IDA recoveries are outside of the control limits. Re-extraction of the blank, other batch QC and the affected samples are required when the method blank is deemed unacceptable. See policy WS-PQA-003 for specific acceptance criteria.

- 9.3.1. If the MB produces a peak within the retention time window of any of the analytes, determine the source of the contamination and eliminate the interference before processing samples.
 - 9.3.2. The method blank must not contain any analyte at or above the reporting limit, or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher.
 - 9.3.3. 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. Such action should be taken in consultation with the client.
 - 9.3.4. Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.
 - 9.3.5. Refer to WS-PQA-003 for further details of the corrective actions.
 - 9.3.6. Projects performed under the auspices of the DOD/DOE must meet QSM specific criteria for method blanks. Results are acceptable if the blank contamination is less than $\frac{1}{2}$ of the reporting limit/LOQ for each analyte, or less than $\frac{1}{10}$ of the regulatory limit, or less than $\frac{1}{10}$ of the sample result for the same analyte, whichever is greater. If the method blank does not meet the acceptance criteria, the source of contamination must be investigated and measures taken to correct, minimize or eliminate the problem. Reprepare and reanalyze all field and QC samples associated with the contaminated method blank.
- 9.4. A laboratory control sample (LCS) must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. The LCS is an aliquot of laboratory matrix (e.g. water for aqueous samples and Ottawa sand for solids) spiked with analytes of known identity and concentration. The LCS must be processed in the same manner and at the same time as the associated samples. Corrective actions must be documented on a Non-Conformance memo, then implemented when recoveries of any spiked analyte is outside of the control limits. Re-extraction of the blank, other batch QC, and all associated samples are required if the LCS is deemed unacceptable. See WS-PQA-0003 for specific acceptance criteria. The control limits for the LCS are stored in TALS.
- 9.4.1. Projects performed for the state of New Jersey: LCS (mid and high spike) recovery limits are 70-130%. Low level LCS recovery limits are 50-150%. The spike level must rotate between low, medium and high.
- 9.5. A matrix spike/matrix spike duplicate (MS/MSD or MS/SD) pair must be extracted with every process batch of similar matrix, not to exceed twenty (20) samples. An

MS/MSD pair is aliquots of a selected field sample spiked with analytes of known identity and concentration. The MS/MSD pair must be processed in the same manner and at the same time as the associated samples. Spiked analytes with recoveries or precision outside of the control limits must be within the control limits in the LCS. Corrective actions must be documented on a nonconformance memo, and then implemented when recoveries of any spiked analyte are outside of the control limits provided by TALS or by the client.

- 9.5.1. Projects performed for the state of New Jersey: MS/MSD (mid and high spike) recovery limits are 70-130%. Low level MS/MSD recovery limits are 50-150%. The spike level must rotate between low, medium and high.
- 9.6. A duplicate control sample (LCSD or DCS) may be added when insufficient sample volume is provided to process an MS/MSD pair, or is requested by the client. The LCSD is evaluated in the same manner as the LCS. See WS-PQA-003 for specific acceptance criteria.
- 9.7. Initial calibration verification (ICV) –A second source standard is analyzed with the initial calibration curve. The concentration should be at the mid range of the curve. Corrective actions for the ICV include:
- Rerun the ICV.
 - Remake or acquire a new ICV.
 - Evaluate the instrument conditions.
 - Evaluate the initial calibration standards.
 - Rerun the initial calibration.
- 9.8. Isotope Dilution Analytes
- 9.8.1. The IDA solution is added to each field and QC sample at the time of extraction, as described in Section 11. As described in Section 7, this solution consists of isotopically labeled analogs of the analytes of interest.
- 9.8.2. IDA recoveries are flagged if they are outside of the acceptance limits (25–150%). Quantitation by isotope dilution generally precludes any adverse effect on data quality due to IDA recoveries being outside of the acceptance limits as long as the signal-to-noise ratio is greater than 10:1.
- 9.8.2.1. Evaluate data quality for usability, flag and submit a non-conformance memo for any analytes outside of the recovery criteria, and report if data is deemed not adversely effected.

9.8.2.2. Re-extraction of samples should be performed if the signal-to-noise for any IDA is less than 10:1 or if the IDA recoveries fall below 10%.

9.8.2.2.1. Re-extraction may be necessary under other circumstances when data quality has been determined to be adversely affected.

9.8.2.3. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for IDA recoveries which are 50-150%. If QC or field samples do not meet these criteria then re-extraction is required.

9.9. Internal Standard

9.9.1. The Internal Standard (IS) is added to each field and QC samples prior to analysis. The CCV IS response (peak area) must not deviate by more than 50% from the average response (peak area) of the initial calibration.

9.9.2. Sample IS response (peak area) must be within $\pm 50\%$ of the response (peak area) in the most recent CCV.

9.9.3. If the IS does not meet criteria, re-analyze the extract. If the IS meets criteria in the second analysis, report that analysis. If the IS does not meet criteria in the second analysis, report the first analysis with narration.

9.10. TOP Oxidation Efficiency

9.10.1. If the data indicates incomplete oxidation (i.e. the Post-TOP M2-4:2 FTS recovery is greater than 10% or the Post-TOP precursor concentration is greater than 10% of the Pre-TOP concentration) then a second aliquot (10 mL or a 0.2g equivalent) should be processed.

9.10.2. A reduced sample size may be used initially if sample history or other information indicates the sample is grossly contaminated.

9.11. Ion Ratio

9.11.1. Compare the quantifier/qualifier SRM transition ratio in the sample to the SRM transition ratio in the standard.

9.11.2. The quantifier/qualifier SRM ion ratio should be within $\pm 50\%$ of the average of the quantifier/qualifier SRM ion ratios calculated from the midlevel ICAL point or from the CCV, if an ICAL is not run.

9.11.3. At this time the ion ratio evaluation is a quantitative identification tool.

Analyst judgement should be used if the ratio does not meet criteria. Data should be qualified "I" if the ratio is not met.

10. CALIBRATION

10.1. For details of the calculations used to generate the regression equations, and how to use the factors generated by these equations, refer to SOP CA-Q-P-003 "Calibration Curves and Selection of Calibration Points".

10.2. Routine instrument operating conditions are listed in the table in Section 11.18.

10.3. Instrument Tuning

Instrument tuning is done initially when the method is first developed and thereafter as needed to maintain the sensitivity and selectivity of the method. Tuning is done by infusing each individual compound (native and IDA) into the mobile phase using a tee fitting at a point just before the entrance to the electrospray probe. The responses for the parent and daughter ions for each compound are observed and optimized for sensitivity and resolution. Mass assignments are reviewed and calibrated if necessary. The mass assignments must be within ± 0.5 amu of the values shown in the table in Section 11.18.

10.3.1. Once the optimal mass assignments (within ± 0.5 amu of true) are made immediately following the initial tune, the lowest level standard from the initial calibration curve is assessed to ensure that a signal to noise ratio greater than 10 to 1 ($S/N > 10:1$) is achieved for each PFAS analyte. The first level standard from the initial calibration curve is used to evaluate the tune stability on an ongoing basis. The instrument mass windows are set initially at ± 0.5 amu of the true value; therefore, continued detection of the analyte transition with $S/N > 10:1$ serves as verification that the assigned mass remains within ± 0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion. For QSM work, the instrument sensitivity check (section 10.12.4) is also evaluated to ensure that the signal to noise criteria is met.

10.4. 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, but are not limited to, new columns or pump seals. A new calibration is not required after minor maintenance.

10.5. With the exception of the circumstances delineated in policy CA-Q-P-003, it is not acceptable to remove points from a calibration curve. In any event, at least five points must be included in the calibration curve. Average Response Factor and linear fit calibrations require five points, whereas Quadratic (second order) calibrations require six points.

- 10.6. A fixed injection volume is used for quantitation purposes and is to be the same for both the sample and standards.
- 10.7. All units used in the calculations must be consistently uniform, such as concentration in ng/mL.
- 10.8. Initial Calibration
 - 10.8.1. A number of analytical standards of different analyte concentrations are used to generate the curve. Each standard is injected once to obtain the peak response for each analyte at each concentration. These standards define the working range of the analysis.
 - 10.8.1.1. A minimum of five analytical standards is used when using average response factor and/or linear calibration fits.
 - 10.8.1.2. A minimum of six analytical standards is used when a quadratic fit is used to generate the curve.
 - 10.8.2. Calibration is by average response factor, linear fit, or by quadratic fit. Quadratic fit is used for the analyte if the response is non-linear.
 - 10.8.2.1. For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated against an identically labeled analog must be < 35% for the curve to be valid.
 - 10.8.2.2. For average response factor (RFa), the relative standard deviation (RSD) for all compounds quantitated against a closely related labeled analog IDA must be < 50% for the curve to be valid.
 - 10.8.2.3. For linear fit, the intercept of the line must be less than $\frac{1}{2}$ the reporting limit, and the coefficient of determination (r^2) must be greater than or equal to 0.990 for the curve to be considered valid (or the correlation coefficient (r) > 0.995).
 - 10.8.2.4. The Internal Standard (IS) response (peak area) must not deviate by more than 50% from the average response (peak area) of the initial calibration.
 - 10.8.2.5. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for initial calibration: The %RSD of the RFS for all analytes must be <20%. Linear or non-linear calibrations must have $r^2 > 0.99$ for each analyte. Analytes must be within 70-130% of their true value for each calibration standard.

- 10.8.2.6. Projects performed for the state of New Jersey: Each calibration point, except the lowest point, of each analyte should be calculated to be within 70-130% of the true value. The lowest calibration point that is at or below the MRL should be within 50-150% of its true value.

10.9. Calibration Curve Fits

- 10.9.1. Linear regression or quadratic curves may be used to fit the data to a calibration function. Detailed descriptions and formulas for each fitting type can be found in SOP CA-Q-P-003, "Calibration Curves and Selection of Calibration Points".

- 10.9.2. The linear curve uses the following function:

Equation 1

$$y = bx + c$$

Where:

$$y = \frac{\text{Area(analyte)}}{\text{Area(IS)}} \times \text{Concentration (IS)}$$

$$x = \text{concentration}$$

$$b = \text{slope}$$

$$c = \text{intercept}$$

- 10.9.3. The quadratic curve uses the following function:

Equation 2

$$y = ax^2 + bx + c$$

Where y, x, b, and c are the same as above, and a = curvature.

- 10.9.4. Evaluation of Calibration Curves

The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- The absolute value of the intercept of a regression line (linear or non-linear) at zero response must be less than the reporting limit.
- There should be no carryover at or above 1/2 MRL after a high CAL standard.

If these criteria are not met, instrument conditions and standards will be checked, and the ICAL successfully repeated before continuing.

- 10.9.5. Weighting of Calibration Points

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. Because accuracy at the low end of the

curve is very important for this analysis, it is preferable to increase the weighting of the lower concentration points. $1/\text{concentration}$ or $1/x$ weighting is encouraged. Visual inspection of the line fitted to the data is important in selecting the best fit.

10.10. Initial Calibration Blank (ICB)

- 10.10.1. Immediately following the ICAL, a calibration blank is analyzed that consists of an injection of 80:20 methanol:water blank containing both IDA and IS.
- 10.10.2. The result for the calibration blank must be less than the reporting limit.
- 10.10.3. If the ICB is greater than the reporting limit then the source of contamination must be identified and any necessary cleaning completed, and then the instrument should be recalibrated.
- 10.10.4. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for instrument blanks. One is required immediately following the highest standard analyzed and *daily prior to sample analysis*. The instrument blank must be $< \frac{1}{2}$ the LOQ.

10.11. Initial Calibration Verification (ICV)

- 10.11.1. Following the ICAL and the ICB, an ICV standard obtained from a different source or vendor than the ICAL standards is analyzed. This ICV standard is a mid-range standard.
- 10.11.2. The recovery for the ICV must meet the appropriate following criteria:
 - 10.11.2.1. The native analyte must be within or equal to 60-140% for all native analytes quantitated against an identically labeled analog IDA.
 - 10.11.2.2. The native analyte must be within or equal to 50-150% for all native analytes quantitated against a closely related labeled analog IDA.
 - 10.11.2.3. The IDA must be within or equal to 50-150%.
- 10.11.3. Projects performed under the auspices of the DoD/DOE QSM (Version 5.1) and the state of New Jersey must meet these criteria for the ICV: Analyte concentrations must be within $\pm 30\%$ of their true values for all analytes, IDA and target.
- 10.11.4. See Section 9.7 for corrective actions in the event that the ICV does not meet

the criteria above.

10.12. Continuing Calibration Verification (CCV)

Analyze a CCV at the beginning of a run, the end of a run, and after every 10 samples to determine if the calibration is still valid. The exception is after an acceptable curve and ICV are run 10 samples can be analyzed before a CCV is required. The CCVs are usually at the mid-level range of the curve and should vary throughout the run from low level (LOQ/RL) to mid level. The curve and ICV do not need to be run every day. To start an analytical run a CCV can be analyzed and if it meets acceptance criteria a run can be started. In addition, the low standard in the curve must be analyzed and must be within $\pm 50\%$ of the expected value.

- 10.12.1. The recovery for the CCV standards must be equal to or within 60-140% for all natives quantitated against an identically labeled analog and equal to or within 50% to 150% for all natives quantitated against a closely related labeled analog. The recovery for the IDA must be within or equal to 50-150%.
- 10.12.2. The Internal Standard (IS) response (peak area) must be within $\pm 50\%$ from the response (peak area) from the midpoint of the initial calibration.
 - 10.12.2.1. Sample IS response (peak area) must be within $\pm 50\%$ of the response (peak area) in the most recent CCV.
- 10.12.3. If this is not achieved, the instrument has drifted outside the calibration limits. The instrument must be recalibrated.
- 10.12.4. Projects performed under the auspices of the DoD/DOE must meet QSM 5.1 specific criteria for CCV. All analyte concentrations must be within $\pm 30\%$ of their true value. Additionally, prior to analysis and at least once every 12 hours an instrument sensitivity check (ISC/CCVL) must be analyzed. The analyte concentrations must be at LOQ and the concentrations must be within $\pm 30\%$ of their true value. This can be used as a CCV.
- 10.12.5. Projects performed for the state of New Jersey: All analyte concentrations in the CCV must be within $\pm 30\%$ of their true value. All analyte concentrations in the low level CCV must be within $\pm 50\%$ of their true value.

11. PROCEDURE

- 11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor 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 (NCM). The NCM process

is described in more detail in SOP WS-QA-0023. The NCM shall be filed in the project file and addressed in the case narrative.

Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.2. Water Sample Preparation

- 11.2.1. Visually inspect samples for the presence of settled and/or suspended sediment/particulates. If present or if the sample is biphasic add IDA prior to any sample decanting or centrifugation. If the sample requires decanting or centrifugation contact the client for guidance prior to such action. Decanting or filtering of the sample can lead to a low bias.
- 11.2.2. If authorized by the client to filter the sample, filter the water sample through a glass fiber filter (Whatman GF/F Cat No 1825 090 or equivalent). Gravity or vacuum can be used to pass the sample through the filter. Prepare a filtration blank with any samples requiring filtration. File an NCM noting the need for filtration.

Warning: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

- 11.2.3. Weigh the sample container prior to extraction and then weigh the sample container after extraction to determine the initial volume. Unless otherwise directed by client, use the entire sample volume.
- 11.2.4. Prepare additional aliquots of a field sample for the MS/MSD, if requested.
- 11.2.5. Prepare two 250 mL aliquots of HPLC-grade water for the method blank and LCS.
- 11.2.6. Spike the LCS and MS/MSD (if requested) with 0.5 mL of the LCS/Matrix PFC Spike solution (Section 7.6). This will result in a sample concentration of 40 ng/L.
- 11.2.7. Add 0.5 mL of the IDA PFC solution (Section 7.7) into each sample and QC sample, for a fixed concentration of 50 ng/mL in the final sample vial.

11.3. Solid Phase Extraction (SPE) of Aqueous Samples

The automated Zymark Auto-Trace Workstation can be used as long as the program follows these conditions and passes the background check.

- 11.3.1. Condition the SPE cartridges (Waters WAX, 500 mg/6 cc) by passing the following without drying the column.

***Note:** The cartridges should not be allowed to go dry until the final elution step with methanol. At all of the other transition steps, the solvent/sample level should be stopped at the top of the column before the next liquid is added.*

WARNING: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

- 11.3.2. Wash with 5.0 mL of 0.3% NH₄OH/methanol.
- 11.3.3. Wash with 5.0 mL of 0.1N NaOH/water. Close valve when ~ 200 uL remains on top to keep column wet. After this step, the columns cannot go dry until the completion of loading and rinsing samples.
- 11.3.4. Appropriately label the columns and add the reservoir to the column.
- 11.3.5. Add samples to the columns and with vacuum, pull the entire 250 mL aliquot of the sample through the cartridge at a rate of approximately 2 to 5 drops per second.
 - 11.3.5.1. If the SPE column should plug (flow rate <1 drop per minute) prior to the entire content of the sample container passing through the column do the following:
 - 1. Stop adding sample to the reservoir.
 - 2. Return any remaining sample volume back to the original container.
 - 3. Weigh the original container and record this weight into the worksheet notes field within the TALS extraction batch.
 - 4. Determine the full volume of sample fortified by using the “Gross Weight” – (remaining sample volume – default tare weight of a sample container (26.1 g)).
 - 5. Enter this value into the “Initial Amount” field in the TALS extraction batch.
 - 6. Proceed to Section 11.4, noting that additional vacuum or pressure might be needed to elute the SPE column.
- 11.3.6. After the entire sample has been loaded onto the column, rinse the sample bottle with two 5 mL aliquots of reagent water and pour onto the column reservoir.
- 11.3.7. After the final loading of the sample but before completely passed through the column, rinse the SPE column with 1 mL of water.
- 11.3.8. After the sample and water rinse have completely passed through the cartridge, allow the column to dry well with vacuum for 15 minutes.

11.4. SPE Column Wash of Aqueous Samples with Hexane

- 11.4.1. Load the first 5 mL of hexane to soak for five minutes and then elute to waste.
- 11.4.2. Load the second 5 mL of hexane and elute to waste (without a soaking period).
- 11.4.3. Allow the column to dry with vacuum for 5 to 10 minutes. Columns must be dried before continuing.

11.5. SPE Elution of Aqueous Samples – using 15 mL polypropylene test tubes as receiving tubes in the SPE manifold.

- 11.5.1. Rinse sample bottles with 5 mL of 0.3% NH_4OH /methanol and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.
- 11.5.2. Repeat sample bottle to column reservoir rinse and cartridge elution with a second 5 mL aliquot of 0.3% NH_4OH /methanol. The total collection should be approximately 10 mL.
- 11.5.3. **Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH_4OH /methanol.**
- 11.5.4. Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This required for all DoD/DOE extracts.

11.6. Extract Concentration for Aqueous Extracts (Note, if the extract will not be concentrated, proceed to Section 11.7.)

- 11.6.1. Prior to concentrating each sample, add 100 μL of water.
- 11.6.2. Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 100 μL of water remains.
 - 11.6.2.1. This blow down must take a minimum of 3.5 hours.
 - 11.6.2.2. Extracts can not remain in the water bath longer than 5 minutes once concentrated.
- 11.6.3. Add 300 μL of methanol and mix the contents well using a vortex mixer.
- 11.6.4. Add 100 μL of Internal Standard (IS) 250 ng/mL concentration solution to each extract and vortex to mix.

- 11.6.5. This will create an extract with a final solvent composition of 80:20 methanol:water.
 - 11.6.6. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.
 - 11.6.7. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps can not be used due to detection of low level concentration of PFAS.
- 11.7. Final volume for non-concentrated extract
- 11.7.1. If the extract does not undergo concentration add 0.5 mL of IS 50 ng/mL concentration and 2 mL of water to the extract. This will create an extract with a final solvent composition of 80:20 methanol:water.
 - 11.7.1.1. Seal the test tube tightly. Invert container several times and then vortex. Allow extract to settle for 10 minutes prior to moving to the next step.
 - 11.7.2. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.
 - 11.7.3. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps cannot be used due to detection of low level concentration of PFAS.
- 11.8. Soil, Sediment and Tissue Sample Preparation and Extraction
- 11.8.1. Visually inspect soil samples for homogeneity.
 - 11.8.1.1. Projects performed under the auspices of the DoD/DOE must have the entire sample homogenized prior to subsampling in accordance with QSM 5.1 criteria (see SOP WS-QA-0018).
 - 11.8.2. Weigh a representative 5 g aliquot of soil, sediment or 1 g of tissue sample into a 50 mL HDPE wide-mouth bottle. Weigh additional sample amounts for the matrix spike and matrix spike duplicate analyses if they are requested.
 - 11.8.3. For the method blank and LCS matrix, use 5 g each of Ottawa sand or 0.1 g of oil.
 - 11.8.4. Spike the LCS and MS/MSD (if requested) with 1.0 mL of the LCS/Matrix PFC Spike solution (Section 7.6). This will result in a sample concentration of 4.0 ng/g.

- 11.8.4.1. Spike non-concentrated samples at 0.5 mL of LCS/Matrix PFC Spike Solution.
- 11.8.5. Add 1.0 mL of the IDA PFC solution (Section 7.7) into each sample and QC sample, for a fixed concentration of 50 ng/mL in the final sample vial.
 - 11.8.5.1. Spike non-concentrated samples at 0.5 mL of IDA PFC Solution.
- 11.8.6. Cap the bottles and allow the spike to settle into the sample matrix. Gently shake the bottles to mix the spike into the matrix.
- 11.8.7. Add 20 mL of 0.4% KOH/methanol to each sample.
- 11.8.8. Shake each sample on an orbital shaker at room temperature for 3 hours.
- 11.8.9. Following the shaking, extract the samples in an ultrasonic water bath for an additional 12 hours.
- 11.8.10. After the completion of extraction, centrifuge each sample at 3500 rpm for 15 minutes.
- 11.8.11. Collect and decant the KOH/methanol extract to a new 50 mL centrifuge tube.
- 11.8.12. Add another 2 mL of 0.4% KOH/methanol solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.
- 11.8.13. Combine the rinsate to the first corresponding tubes.
- 11.8.14. To the final KOH/methanol extract, add 2 mL of water to each.
- 11.8.15. Concentrate the KOH/methanol/water extract under nitrogen to less than 2 mL, and dilute with water to 15 mL final volume.
- 11.8.16. Acidify with 80 uL of glacial acetic acid, and mix the contents well with vortex mixer. Check the pH to ensure pH is between 6 to 8.
- 11.8.17. Centrifuge at 3500 rpm for 15 minutes.
- 11.9. Solid Extract Cleanup by SPE
 - Set up WAX 150 mg/6 cc SPE columns for sample cleanup using vacuum manifold.
 - 11.9.1. Condition the SPE cartridges by passing the following without drying the column.

***Note:** The cartridges should not be allowed to go dry until the final elution step with methanol. At all of the other transition steps, the solvent/sample level should be stopped at the top of the column before the next liquid is added.*

WARNING: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

11.9.2. Wash with 5.0 mL of 0.3% NH₄OH/methanol.

11.9.3. Wash with 10 mL of 0.1N NaOH/water. Close valve when ~ 500uL remains on top of column to keep column wet. *After this step, the columns cannot go dry until the completion of loading and rinsing samples.*

11.9.4. Add extracts to the columns and with vacuum, pull the entire extracts through the cartridge at rate of approximately 3 to 5 drops per second.

11.9.5. Rinse the sample tube with 5 mL of water and add to the SPE column.

11.9.6. Dry the columns with vacuum for 15 minutes.

11.10. SPE Column Wash of Solid Extracts with Hexane

11.10.1. Load the first 5 mL of hexane to soak for five minutes, and elute to waste.

11.10.2. Load the second 5 mL of hexane and elute to waste (without a soaking period).

11.10.3. Allow the column to dry with vacuum for 10 minutes. Columns must be dried before continuing.

11.11. SPE Elution of Solid Extracts – using 15 mL polypropylene test tube as receiving tube in the SPE manifold.

11.11.1. Rinse extraction bottles with 5 mL of 0.3% NH₄OH/methanol and transfer to the column reservoir onto the cartridge. Allow the solution to soak for 5 minutes and then elute into the 15 mL collection tube.

11.11.2. Repeat extract bottle to column reservoir rinse and cartridge elution with a second 5 mL aliquot of 0.3% NH₄OH/methanol. The total collection should be approximately 10 mL.

11.11.3. **Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH₄OH/methanol.**

11.11.4. Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This is

required for all DoD/DOE extracts.

11.12. Extract Concentration for Solid Samples (Note, if the extract will not be concentrated, proceed to Section 11.7)

11.12.1. Prior to concentrating each sample, add 200 uL of water.

11.12.2. Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 200 uL of water remains.

11.12.2.1. This blow down must take a minimum of 3.5 hours.

11.12.2.2. Extracts can not remain in the water bath longer than 5 minutes once concentrated.

11.12.2.3. Add 600 uL of methanol and mix the contents well using a vortex mixer.

11.12.2.4. Add 200 uL of Internal Standard (IS) 250 ng/mL concentration solution to each extract and vortex to mix.

11.12.3. Transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.

11.12.4. Seal the vial with a polypropylene screw cap. *Note: Teflon lined caps can not be used due to detection of low level concentration of PFAS.*

11.13. Product/Dispersion Samples

11.13.1. Check the solubility of the material in both methanol and water

11.13.1.1. If the material is soluble in water, dilute 0.5 mL of sample into 250 mL of DI water and proceed to Section 11.3 (follow water extraction procedures). Fortify sample appropriately with IDA or PFC spike solution, see Section 11.2.

11.13.1.2. If the material is soluble in methanol, dilute 1 g (if solid) or 1 mL (if liquid) of material into 10 mL of methanol (MeOH).

11.13.1.2.1. If the material does not completely dissolve, contact your immediate supervisor.

11.13.2. Take 100 uL of the 10 mL solution and dilute it to 10 mL in MeOH.

11.13.3. Take a 1 mL aliquot of this solution (effective dilution of 1000x (1 mg for solid or 0.001 mL for liquid)) and fortify with 0.5 mL of labeled IDA

solution (Section 7.7).

11.13.4. DO NOT PASS EXTRACT THROUGH SPE CARTIRIDGE (omit steps 11.9 – 11.11).

11.13.5. Proceed to Section 11.6 of this SOP for extract concentration.

11.14. TOP (Total Oxidizable Precursor) Assay for Aqueous Samples

11.14.1. Prepare 3-250 mL HDPE containers with HPLC grade water to create the needed QC Samples (MB, LCS/LCSD).

11.14.2. Prepare enough 125 mL HDPE containers as needed for all “Pre” and “Post” samples, including QC. Label each appropriately.

11.14.3. Spike the “Pre” and “Post” MB 125 mL containers with 25 uL of the reverse surrogate solution of M2-4:2 FTS (Section 7.8).

11.14.4. Spike the “Pre” and “Post” LCS/LCSD 125 mL containers with 0.5 mL of the LCS Spike solution (Section 7.6), both regular and “add-on”, and 25 uL of the reverse surrogate solution (Section 7.8).

11.14.5. Remove the methanol solvent from all Post QC sample 125 mL containers (MB and LCS/LCSD) by using N₂ evaporation.

11.14.6. Add 2g of potassium persulfate and 1.9 mL of 10 M NaOH to each “Post” sample container.

11.14.7. Subsample 100 mL aliquots of water from each field sample and QC from the 250 mL containers into each of the corresponding 125 mL containers for both the “Pre” and “Post” samples. Spike all “Pre” and “Post” samples with 25uL of the reverse surrogate solution (Section 7.8).

11.14.8. Set aside all “Pre” sample containers.

11.14.9. Cap each “Post” sample container, invert 2-3 times prior to placing container into water bath.

11.14.10. Add 2 g of potassium persulfate and 1.9 mL of 10N NaOH to each “Post” sample container.

11.14.11. Heat each “Post” sample container in a water bath (KD) at 85°C for 6 hours.

11.14.12. After digestion for 6 hours, place the “Post” sample containers in an ice bath for 30 minutes.

- 11.14.13. Adjust the pH of “Post” samples and associated QC aliquots to 7 with concentrated HCl. Use pH paper to determine the pH.
- 11.14.14. Spike both “Pre” and “Post” samples and their associated QC samples with 0.5 mL of PFC IDA solution (Section 7.7), both regular and add-on.
- 11.14.15. Use the following SPE procedure for both “Pre” and “Post” samples:
 - 11.14.15.1. Set up WAX 150 mg/6 cc SPE columns for sample extraction using a vacuum manifold.
 - 11.14.15.2. Establish a sample loading flow rate of 3-5 drops per second for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.
 - 11.14.15.3. Wash/condition the SPE column with 5 mL of 0.3% NH₄OH/Methanol, then 5 mL water.
 - 11.14.15.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 3-5 drops per second.
 - 11.14.15.5. Add 5 mL rinse water
 - 11.14.15.6. After the sample and water rinse have completely passed through the column, allow it to dry well using vacuum with a flow rate of 1 mL/minute for 15 minutes.
 - 11.14.15.7. Wash the SPE column with 10 mL hexane rinse eluting all to waste.
 - 11.14.15.8. Allow the column to dry well using vacuum for 5 minutes. Columns must be dry before continuing.
 - 11.14.15.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 5 mL of 0.3% NH₄OH/methanol, and add to the SPE cartridge as eluent.
 - 11.14.15.10. Repeat with another 5 mL of 0.3% NH₄OH/methanol.
 - 11.14.15.11. Collect the 10 mL of eluent and concentrate per Section 11.6.
- 11.15. TOP (Total Oxidizable Precursor) Assay for Soil Samples
 - 11.15.1. Weigh representative 2 g aliquots of soil for each “Pre” and “Post” sample into a 50 mL centrifuge tube.
 - 11.15.2. For the method blank and LCS matrix, use 2 g each of Ottawa sand for each

“Pre” and “Post” QC sample.

- 11.15.3. Add 20 mL of 0.4% KOH/methanol to each sample.
- 11.15.4. Shake each sample on an orbital shaker at room temperature for 3 hours.
- 11.15.5. Following the shaking, extract the samples in an ultrasonic water bath for an additional 12 hours.
- 11.15.6. After the completion of extraction, centrifuge each sample at 3500 rpm for 15 minutes.
- 11.15.7. Collect and decant the KOH/methanol extract to a new 50 mL centrifuge tube.
- 11.15.8. Add another 2 mL of 0.4% KOH/methanol solution to the residue, briefly shake to mix and centrifuge at 3500 rpm for 15 minutes.
- 11.15.9. Combine the rinsate to the first corresponding tubes.
- 11.15.10. Proceed to Section 11.16.2 (Envi-carb clean up)
- 11.15.11. To the final KOH/methanol extract, add 0.5 mL of water to each.
- 11.15.12. Concentrate the KOH/methanol/water extract under nitrogen to less than 0.25 mL.
- 11.15.13. Dilute extract up to 50 mL with water in the centrifuge tube and vortex.
- 11.15.14. Prepare enough 125 mL HDPE containers as needed for all “Pre” and “Post” samples, including QC. Label each appropriately.
- 11.15.15. Spike the “Pre” and “Post” MB 125 mL containers with 25 uL of the reverse surrogate solution of M2-4:2 FTS (Section 7.8).
- 11.15.16. Spike the “Pre” and “Post” LCS/LCSD 125 mL containers with 0.5 mL of the LCS Spike solution and 25 uL of the reverse surrogate solution (Section 7.8).
- 11.15.17. Remove the methanol solvent from all “Post” QC sample 125 mL containers (MB and LCS/LCSD) by using N₂ evaporation.
- 11.15.18. Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each “Post” sample container.
- 11.15.19. Transfer extract from the centrifuge tube to the appropriate 125 mL

container.

- 11.15.20. Rinse the centrifuge container with an additional 50 mL of water and transfer to the appropriate 125 mL container.
- 11.15.21. Set aside all “Pre” sample containers.
- 11.15.22. Cap each “Post” sample container, invert 2-3 times prior to placing container into water bath.
- 11.15.23. Heat each “Post” sample container in a water bath (KD) at 85°C for 6 hours.
- 11.15.24. After digestion for 6 hours, place the “Post” sample containers in an ice bath for 30 minutes.
- 11.15.25. Adjust the pH of “Post” samples and associated QC aliquots to 7 with concentrated HCl. Use pH paper to determine the pH.
- 11.15.26. Spike both “Pre” and “Post” samples and their associated QC samples with 0.5 mL of PFC IDA solution (Section 7.7).
- 11.15.27. Use the following SPE procedure for both “Pre” and “Post” samples:
 - 11.15.27.1. Set up WAX 150 mg/6 cc SPE columns for sample extraction using a vacuum manifold.
 - 11.15.27.2. Establish a sample loading flow rate of 3-5 drops per second for each port of the vacuum manifold, for as many ports as will be used simultaneously during sample loading.
 - 11.15.27.3. Wash/condition the SPE column with 5 mL of 0.3% NH₄OH/Methanol, then 5 mL water.
 - 11.15.27.4. Load 100 mL of sample onto the SPE cartridge at a flow rate of 3-5 drops per second.
 - 11.15.27.5. Add 5 mL rinse water
 - 11.15.27.6. After the sample and water rinse have completely passed through the column, allow it to dry well using vacuum with a flow rate of 1 mL/minute for 15 minutes.
 - 11.15.27.7. Wash the SPE column with 10 mL hexane rinse eluting all to waste.
 - 11.15.27.8. Allow the column to dry well using vacuum for 5 minutes. Columns must be dry before continuing.

11.15.27.9. Elute the samples into 15 mL polypropylene test tubes in the SPE manifold by rinsing each 125 mL sample container with 5 mL of 0.3% NH_4OH /methanol, and add to the SPE cartridge as eluent.

11.15.27.10. Repeat with another 5 mL of 0.3% NH_4OH /methanol.

11.15.27.11. Collect the 10 mL of eluent and concentrate per Section 11.6.

Note: *If the extracts will not be concentrated elute extract with a total of 8 mL (2 4 mL rinses) of 0.3% NH_4OH /methanol.*

11.16. Other Types of Sample Cleanup

11.16.1. Freezing technique to remove lipids.

If samples contain lipids then freeze the methanolic extract and QC extracts at -20°C for at least 1 hour. Collect the solvent layer.

11.16.2. Cleanup with graphitized carbon will be applied to all samples as needed but is required for all DoD/DOE extracts.

11.16.2.1. Add 100 mg of graphitized carbon to each sample extract and QC extracts.

11.16.2.2. Shake vigorously and then let sit for 10 minutes.

11.16.2.3. Centrifuge each sample for 2 minutes at 1000 rpm.

11.16.2.4. Decant the solvent layer.

11.16.2.5. Proceed to Section 11.6, 11.7 or 11.12 as applicable.

11.17. AFFF Sample Preparation

11.17.1. QC for AFFF samples consists of a method blank, a laboratory control sample and a sample or matrix duplicate only. No matrix spike or matrix spike duplicate is needed.

11.17.2. Perform a 1,000,000 X serial dilution of the AFFF sample. Dilute 1 mL of AFFF sample to 1L with laboratory supplied water. Then dilute 1mL of this dilution to 1L with laboratory supplied water.

11.17.2.1. Be sure to retain all dilutions should the initial analysis warrant re-analysis at higher concentration.

11.17.3. Subsample 2.0 mL of this dilution and fortify with 0.5 mL IDA solution and 0.5mL of IS (50 ng/mL) solution: then add 7.0 mL of methanol.

11.17.4. Transfer a portion of the sample to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately ½ filled is sufficient). Archive the rest of the sample for re-injection or dilution.

11.18. Instrument Analysis

Suggested operating conditions are listed in Tables 1-7 for the Waters and SCIEX LCMS systems:

Table 1 - Recommended Instrument Operating Conditions				
HPLC Conditions (Shimadzu HPLC)				
Column (Column temp = 45°C)	Phenomenex Gemini 3 µm C18 110Å, 50 X 2 mm			
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol			
Gradient Program	Time	%A	%B	Flow Rate - mL/min
	0	90	10	0.60
	0.1	45	55	0.60
	4.5	1	99	0.60
	4.95	1	99	0.60
	5	90	10	0.60
	Maximum pressure limit = 5,000 psi			
Injection Size	2 µL (fixed amount throughout the sequence). If non-concentrated extract then use 20 uL.			
Run Time	~6.6 minutes			
Mass Spectrometer Interface Settings (SCIEX 5500)				
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.			
Ion Spray Voltage (kV)	4.5			
Entrance Potential (V)	5			
Declustering Potential (V)	25			
Desolvation Temp	600°C			
Curtain Gas	35 psi			
Collision Gas	8 psi			

Table 2 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500)								
Compound	Comments	Reaction (MRM)	Dwel 1 (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
PFBA	Native analyte	212.9 > 169	0.011	-5	-12	-25	-31	1.74
13C4-PFBA	IDA	217 > 172	0.011	-5	-12	-25	-31	1.74
PFBS	Native analyte	298.9 > 80	0.011	-6	-58	-55	-37	1.76
PFBS_2	Native analyte	298.9 > 99	0.011	-5	-40	-55	-12	1.76

Table 2 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500)								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Decl. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
13C3-PFBS	IDA	301.9 > 83	0.011	-5	-40	-55	-12	1.76
PFPeA	Native analyte	262.9 > 219	0.011	-7	-12	-20	-34	1.99
13C5-PFPeA	IDA	267.9 > 223	0.011	-7	-12	-20	-35	1.99
4:2 FTS	Native analyte	327 > 307	0.011	-7	-32	-50	-10	2.06
M2-4:2FTS	IDA or Reverse Surrogate for TOP	329 > 81	0.011	-7	-32	-50	-10	2.06
PFHxA	Native analyte	313 > 269	0.011	-5	-12	-25	-37	2.25
PFHxA 2	Native analyte	313 > 119	0.011	-5	-12	-25	-37	2.25
13C2-PFHxA	IDA	315 > 270	0.011	-5	-12	-25	-38	2.25
PFHpA	Native analyte	363 > 319	0.011	-6	-12	-25	-41	2.57
PFHpA 2	Native analyte	363 > 169	0.011	-6	-12	-25	-41	2.57
13C4-PFHpA	IDA	367 > 322	0.011	-6	-12	-25	-41	2.57
PFPeS	Native analyte	349 > 80	0.011	-9	-66	-57	-40	2.15
PFPeS 2	Native analyte	349 > 99	0.011	-9	-40	-57	-12	2.15
PFHxS	Native analyte	399 > 80	0.011	-12	-74	-60	-43	2.59
PFHxS 2	Native analyte	399 > 99	0.011	-12	-74	-60	-43	2.59
18O2-PFHxS	IDA	403 > 84	0.011	-12	-74	-60	-43	2.59
6:2 FTS	Native analyte	427 > 407	0.011	-7	-32	-50	-10	2.91
M2-6:2FTS	IDA	429 > 81	0.011	-7	-32	-50	-10	2.91
PFOA	Native analyte	413 > 369	0.011	-6	-14	-25	-44	2.93
PFOA 2	Native analyte	413 > 169	0.011	-5	-22	-25	-12	2.93
13C4-PFOA	IDA	417 > 372	0.011	-6	-14	-25	-44	2.93
13C2-PFOA	IS	415 > 370	0.011	-6	-14	-25	-44	2.93
PFHpS	Native analyte	449 > 80	0.011	-11	-88	-65	-46	2.94
PFHpS 2	Native analyte	449 > 99	0.011	-11	-88	-65	-46	2.94
PFNA	Native analyte	463 > 419	0.011	-6	-14	-25	-47	3.29
PFNA 2	Native analyte	463 > 169	0.011	-6	-14	-25	-47	3.29
13C5-PFNA	IDA	468 > 423	0.011	-6	-14	-25	-48	3.29
PFOS	Native analyte	499 > 80	0.011	-9	-108	-65	-50	3.29
PFOS 2	Native analyte	499 > 99	0.011	-5	-58	-65	-12	3.29
PFNS	Native analyte	549 > 80	0.011	-10	-113	-75	-52	3.40
PFNS 2	Native analyte	549 > 99	0.011	-8	-71	-75	-12	3.40
PFDoS	Native analyte	699 > 80	0.011	-11	-76	-10	-11	4.48
PFDoS 2	Native analyte	699 > 99	0.011	-11	-130	-10	-5	4.48
13C4-PFOS	IDA	503 > 80	0.011	-9	-108	-65	-50	3.29
PFDA	Native analyte	513 > 469	0.011	-6	-16	-25	-51	3.65
PFDA 2	Native analyte	513 > 169	0.011	-6	-16	-25	-51	3.65
13C2-PFDA	IDA	515 > 470	0.011	-6	-16	-25	-51	3.65
8:2 FTS	Native analyte	527 > 507	0.011	-7	-40	-50	-15	3.65
10:2 FTS	Native analyte	627 > 607	0.011	-7	-38	-110	-5	4.25

Table 2 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500)								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Decl. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
M2-8:2FTS	IDA	529 > 81	0.011	-7	-40	-50	-15	3.65
PFOSA	Native analyte	498 > 78	0.011	-8	-85	-60	-50	3.7
13C8-PFOSA	IDA	506 > 78	0.011	-8	-85	-60	-50	3.7
N-MeFOSAA	Native analyte	570 > 419	0.011	-7	-36	-40	-15	3.82
d3-MeFOSAA	IDA	573 > 419	0.011	-7	-36	-40	-15	3.82
PFDS	Native analyte	599 > 80	0.011	-11	-118	-85	-54	3.96
PFDS_2	Native analyte	599 > 99	0.011	-11	-118	-85	-54	3.96
PFUdA	Native analyte	563 > 519	0.011	-7	-18	-25	-54	3.97
PFUdA_2	Native analyte	563 > 169	0.011	-7	-18	-25	-54	3.97
13C2-PFUdA	IDA	565 > 520	0.011	-7	-18	-25	-54	3.97
N-EtFOSAA	Native analyte	584 > 419	0.011	-7	-36	-50	-15	3.99
d5-EtFOSAA	IDA	589 > 419	0.011	-7	-36	-50	-15	3.99
PFDaA	Native analyte	613 > 569	0.011	-5	-18	-25	-54	4.3
PFDaA_2	Native analyte	613 > 169	0.011	-5	-18	-25	-54	4.3
13C2-PFDaA	IDA	615 > 570	0.011	-5	-18	-25	-54	4.3
PFTTrDA	Native analyte	663 > 619	0.011	-7	-20	-25	-54	4.56
PFTTrDA_2	Native analyte	663 > 169	0.011	-7	-20	-25	-54	4.56
PFTeDA	Native analyte	713 > 169	0.011	-2	-22	-25	-10	4.79
PFTeDA_2	Native analyte	713 > 219	0.011	-7	-36	-25	-30	4.79
13C2-PFTeDA	IDA	715 > 670	0.011	-2	-22	-25	-10	4.79
PFHxDA	Native analyte	813 > 769	0.011	-7	-24	-25	-54	5.25
PFHxDA_2	Native analyte	813 > 169	0.011	-7	-24	-25	-54	5.25
13C2-PFHxDA	IDA	815 > 770	0.011	-7	-24	-25	-54	5.25
PFODA	Native analyte	913 > 869	0.011	-7	-26	-25	-54	5.55
PFODA_2	Native analyte	913 > 169	0.011	-7	-26	-25	-54	5.55

Table 3 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals								
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Decl. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
HFPO-DA	Native analyte	329.1 > 285	0.011	-10	-6	-48	-17	2.06
13C3-HFPO-DA	IDA	332.1 > 287	0.011	-10	-10	-40	-17	2.06
9Cl-PF3ONS (F53B major)	Native analyte	531 > 351	0.011	-10	-30	-120	-17	3.23

Table 3 - Recommended Instrument Operating Conditions								
Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals								
Compound	Comments	Reaction (MRM)	Dwell 1 (sec)	Ent. Pot. (V)	Col. Energy (V)	Decl. Pot. (V)	Cell Exit Pot. (V)	Typ RT (Min)
11Cl-PF3OUdS (F53B minor)	Native analyte	631 > 451	0.011	-10	-40	-160	-17	3.84
Dona	Native analyte	377 > 251	0.011	-10	-16	-55	-17	2.33
Dona_2	Native analyte	377 > 85	0.011	-10	-35	-55	-17	2.33

Table 4 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	Typical Native RT (minutes)	IDA analog	Typical IDA RT (minutes)	Quantitation Method
PFBA	1.54	13C4-PFBA	1.54	Isotope Dilution
PFPeA	1.56	13C5-PFPeA	1.56	Isotope Dilution
PFBS	1.78	13C3-PFBS	1.78	Isotope Dilution
PFHxA	2.03	13C2-PFHxA	2.03	Isotope Dilution
PFPeS	2.06	13C3-PFBS	1.78	Isotope Dilution
PFHpA	2.36	13C4-PFHpA	2.36	Isotope Dilution
PFHxS	2.37	18O2-PFHxS	2.37	Isotope Dilution
PFOA	2.71	13C4-PFOA	2.71	Isotope Dilution
PFHpS	2.72	13C4-PFOS	3.09	Isotope Dilution
PFNA	3.09	13C5-PFNA	3.09	Isotope Dilution
PFOS	3.09	13C4-PFOS	3.09	Isotope Dilution
PFNS	3.40	13C4-PFOS	3.09	Isotope Dilution
PFDA	3.45	13C2-PFDA	3.45	Isotope Dilution
FOSA	3.43	13C8-FOSA	3.43	Isotope Dilution
PFDS	3.77	13C4-PFOS	3.09	Isotope Dilution
PFUdA	3.78	13C2-PFUdA	3.78	Isotope Dilution
PFDoA	4.07	13C2-PFDoA	4.07	Isotope Dilution
PFTTrDA	4.34	13C2-PFDoA	4.07	Isotope Dilution
PFDoS	4.48	13C4-PFOS	3.09	Isotope Dilution
PFTeDA	4.58	13C2-PFTeDA	4.58	Isotope Dilution
PFHxDA	4.99	13C2-PFHxDA	4.99	Isotope Dilution
PFODA	5.34	13C2-PFHxDA	4.99	Isotope Dilution
EtFOSAA	3.78	d5-EtFOSAA	3.78	Isotope Dilution
MeFOSAA	3.61	d3-MeFOSAA	3.60	Isotope Dilution
4:2 FTS	1.98	M2-4:2 FTS (If TOP then 13C-PFBS)	1.78	Isotope Dilution
6:2FTS	2.69	M2-6:2FTS	2.69	Isotope Dilution
8:2FTS	3.44	M2-8:2FTS	3.44	Isotope Dilution
HFPO-DA	2.06	13C3-HFPO-DA	2.06	Isotope Dilution

Table 4 - Retention Times & Quantitation (SCIEX 5500)				
Native Compounds	Typical Native RT (minutes)	IDA analog	Typical IDA RT (minutes)	Quantitation Method
9Cl-PF3ONS (F53B major)	3.23	13C4-PFOS	3.09	Isotope Dilution
11Cl-PF3OUdS (F53B minor)	3.84	13C4-PFOS	3.09	Isotope Dilution
Dona	2.33	13C4-PFOS	3.09	Isotope Dilution
10:2 FTS	4.25	M2-8:2 FTS	3.44	Isotope Dilution

Table 5 - Recommended Instrument Operating Conditions					
HPLC Conditions (Waters Acquity UPLC)					
Column (Column temp = 50°C)	Waters Acquity BEH 1.7µm C18, 3.0 x 150 mm				
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol				
Gradient Program	Time	%A	%B	Curve	Flow Rate - mL/min.
	0	98	2	6	0.30
	1	98	2	6	0.30
	2	50	50	6	0.30
	12	10	90	6	0.30
	12.5	0	100	6	0.30
	16	0	100	6	0.30
	16.2	98	2	6	0.30
	Maximum pressure limit = 15,000 psi				
Injection Size	10 µL (fixed amount throughout the sequence)				
Run Time	~20 minutes				
Mass Spectrometer Interface Settings (Quattro Premier XE)					
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.				
Capillary (kV)	2.8				
Cone (V)	Varies from 8.0 to 65				
Extractor (V)	3				
Source Temp	135°C				
Desolvation Temp	350°C				
Cone Gas (nitrogen) Flow	25 L/hour				
Desolvation Gas (nitrogen) Flow	1100 L/hour				

Table 6 - Recommended Instrument Operating Conditions						
Mass Spectrometer Scan Settings (Quattro Premier XE)						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Cone Volt.	Col. Energy	Function Number
PFBA	Native analyte	213 > 169	0.02	8	10	1
13C4-PFBA	IDA	217 > 172	0.02	12	10	1
PFPeA	Native analyte	263 > 219	0.02	10	10	2
13C5-PFPeA	IDA	268 > 223	0.02	11	9	2
PFBS	Native analyte	299 > 80	0.02	45	35	2
PFBS_2	Native analyte	299 > 99	0.02	45	35	2
13C3-PFBS	IDA	302 > 83	0.02	45	35	2
PFHxA	Native analyte	313 > 269	0.02	10	10	3
PFHxA_2	Native analyte	313 > 119	0.02	10	10	3
13C2-PFHxA	IDA	315 > 270	0.02	12	9	3
PFHpA	Native analyte	363 > 319	0.02	10	10	4
PFHpA_2	Native analyte	363 > 169	0.02	10	10	4
13C4-PFHpA	IDA	367 > 322	0.02	12	10	4
PFHxS	Native analyte	399 > 80	0.02	55	35	4
PFHxS_2	Native analyte	339 > 99	0.02	55	35	4
18O2-PFHxS	IDA	403 > 84	0.02	50	40	4
PFOA	Native analyte	413 > 369	0.02	12	10	5
PFOA_2	Native analyte	413 > 169	0.02	12	10	5
13C2-PFOA	IS	415 > 370	0.02	12	12	5
13C4-PFOA	IDA	417 > 372	0.02	12	12	5
PFHpS	Native analyte	449 > 80	0.02	60	38	5
PFHpS_2	Native analyte	449 > 99	0.02	60	38	5
PFNA	Native analyte	463 > 419	0.02	16	10	7
PFNA_2	Native analyte	463 > 169	0.02	16	10	7
13C5-PFNA	IDA	468 > 423	0.02	12	12	7
PFOS	Native analyte	499 > 80	0.02	60	40	6
PFOS_2	Native analyte	499 > 99	0.02	60	40	6
PFNS	Native analyte	549 > 80	0.02	60	40	6
PFNS_2	Native analyte	549 > 99	0.02	60	40	6
13C4-PFOS	IDA	503 > 80	0.02	35	48	6
PFDA	Native analyte	513 > 469	0.02	16	12	8
PFDA_2	Native analyte	513 > 169	0.02	16	12	8
13C2-PFDA	IDA	515 > 470	0.02	14	12	8
PFUdA	Native analyte	563 > 519	0.02	15	12	10
PFUdA_2	Native analyte	563 > 169	0.02	15	12	10

Table 6 - Recommended Instrument Operating Conditions						
Mass Spectrometer Scan Settings (Quattro Premier XE)						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Cone Volt.	Col. Energy	Function Number
13C2-PFUdA	IDA	565 > 520	0.02	14	12	10
PFDS	Native analyte	599 > 80	0.02	74	48	10
PFDS_2	Native analyte	559 > 99	0.02	74	48	10
FOSA	Native analyte	498 > 78	0.02	40	32	9
13C8-FOSA	IDA	506 > 78	0.02	48	32	9
PFDaA	Native analyte	613 > 569	0.02	15	14	11
PFDaA_2	Native analyte	613 > 169	0.02	15	14	11
13C2-PFDaA	IDA	615 > 570	0.02	16	12	11
PFTTrDA	Native analyte	663 > 619	0.02	12	12	11
PFTTrDA_2	Native analyte	663 > 169	0.02	12	12	11
PFTeDA	Native analyte	713 > 169	0.02	12	18	11
PFTeDA_2	Native analyte	713 > 219	0.02	12	18	11
13C2-PFTeDA	IDA	715 > 670	0.02	15	15	11
PFHxDA	Native analyte	813 > 769	0.02	18	15	12
PFHxDA_2	Native analyte	813 > 169	0.02	18	15	12
PFODA	Native analyte	913 > 869	0.02	20	16	12
PFODA_2	Native analyte	913 > 169	0.02	20	16	12
13C2-PFHxDA	IDA	815 > 770	0.02	18	15	12
EtFOSAA	Native analyte	584 > 419	0.02	35	20	9
d5-EtFOSAA	IDA	589 > 419	0.02	30	25	9
MeFOSAA	Native analyte	570 > 419	0.02	30	28	9
d3-MeFOSAA	IDA	573 > 419	0.02	30	25	9
4:2FTS	Native analyte	327 > 307	0.02	40	30	5
M2-4:2FTS	IDA or Reverse Surrogate for TOP	329 > 81	0.02	40	30	5
6:2FTS	Native analyte	427 > 407	0.02	40	30	5
M2-6:2FTS	IDA	429 > 81	0.02	40	28	5
8:2FTS	Native analyte	527 > 507	0.02	40	28	8
M2-8:2FTS	IDA	529 > 81	0.02	40	28	8

Table 7 - Recommended Instrument Operating Conditions				
Retention Times & Quantitation (Quattro Premier XE)				
Native Compounds	Typical Native RT (minutes)	IDA analog	Typical IDA RT (minutes)	Quantitation Method
PFBA	4.77	13C4-PFBA	4.79	Isotope Dilution

Table 7 - Recommended Instrument Operating Conditions				
<i>Retention Times & Quantitation (Quattro Premier XE)</i>				
Native Compounds	Typical Native RT (minutes)	IDA analog	Typical IDA RT (minutes)	Quantitation Method
PFPeA	5.90	13C5-PFPeA	5.92	Isotope Dilution
PFBS	6.01	13C3-PFBS	6.01	Isotope Dilution
PFHxA	7.22	13C2-PFHxA	7.25	Isotope Dilution
PFPeS	7.20	18O2-PFHxS	8.64	Isotope Dilution
PFHpA	8.57	13C4-PFHpA	8.59	Isotope Dilution
PFHxS	8.60	18O2-PFHxS	8.64	Isotope Dilution
PFOA	9.80	13C4-PFOA	9.83	Isotope Dilution
PFHpS	9.80	13C4-PFOS	10.90	Isotope Dilution
PFNA	10.88	13C5-PFNA	10.92	Isotope Dilution
PFOS	10.87	13C4-PFOS	10.90	Isotope Dilution
PFNS	11.70	13C4-PFOS	10.90	Isotope Dilution
PFDA	11.82	13C2-PFDA	11.86	Isotope Dilution
FOSA	12.41	13C8-FOSA	12.46	Isotope Dilution
PFDS	12.57	13C4-PFOS	10.90	Isotope Dilution
PFUdA	12.62	13C2-PFUdA	12.66	Isotope Dilution
PFDoA	13.32	13C2-PFDoA	13.34	Isotope Dilution
PFTTrDA	13.91	13C2-PFDoA	13.34	Isotope Dilution
PFTeDA	14.39	13C2-PFTeDA	14.39	Isotope Dilution
PFHxDA	15.16	13C2-PFHxDA	15.16	Isotope Dilution
PFODA	15.57	13C2-PFHxDA	15.16	Isotope Dilution
EtFOSAA	12.63	d5-EtFOSAA	12.62	Isotope Dilution
MeFOSAA	12.3	d3-MeFOSAA	12.28	Isotope Dilution
4:2FTS	7.02	M2-4:2 FTS (If TOP then 13C-PFBS)	6.01	Isotope Dilution
6:2FTS	10.08	M2-6:2FTS	10.08	Isotope Dilution
8:2FTS	11.95	M2-8:2FTS	11.95	Isotope Dilution

11.18.1. Post Spike Sample Analysis for AFFF samples

- 11.18.1.1. This section only applies to aqueous samples prepared by serial dilution instead of SPE that have reported value of <LOQ (RL) for any analyte.
- 11.18.1.2. Spike aliquots of the sample at the final dilution reported for the sample with all analytes that have reported of <LOQ in the final dilution. The spike must be at the LOQ concentration to be reported with the sample (the < LOQ value).
- 11.18.1.3. When analyte concentrations are calculated as <LOQ, the spike must recover within 70-130% of its true value.

- 11.18.1.4. If the recovery does not meet this criteria, the sample, sample duplicate and post spike sample must be reanalyzed at consecutively higher dilutions until the criteria is met.
- 11.18.2. Tune and calibrate the instrument as described in Section 10.
- 11.18.3. A typical run sequence is as follows:
- Rinse Blank (RB, not linked to anything)
 - Start ICAL with CCVL but called IC in TALS (starts the 12 hour clock or time 0:00)
 - Rest of ICAL
 - ICB: link to midpoint of ICAL and samples
 - ICV: link to midpoint of ICAL and samples (If ICAL good)
 - CCB: link to midpoint of ICAL and samples
 - PFOA RT marker
 - Rinse Blank (RB, not linked to anything)
 - 10 samples: link to midpoint of ICAL
 - CCV: link to midpoint of ICAL
 - 10 more samples: link to midpoint of ICAL
 - CCV: link to midpoint of ICAL
 - Etc.
 - CCVL (within 12 hours from CCVL in ICAL, can be the ending CCV and starts 12 hours all over again): if this occurs link to the midpoint of the ICAL/toggle it as opening/closing CCV.
 - CCV: link to midpoint of ICAL
 - 10 samples: link to midpoint of ICAL
 - CCV: link to midpoint of ICAL
 - If no ICAL run that day
 - CCB: link to CCVIS
 - CCVL (starts 12 hour clock): link to CCVIS
 - CCVIS: link to midpoint of ICAL
 - 10 samples: link to CCVIS
 - CCV: link to CCVIS
 - 10 samples: link to CCVIS
 - CCV: link to CCVIS
 - Etc.

- If going over 12 hours in the sequence: CCVL (within 12 hours from CCVL at item 2 above, can be the ending CCV and starts 12 hours all over again): if this occurs link to the CCVIS /toggle as opening and closing CCV.
- CCV: link to CCVIS
- 10 samples: link to CCVIS
- CCV: link to CCVIS

12. CALCULATIONS

12.1. If the concentration of the analyte ions exceeds the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. It may be necessary to dilute samples due to matrix.

12.2. Qualitative Identification

12.2.1. The retention times of PFAS with labeled standards should be the same as that of the labeled IDA's to within 0.05 min. For PFAS with no labeled standards, the RT must be within ± 0.3 minutes of the ICV and CCV standards. **Note:** *The IDA RT and native RT may be offset by 0.02 to 0.04 minutes.*

12.3. The ICAL established in Section 10 is used to calculate concentrations for the extracts.

12.4. Extract concentrations are calculated as below. The first equation applies to the linear fit, the second to the quadratic line fit.

Equation 3 Concentration, ng/mL = $\frac{y - c}{b}$

Equation 4 Concentration, ng/mL = $\frac{-b + \sqrt{b^2 - 4a(c - y)}}{2a}$

Where:

$$y = \frac{\text{Area(analyte)}}{\text{Area(IS)}} \times \text{Concentration (IS)}$$

x = concentration
 a = curvature
 b = slope
 c = intercept

12.5. Water Sample Result Calculation:

Equation 5 Concentration, ng/L = $\frac{C_{ex}V_t}{V_o}$

Where:

$$\begin{aligned} C_{ex} &= \text{Concentration measured in sample extract (ng/mL)} \\ V_t &= \text{Volume of total extract (mL)} \\ V_o &= \text{Volume of water extracted (L)} \end{aligned}$$

12.6. Soil Sample Result Calculation:

Equation 6 Concentration, ng/g = $\frac{C_{ex}V_t}{W_sD}$

Where ng/g = µg/kg and:

$$\begin{aligned} C_{ex} &= \text{Concentration measured in sample extract (ng/mL)} \\ V_t &= \text{Volume of total extract (mL)} \\ W_s &= \text{Weight of sample extracted (g)} \\ D &= \text{Fraction of dry solids, which is calculated as follows:} \\ &\quad \frac{100 - \% \text{ moisture in sample}}{100} \quad (\text{for dry weight result}) \end{aligned}$$

12.7. IDA Recovery Calculation:

Equation 7 % Recovery = $\frac{A_t Q_{is}}{A_{is} Q_t RRF_{IDA}} \times 100$

Where ng/g = µg/kg and:

$$\begin{aligned} RRF_{IDA} &= \text{Response Factor for IDA compound} \\ A_t &= \text{Area response for IDA compound} \\ A_{is} &= \text{Area Response for IS compound} \\ Q_{is} &= \text{Amount of IS added} \\ Q_t &= \text{Amount of IDA added} \end{aligned}$$

12.8. Raw data, calibration summaries, QC data, and sample results are reviewed by the analyst. These must also be reviewed thoroughly by a second qualified person. See the Data Review Policy (WS-PQA-0012). These reviews are documented on the Data Review Checklist.

13. METHOD PERFORMANCE

13.1. 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 expertise.

13.2. Method Detection Limit

The 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 WS-QA-0006 and policy WS-PQA-003. MDLs are available in the Quality Assurance Department.

13.3. Initial Demonstration of Capability (IDOC)

Each analyst performing this procedure must successfully analyze four LCS QC samples using current laboratory LCS control limits. IDOCs are approved by the Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files.

13.4. The 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 WS-QA-0006 and policy WS-PQA-003.

14. POLLUTION PREVENTION

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations.

14.2. Solid phase extraction used for water samples greatly reduces the amount of solvent used compared to liquid-liquid extraction.

14.3. Standards and reagents are purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.4. 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 Safety Manual for "Waste Management and Pollution Prevention."

14.5. Do not allow waste solvent to vent into the hoods. All solvent waste is stored in capped containers unless waste is being transferred.

14.6. Transfer waste solvent from collection cups (tri-pour and similar containers) to jugs and/or carboys as quickly as possible to minimize evaporation.

15. WASTE MANAGEMENT

The following waste streams are produced when this method is carried out:

- 15.1. Assorted test tubes, autovials, syringes, filter discs and cartridges. Dump the solid waste into a yellow contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the hazardous waste – landfill steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.
- 15.2. Extracted soil samples, used sodium sulfate, paper funnel filters, glass wool, thimbles, and extracted solids saturated with solvents. Dump these materials into an orange contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the incineration steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.
- 15.3. Waste Methanol. Collect the waste solvents in tripours during use. Empty the tripours into a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the steel flammable solvent drum in the H3 closet. When full to no less than six inches of the top, or after no more than 75 days, move the steel flammable solvent drum to the waste collection area for shipment.
- 15.4. Mixed water/methanol waste from soil extraction. Collect the waste in the HPLC waste carboy. When full, or after no more than one year, dump into the blue plastic HPLC collection drum in the H3 closet. When the drum is full, to no less than six inches of the top, or after no more than 75 days, move it to the waste collection area for shipment.
- 15.5. Aqueous acidic waste from the LCMS instrument contaminated with methanol. This is collected in a 1-gallon carboy at the instrument. When the carboy is full, or after no more than one year, it is emptied into the blue plastic HPLC collection drum in the H3 closet. When the drum is full to between two and six inches of the top, or after no more than 75 days, move it to the waste collection area for shipment.
- 15.6. Autovials contaminated with methanol. As the autovials are removed from the instrument after analysis, they are collected in open containers at the instrument. After all autovials are removed, the open container must be dumped into a closed satellite collection container in a fume hood, as the punctured septa in the autovial can allow methanol and other contaminants to evaporate into the atmosphere. The satellite collection containers are transferred to the waste disposal area when full or after no more than one year, where they are disposed through the vial eater.

16. REFERENCES

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- 16.9. Erika F. Houtz and David L. Sedlak, “Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff,” Environmental Science and Technology 46, no. 17 (2012): 9342-49.

17. METHOD MODIFICATIONS

- 17.1. Modifications from Method 537 are detailed below:

- 17.1.1. Water sample containers are not preserved with Trizma.

- 17.1.2. The method has been modified to address soil/solid matrices. The extraction

holding time is set at 14 days.

- 17.1.3. The analyte list has been expanded. The number of labeled analytes has been expanded as well to improve quantitation.
- 17.1.4. The reporting limits differ as they are all set at one consistent value.
- 17.1.5. Calibration levels differ from the referenced method.
- 17.1.6. More labeled analytes are fortified into the samples prior to the extraction process. Most target analytes are quantitated against a labeled analyte.
- 17.1.7. There is no symmetry requirement.
- 17.1.8. Calibration, both initial and continuing, has different acceptance criteria due to the longer list of analytes, and the use of isotope dilution quantitation.
- 17.1.9. The eluents and HPLC configuration differs. As a result the final extract is in 80:20 methanol:water.
- 17.1.10. The LCS and MS/MSD are spiked at one concentration and do not rotate between a low to high levels.
- 17.1.11. Samples are not checked for residual chlorine or pH.
- 17.1.12. A different SPE cartridge (Waters OASIS WAX) is used for the extraction process. As a result solvents and elution procedures are different.

18. ATTACHMENTS

- 18.1. Attachment 1 - Analysis of Perfluorinated Compounds (PFAS) in Water via In Line Solid Phase Extraction (SPE).

19. REVISION HISTORY

Revisions to Attachment 1 are documented in the attachment.

Revisions prior to 05/01/2017 have been removed and are available in previous versions of this SOP.

- 19.1. WS-LC-0025, Revision 3.5, Effective 02/27/2019
 - 19.1.1. Added Section 11.3.6, "After the entire sample has been loaded onto the column, rinse the sample bottle with two 5 mL aliquots of reagent water and pour onto the column reservoir."
 - 19.1.2. Editorial changes.

19.2. WS-LC-0025, Revision 3.4, Effective 02/13/2019

- 19.2.1. Section 6.4 added, “The average weight of the HDPE bottles with HDPE screw caps are calibrated once a year. The calibration is performed by weighing 10 bottles with caps and dividing by 10 to get the average weight. The average weight is used in section (11.3.5.1.d).”
- 19.2.2. Section 7.4.1 revised, “an” to “every” and removed “or when a new column is installed”.
- 19.2.3. Add Section 7.4.1.1, “Attach this document to the ICV from the associated ICAL by scanning the document and associating it to the file as a document type of High Res MS Tune in TALS. Use the following naming convention: “_ZbatchnumberTPFOA”.”
- 19.2.4. Added Section 8.2.1, “Projects performed for the state of New Jersey have an analytical holding time 28 days from the extraction date.”
- 19.2.5. Added Section 8.2.2, “For projects performed for the state of New Jersey a field reagent blank (FRB) must be collected with each sample set. Acceptance limits are <RL for each analyte.”
- 19.2.6. Added Section 9.4.1, “Projects performed for the state of New Jersey: LCS (mid and high spike) recovery limits are 70-130%. Low level LCS recovery limits are 50-150%. The spike level must rotate between low, medium and high.”
- 19.2.7. Added Section 9.5.1, “Projects performed for the state of New Jersey: MS/MSD (mid and high spike) recovery limits are 70-130%. Low level MS/MSD recovery limits are 50-150%. The spike level must rotate between low, medium and high.”
- 19.2.8. Added Section 9.10, “TOP Oxidation Efficiency” and its associated subsections.
- 19.2.9. Added Section 9.11, “Ion Ratio” and associated subsections.
- 19.2.10. Added Section 10.8.2.6, “Projects performed for the state of New Jersey: MS/MSD (mid and high spike) recovery limits are 70-130%. Low level MS/MSD recovery limits are 50-150%. The spike level must rotate between low, medium and high.”
- 19.2.11. Section 10.11.3 added, “and the state of New Jersey”.
- 19.2.12. Added Section 10.12.5, “Projects performed for the state of New Jersey: All

analyte concentrations in the CCV must be within + 30% of their true value. All analyte concentrations in the low level CCV must be within + 50% of their true value.”

- 19.2.13. Added Section 11.3.5.1, “If the SPE column should plug (flow rate <1 drop per minute) prior to the entire content of the sample container passing through the column do the following:” and its associated subsections.
- 19.2.14. Sections 11.14.15.8 and 11.15.27.8 removed, “with a flow rate of 1 mL/minute”.
- 19.2.15. Section 11.18.3 removed, “(as needed)” from the PFOA RT marker.
- 19.2.16. Throughout SOP revised, “1 mL/minute” to “3-5 drops per second”.
- 19.2.17. Editorial changes.
- 19.3. WS-LC-0025, Revision 3.3, Effective 12/03/2018
 - 19.3.1. Added Section 6.9, “Phenomenex Gemini 3 μ m C18 110A, 50 X 3 mm, Part No. 00B-4439-Y0.”
 - 19.3.2. Tables 2 and 6 revised comment for M2-4:2 FTS to, “IDA or Reverse Surrogate for TOP”.
 - 19.3.3. Tables 4 and 7 revised header from “IS Analog” to “IDA Analog”, and revised “4:2 FTS” entry to “M2-4:2 FTS (If TOP then 13C-PFBS)”.
 - 19.3.4. Editorial changes.
- 19.4. WS-LC-0025, Revision 3.2, Effective 08/20/2018
 - 19.4.1. Section 1 added, “1H,1H,2H,2H-perfluorododecane sulfonate” and “Perfluoro-1-dodecansulfonic acid” entries to table.
 - 19.4.2. Section 1.2 revised table entry for “Adona” to “Dona”.
 - 19.4.3. Section 7.4 added, “PFDoS” and “10:2 FTS” entries to table.
 - 19.4.4. Section 7.4 revised, “Adona” entry to “Dona”.
 - 19.4.5. Table 2 added, “PFDoS”, “PFDoS_2”, and “10:2 FTS” entries to table.
 - 19.4.6. Table 3 revised, “Adona” and “Adona_2” entries to “Dona” and “Dona_2”.
 - 19.4.7. Table 4 added, “PFDoS” and “10:2 FTS” entries to table.

- 19.4.8. Table 4 revised, “Adona entry to “Dona”.
- 19.4.9. Editorial changes.
- 19.5. WS-LC-0025, Revision 3.1, Effective 06/21/2018
 - 19.5.1. Section 11.2.1 revised to, “Visually inspect samples for the presence of settled and/or suspended sediment/particulates. If present or if the sample is biphasic add IDA prior to any sample decanting or centrifugation. If the sample requires decanting or centrifugation contact the client for guidance prior to such action. Decanting or filtering of the sample can lead to a low bias.”
 - 19.5.2. Editorial changes.
- 19.6. WS-LC-0025, Revision 3.0, Effective 04/13/2018
 - 19.6.1. Section 1.1 updated table with PFPeS and PFNS analytes.
 - 19.6.2. Added Section 2.2, which details the analytes that can be covered by the method under special request.
 - 19.6.3. Added Section 3.13, “AFFF: Aqueous Film Forming Foam”.
 - 19.6.4. Section 6.19 added, “Create all eluents in Reagent module, label eluent containers with TALS label and place 2nd label into maintenance log when put into use” to table.
 - 19.6.5. Section 7.1.2 added, “Prepared by weighing 1.509g of ammonium acetate and dissolving in 1L of water. The resultant solution is filtered through a 0.22um filter before use. This solution has volatile components, thus it should be replaced every 7 days or sooner.”
 - 19.6.6. Section 7.1.3 added, “Prepared by diluting 12mL of ammonium hydroxide into 4L of methanol.”
 - 19.6.7. Section 7.1.8 added, “Prepared by weighing 16g of potassium hydroxide and dissolving in 4L of methanol.”
 - 19.6.8. Section 7.1.11 added, “Prepared by diluting 400mL of 1N NaOH into 3.6L of water for a total volume of 4L.”
 - 19.6.9. Section 7.4 updated table with PFPeS and PFNS analytes.
 - 19.6.10. Section 7.4, added table to detail ICAL for Fluorinated Replacement Compounds.

- 19.6.11. Added Section 8.1.1, "Water samples collected from a known chlorinated source should be preserved with Trizma."
- 19.6.12. Added Section 9.9.3, "If the IS does not meet criteria, re-analyze the extract. If the IS meets criteria in the second analysis, report that analysis. If the IS does not meet criteria in the second analysis, report the first analysis with narration."
- 19.6.13. Added Section 11.14.6, "Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each "Post" sample container."
- 19.6.14. Removed Section 11.14.8, "Add 2g of potassium persulfate and 1.9 mL of 10N NaOH to each "Post" sample container."
- 19.6.15. Added Section 11.14.9, "Cap each "Post" sample container, invert 2-3 times prior to placing container into water bath."
- 19.6.16. Added Section 11.5 and associated subsections, which detail the "TOPS (Total Oxidizable Precursor) Assay for Soil Sample".
- 19.6.17. Section 11.8 updated Table labeling, added PFPeS and PFNS analytes throughout Tables where applicable, and updated Table 7 to reflect current retention times and quantitation.
- 19.6.18. Section 11.8 added Table 6, "Recommended Instrument Operating Conditions Mass Spectrometer Scan Settings (SCIEX 5500) for Fluorinated Replacement Chemicals"
- 19.6.19. Section 11.18.3 removed outdated run sequence and replaced with current run sequence.
- 19.6.20. Editorial changes.
- 19.7. WS-LC-0025, Revision 2.9, Effective 11/22/2017
 - 19.7.1. Section 1.2, table updated to reflect ranges after removing MeFOSA and EtFOSA from the SOP in the previous revision.
 - 19.7.2. Section 9.3.6, last sentence changed to read, "Reprepare and reanalyze all field and QC samples associated with the contaminated method blank."
 - 19.7.3. Section 9.7, first sentence changed to read, "Initial calibration verification (ICV) – A second source standard is analyzed with the initial calibration curve."

- 19.7.4. Section 1.3.1 revised to read, “Once the optimal mass assignments (within ± 0.5 amu of true) are made immediately following the initial tune, the lowest level standard from the initial calibration curve is assessed to ensure that a signal to noise ratio greater than 10 to 1 ($S/N > 10:1$) is achieved for each PFAS analyte. The first level standard from the initial calibration curve is used to evaluate the tune stability on an ongoing basis. The instrument mass windows are set initially at ± 0.5 amu of the true value; therefore, continued detection of the analyte transition with $S/N > 10:1$ serves as verification that the assigned mass remains within ± 0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion. For QSM work, the instrument sensitivity check (section 10.12.4) is also evaluated to ensure that the signal to noise criteria is met.”
- 19.7.5. Editorial changes.
- 19.8. WS-LC-0025, Revision 2.8, Effective 11/06/2017
- 19.8.1. Revised Section 4.5 to “Both branched and linear PFAS isomers can potentially be found in the environment. Linear and branched isomers are known to exist for PFOS, PFOA, PFHxS, PFBS, EtFOSAA, and MeFOSAA based upon the literature. If multiple isomers are present for one of these PFAS they might be adjacent peaks that completely resolved or not, but usually with a deflection point resolved during peak integration. The later of these peaks match the retention time of its labeled linear analog. In general, earlier peaks are the branched isomers and are not the result of peak splitting.
- At this time only PFOS, PFOA and PFHxS are commercially available as technical mixtures. These reference standards of the technical mixtures for these specific PFAS are used to ensure that all appropriate peaks are included during peak integration.”
- 19.8.2. Sections 4.8 and 7.2.1.1, corrected the in-sample contributions to 0.30 ng/L and 0.015 ug/kg.
- 19.8.3. Removed Section 7.1.14, “Methanol-Water, 78:22 vol./vol., prepared by mixing 780 mL methanol and 220 mL reagent water. Stored in polypropylene bottle and sealed with polypropylene screw cap.” Reagent was added incorrectly.
- 19.8.4. Section 7.2.4, corrected the factor to 0.956 from 1.046.
- 19.8.5. Added Section 7.4.1, “A technical (qualitative) grade PFOA standard which contains both linear and branched isomers is used as a retention time (RT) marker. This is used to integrate the total response for both linear and

branched isomers of PFOA in environmental samples while relying on the initial calibration with the linear isomer quantitative standard. This technical (qualitative) grade PFOA standard is analyzed initially, after an initial calibration when a new column is installed or when significant changes are made to the HPLC parameters.”

- 19.8.6. Section 9.7, added “Rerun the initial calibration” as the last bullet item.
- 19.8.7. Added Section 10.3.1, “The first level standard from the initial calibration curve is used to evaluate the tune criteria. The instrument mass windows are set at ± 0.5 amu; therefore, detection of the analyte serves as verification that the assigned mass is within ± 0.5 amu of the true value, which meets the DoD/DOE QSM tune criterion.
- 19.8.8. Section 10.10.1, appended “containing both IDA and IS” to the end of the paragraph.
- 19.8.9. Sections 11.6.3 and 11.12.2.3, changed “78:22 methanol:water” to “methanol”.
- 19.8.10. Sections 1.1 and 7.4, removed EtFOSA and MeFOSA from tables due to low volume of requests for those analytes.
- 19.8.11. Removed Section 2.2.1, “Optional cleanups may include sample freezing and/or cleanup by SPE cartridge, unless EtFOSA and MeFOSA are requested.”
- 19.8.12. Removed EtFOSA/MeFOSA specific comments in various sections throughout the document.
- 19.8.13. Section 7.4 Note added, “The concentration of the calibration solutions for non-concentrated extracts is $1/20^{\text{th}}$ the levels indicated above.”
- 19.8.14. Section 7.9, changed 1000 ng/mL to 250 ng/mL and replaced final sentence with “The internal standard solution used for the non-concentrated extracts is at a concentration of 50 ng/mL.”
- 19.8.15. Removed Section 11.2.8, “If EtFOSA and/or MeFOSA are requested, add 100uL of IS and then adjust the final volume (FV) of these aliquots to 5.0 mL with MeOH. QC samples, LCS, MS, and MSD will require concentration via nitrogen to adjust the FV to 5.0 mL. Vortex each sample. Then, transfer a portion of the extract to a 300 uL polypropylene autosampler vial (7 drop-wise or approximately $\frac{1}{2}$ filled is sufficient). Archive the rest of the extracts for re-injection and dilution.”

- 19.8.16. Added Section 11.5.4, "Proceed to Section 11.15.2 (Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts."
- 19.8.17. Added Section 11.7.1.1, "Seal the test tube tightly. Invert container several times and then vortex. Allow extract to settle for 10 minutes prior to moving to the next step."
- 19.8.18. Inserted Section 11.8.1.1, "Projects performed under the auspices of the DoD/DOE must have the entire sample homogenized prior to subsampling in accordance with QSM 5.1 criteria."
- 19.8.19. Section 11.11.4, added "(Graphitized Carbon Cleanup) as needed. This is required for all DoD/DOE extracts."
- 19.8.20. Section 11.14.6, added "Spike all "Pre" and "Post" samples with 25uL of the reverse surrogate solution (Section 7.8)."
- 19.8.21. Section 11.15.2, revised to read, "Cleanup with graphitized carbon will be applied to all samples as needed but is required for all DoD/DOE extracts."
- 19.8.22. Added Section 11.15.2.5, "Proceed to Section 11.6, 11.7, or 11.12 as applicable."
- 19.8.23. Removed Sections 11.15.3 through 11.15.6.
- 19.8.24. Added Section 11.16, "AFFF Sample Preparation".
- 19.8.25. Section 11.17, removed EtFOSA, MeFOSA, d5-EtFOSA, and d3MeFOSA from all tables.
- 19.8.26. Section 11.17, changed masses for M2-4:2FTS, M2-6:2FTS, and M2-8:2FTS. Initially assigned daughter masses were bleeding through from the native analog.
- 19.8.27. Section 11.17, all tables on MS Interface Mode Line, added "Minimum of 10 scans/peak."
- 19.8.28. Added Section 11.17.1, "Post Spike Sample Analysis for AFFF Samples".
- 19.8.29. Added Section 11.8.4.1 "Spike non-concentrated samples at 0.5 mL of LCS/Matrix Spike Solution."
- 19.8.30. Added Section 11.8.5.1, "Spike non-concentrated samples at 0.5 mL of IDA PFC Solution."
- 19.8.31. Editorial changes.

19.9. WS-LC-0025, Revision 2.7, Effective 09/20/2017

- 19.9.1. Section 1.1 table, added 1H,1H,2H,2H-perfluorohexane sulfonate (4:2).
- 19.9.2. Section 1.1, removed "Sample results for PFOA may also be reported as APFO, at the request of the client. (See Section 12.7)."
- 19.9.3. Section 1.2 and 11.8.2, updated tissue extracted mass and RL.
- 19.9.4. Section 2.5, removed "and assumes a proportional relationship between the initial calibration and the analyte in the extract. The ratio of the peak response to mass or concentration injected is used to prepare a calibration curve."
- 19.9.5. Added Section 6.6, "Extract concentrator or nitrogen manifold with water bath heating to 50-55°C".
- 19.9.6. Added Section 7.1.14, "Methanol-Water, 78:22 vol./vol., prepared by mixing 780 mL methanol and 220 mL reagent water. Stored in polypropylene bottle and sealed with polypropylene screw cap."
- 19.9.7. Section 7.2.1.1, revised "roughly 0.15 pg/L" to "roughly 0.15 ng/L".
- 19.9.8. Section 7.4 table, added:
- | | | | | | | | |
|---------|-----|-----|-----|----|----|-----|-----|
| 4:2 FTS | 0.5 | 1.0 | 2.0 | 20 | 50 | 200 | 400 |
|---------|-----|-----|-----|----|----|-----|-----|
- 19.9.9. Section 7.4 table, revised Labeled Isotope Dilution Analytes (IDA) Section.
- 19.9.10. Section 7.4 table, added:
- | Internal Standard (IS) | | | | | | | |
|------------------------|----|----|----|----|----|----|----|
| 13C2-PFOA | 50 | 50 | 50 | 50 | 50 | 50 | 50 |
- 19.9.11. Section 7.4, removed "FOSAA may be added to the mix and are added at the same concentration as FOSA."
- 19.9.12. Added Section 7.9, "Internal Standard Solution, 1000 ng/mL. The internal standard solution is prepared by diluting 13C2-PFOA to produce a solution containing this compound at a concentration of 1000 ng/mL in methanol. This is added to all extracts prior to analysis. Non-concentrated extracts are fortified with a 5X dilution of this solution."
- 19.9.13. Section 8.1, changed "250 mL" to "8 oz."
- 19.9.14. Added Sections 9.3.6, 9.8.2.3, 10.10.4, 10.8.2.5, 10.11.3, and 10.12.4 to address DOD QSM 5.1 Table B-15 criteria.

- 19.9.15. Added Section 9.9, "Internal Standard."
- 19.9.16. Updated all tables to indicate target analyte quantitation via isotope dilution. Internal standard quantitation is only used to quantitate the IDA recoveries.
- 19.9.17. Added Section 10.8.2.4, 10.12.2, and 10.12.2.1 to incorporate IS criteria into calibrations.
- 19.9.18. Section 11.2.1, "Evaluate if the sample can be decanted or centrifuged; if not, contact the client for guidance. Filtering the sample can lead to a low bias."
- 19.9.19. Added Section 11.2.3.1, "Alternatively, weigh the sample container prior to extraction and then weigh the sample container after extraction to determine the initial volume."
- 19.9.20. Added Section 11.5.3, "Note: If the extracts will not be concentrated elute extract with a total of 8 mL of 0.3% NH₄OH/methanol."
- 19.9.21. Added Section 11.6.2.3, "Add 300 uL of the 78:22 methanol:water solution and mix the contents well using a vortex mixer."
- 19.9.22. Added Section 11.6.2.4, "Add 100 uL of Internal Standard (IS) solution to each extract and vortex to mix."
- 19.9.23. Added Section 11.7, "Final volume for non-concentrated extract".
- 19.9.24. Revised Section 11.11, "SPE Elution of Solid Extracts".
- 19.9.25. Revised Section 11.12, "Extract Concentration for Solid Samples".
- 19.9.26. Removed Section 12.8, "If results are to be reported as ammonium perfluorooctanoate (APFO), instead of PFOA, apply a multiplier of 1.0406 to the sample results to correct for the molecular weight differences between PFOA and APFO or this adjustment can be made during the preparation of the standards used for calibration. (Use one, not both.)"
- 19.9.27. Removed Section 13.4 – it was a copy of Section 13.2.
- 19.9.28. Various revisions to fulfill requirements based on DOD/DOE QSM 5.1.
- 19.9.29. Editorial changes.
- 19.10. WS-LC-0025, Revision 2.6, Effective 08/15/2017
 - 19.10.1. Section 7.4, added MPFBS, MPFTeDA, and MPFHxDA to the table.

- 19.10.2. Section 11.15, added 13C-PFBS to the Recommended Instrument Operating Conditions table for SCIEX 5500.
 - 19.10.3. Section 11.15 Recommended Instrument Operating Conditions table, changed the mass transitions for native PFTeDA from 713 > 669 (quant) and 713 > 169 (qualifier) to 713 > 169 (quant) and 713 > 219 (qualifier).
 - 19.10.4. Editorial changes.
- 19.11. WS-LC-0025, Revision 2.5, Effective 07/10/2017
- 19.11.1. Revised Section 11.6.1 to read “Prior to concentrating each sample, add 100 uL of water.”
 - 19.11.2. Revised Section 11.6.2 to read “Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 100 uL of water remains.
 - 11.6.2.1 This blow down must take a minimum of 3.5 hours.
 - 11.6.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated.”
 - 19.11.3. Revised Section 11.6.3 to read “Add 400 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water.”
 - 19.11.4. Revised Section 11.11.1 to read “Prior to concentrating each sample, add 200 uL of water.”
 - 19.11.5. Revised Section 11.11.2 to read “Concentrate each sample under a gentle stream of nitrogen until the methanol is evaporated and the 200 uL of water remains.”
 - 11.11.2.1 This blow down must take a minimum of 3.5 hours.
 - 11.11.2.2 Extracts can not remain in the water bath longer than 5 minutes once concentrated.”
 - 19.11.6. Revised Section 11.11.3 to read “Add 800 uL of methanol to each extract, soak, and vortex to mix well. This will create an extract with a final solvent composition of 80:20 methanol:water.”

Analysis of Per- and Polyfluorinated Compounds (PFAS) in Water via In Line Solid Phase Extraction (SPE)**1. SCOPE AND APPLICATION**

- 1.1. This procedure describes the analysis of water samples via in line solid phase extraction (SPE) for the following compounds using liquid chromatography / tandem mass spectrometry (LC/MS/MS) on a SCIEX 5500.

Compound Name	Abbreviation	CAS #
Perfluoroalkylcarboxylic acids (PFCAs)		
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
Perfluoro-n-octanoic acid	PFOA	335-67-1
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluorinated sulfonic acids (PFSAs)		
Perfluoro-1-butanesulfonic acid	PFBS	375-73-5
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-octanesulfonic acid	PFOS	1763-23-1

- 1.2. The working range of the method is listed below. The linear range can be extended by diluting the extracts.

Matrix	Nominal Sample Size	Reporting Limit	Working Range
Water	1.0 mL	2.0 ng/L	2 to 200 ng/L

2. SUMMARY OF METHOD

- 2.1. A 1 mL aliquot of sample is diluted to a 40:60 methanol:water extract and analyzed by LC/MS/MS. PFAS are separated from other components on a C18 column with a solvent gradient program using 20mM ammonium acetate/water and methanol.

3. DEFINITIONS

Refer to Section 3 of the main body of this SOP for a summary of definitions.

4. INTERFERENCES

Refer to Section 4 of the main body of this SOP for interferences.

5. SAFETY

Refer to Section 5 of the main body of this SOP for safety information.

6. EQUIPMENT AND SUPPLIES

Refer to Section 6 of the main body of this SOP for supplies, other than those listed below specific to the in line SPE analysis.

**Analysis of Per- and Polyfluorinated
Compounds (PFAS) in Water via In Line
Solid Phase Extraction (SPE)**

- 6.1. 2 mL auto sampler vials, clear glass, Thermo Scientific Nation surestop vial, part no. C5000-1, or equivalent.
- 6.2. Vial caps, Thermo Scientific National AVCS blue cap, pre slit TEF/STL septa, part no. C5000-55B or equivalent.
- 6.3. Eppendorf 1000 uL epTIPS, part no. 022491954 or equivalent.
- 6.4. Eppendorf 200 uL epTIPS, part no. 022491938 or equivalent.
- 6.5. 50 mL graduated plastic centrifuge tubes, SCP Science DigiTUBES part no. 010-500-263 or equivalent.
- 6.6. 1000 uL Pipette: Eppendorf Research Plus.
- 6.7. 100 uL Pipette: Rainin EDP3-Plus.
- 6.8. 250 mL HDPE bottles with PPE screw caps, ESS part no. 0250-1902-QC or equivalent.
- 6.9. Analytical columns
 - 6.9.1. Phenomenex Gemini C18 3 um, 3.0 mm x 100 mm, Part No. 00D-4439-Y0, or equivalent.
 - 6.9.2. PFAS Isolator column, Phenomenex Luna C18 5 um, 50 mm x 4.6 mm, part no. 00B-4252-E 0 or equivalent.
- 6.10. SCIEX 5500 Triple Quad MS. The system utilizes Chrom Peak Review, version 2.1 or equivalent.
- 6.11. Shimadzu CTO-20AC HPLC equipped with 3 LC-20AD pumps and one DGU-20 degassing unit or equivalent.

7. REAGENTS AND STANDARDS

Refer to Section 7 of the main body of this SOP for reagents and standards, other than those listed below specific to the in line SPE analysis.

- 7.1. Reagent grade chemicals shall be used in all tests whenever available. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on the 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.

Analysis of Per- and Polyfluorinated Compounds (PFAS) in Water via In Line Solid Phase Extraction (SPE)

- 7.1.1. Ammonium acetate, Fisher Optima LCMS grade (20 mM in water), part no. A114-50, or equivalent.
- 7.1.2. Methanol, Baker HPLC grade, part no. 9093-03.
- 7.1.3. Water, Nanopure or Millipore or Fisher Optima LCMS grade, part no. W6-4, must be free of interference and target analytes.

7.2. Calibration Standards

The calibration stock solution is prepared by diluting the appropriate amounts of the stock solutions (Section 7.2 of the main body of this SOP) in 40:60 methanol:water. The calibration stock solution is diluted with methanol to produce initial calibration standards. These are the normal calibration levels used. A different range can be used if needed to achieve lower reporting limits or a higher linear range.

7.3. Initial Calibration (ICAL) Levels (ng/L)

Compound	CS-1	CS-2	CS-3	CS-4	CS-5	CS-6	CS-7	CS-8
Perfluoroalkylcarboxylic acids (PFCAs)								
PFHpA	1.0	2.0	5.0	10	20	50	100	200
PFOA	1.0	2.0	5.0	10	20	50	100	200
PFNA	1.0	2.0	5.0	10	20	50	100	200
Perfluorinated sulfonic acids (PFSA's)								
PFBS	1.0	2.0	5.0	10	20	50	100	200
PFHxS	1.0	2.0	5.0	10	20	50	100	200
PFOS	1.0	2.0	5.0	10	20	50	100	200
Labeled Isotope Dilution Analytes (IDA)								
13C4-PFHpA	50	50	50	50	50	50	50	50
13C4-PFOA	50	50	50	50	50	50	50	50
13C5-PFNA	50	50	50	50	50	50	50	50
18O2-PFHxS	50	50	50	50	50	50	50	50
13C4-PFOS	50	50	50	50	50	50	50	50
13C3-PFBS	50	50	50	50	50	50	50	50

Note: The above calibration levels are provided only as an example. The actual ICAL level used for each analytical batch will depend upon the LOQ requirements of the program.

7.4. LCS/Matrix PFC Spike Solution, 100 ng/mL.

The PFC spike solution is prepared by diluting all PFAS to produce a solution containing each PFAS at 100 ng/mL in methanol.

7.5. PFC Isotope Dilution Analyte (IDA) Spike Solution, 1 ng/mL.

**Analysis of Per- and Polyfluorinated
Compounds (PFAS) in Water via In Line
Solid Phase Extraction (SPE)**

The PFC-IDA solution is prepared by diluting all labeled PFAS to produce a solution containing each at 1 ng/mL in methanol.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1. Water samples are collected in pre-cleaned 250 mL HDPE containers. Other containers may also be suitable. Samples are chilled to 0 - 6 °C for shipment to the laboratory.
- 8.2. Samples are logged in following normal laboratory procedures and are stored under refrigeration at 0 - 6 °C. Water samples must be analyzed within 28 days of collection.

9. QUALITY CONTROL

Refer to Section 9 of the main body of this SOP for Quality Control information.

- 9.1. If potable water samples from the state of New York (NY) are analyzed via this method the control limits for LCS and IDA for PFOS and PFOA recoveries are 70-130%. If these limits are not met, refer to Section 9 of the main body of this SOP for corrective action.
- 9.2. If POST (treatment) samples have positive detections, review the associated PRE and MID (treatment) samples for similar detections. Re-preparation and re-analysis may be needed.
- 9.3. If PFBS is detected in the method blank greater than the RL, evaluate data for impact. PFBS is a known laboratory artifact. Re-preparation and re-analysis may be needed.

10. CALIBRATION

Refer to Section 10 of the main body of the SOP for calibration information.

11. PROCEDURE

Refer to Section 11 of the main body of this SOP for procedures, other than those listed below specific to the in line SPE analysis.

11.1. Water Sample Preparation

- 11.1.1. Visually inspect samples for the presence of settled and or suspended sediment/particulate. Evaluate if the sample can be decanted or centrifuged; if not, contact the client for guidance. Filtering the sample can lead to a low bias.

If authorized by the client to filter the sample, filter the water sample through a glass fiber filter (Whatman GF/F Cat No 1825 090 or equivalent).

**Analysis of Per- and Polyfluorinated
Compounds (PFAS) in Water via In Line
Solid Phase Extraction (SPE)**

Gravity or vacuum can be used to pass the sample through the filter. Prepare a filtration blank with any samples requiring filtration. File an NCM noting the need for filtration.

Warning: The use of a vacuum system creates the risk of glassware implosion. Inspect all glassware prior to use. Glassware with chips, scratches, rub marks or cracks must not be used.

- 11.1.2. Prepare an LCS and method blank by adding 250 mL of HPLC grade water into a 250 mL HDPE bottle.
- 11.1.3. If requested, find the client assigned sample for MS/MSD.
- 11.1.4. Spike directly into the sample bottles for the LCS and MS/MSD (if requested) with 0.050 mL (50 uL) of the LCS/Matrix PFC Spike solution (Section 7.4). This will result in a sample concentration of 20 ng/L. Shake well to disperse spike.
- 11.1.5. Measure 1 mL of each sample using an Eppendorf pipette and pour into a labeled 2.0 mL injection vial. This includes the LCS and method blank samples as well.
- 11.1.6. Be sure to “prepare” the pipette by collecting two 1 mL aliquots and disposing of them, and then collect the aliquot for testing.
- 11.1.7. Add 83 uL of surrogate solution (PFC IDA Spike Solution, Section 7.5) into each vial for each sample and QC sample. This will result in an extract concentration of 50 ng/L for the surrogate.
- 11.1.8. Add 577 uL of methanol to each sample for a final solvent composition of 40:60 methanol:water.
- 11.1.9. Seal the vial with a polypropylene screw cap. Note: Teflon lined caps can not be used due to detection of low level concentration of PFAS.
- 11.1.10. Vortex to mix the mixture well.

11.2. Instrument Analysis

- 11.2.1. Suggested operation conditions are listed in Tables 1A-1C below:

Table 1A - Routine Instrument Operating Conditions	
<i>HPLC Conditions (Shimadzu HPLC)</i>	
Column (Column temp = 35°C)	Phenomenex Gemini C18 3 um, 3.0 mm x 100 mm
Mobile Phase Composition	A = 20 mM Ammonium Acetate in Water B = Methanol

**Analysis of Per- and Polyfluorinated
Compounds (PFAS) in Water via In Line
Solid Phase Extraction (SPE)**

Table 1A - Routine Instrument Operating Conditions					
<i>HPLC Conditions (Shimadzu HPLC)</i>					
Gradient Program	Time (min)	%A	%B	Curve	Flow Rate (mL/min)
	0	90	10	6	0.60
	1	90	10	6	0.60
	1.5	35	65	6	0.60
	8	5	95	6	0.60
	8.1	1	99	6	0.60
	12	1	99	6	0.60
	12.5	90	10	6	0.60
	Maximum Pressure limit = 5,000 psi				
Injection Size	950 uL (fixed amount throughout the sequence)				
Run Time	17.1 minutes				
MS Interface Mode	ESI Negative Ion. Minimum of 10 scans/peak.				
Ion Spray Voltage (kV)	4.5				
Entrance Potential (V)	5				
Declustering Potential (V)	25				
Desolvation Temp	550 °C				
Curtain Gas (nitrogen) Flow	35 psi				
Collision Gas (nitrogen) Flow	8 psi				

Table 1B - Routine Instrument Operating Conditions						
<i>Mass Spectrometer Scan Settings (SCIEX 5500)</i>						
Compound	Comments	Reaction (MRM)	Dwell (sec)	Ent. Pot. (V)	Col. Energy (V)	Declu. Pot. (V)
PFBS	Perfluorobutanesulfonate	299 > 80	0.02	6	58	55
13C3-PFBS	IDA	302 > 83	0.02	12	74	60
PFHpA	Perfluoroheptanoic acid	363 > 319	0.02	6	12	25
13C4-PFHpA	IDA	367 > 322	0.02	6	12	25
PFHxS	Perfluorohexanesulfonate	399 > 80	0.02	12	74	60
18O2-PFHxS	IDA	403 > 84	0.02	12	74	60
PFOA	Perfluorooctanoic acid	413 > 369	0.02	6	14	25
13C4PFOA	IDA	417 > 372	0.02	6	14	25
PFNA	Perfluorononanoic acid	463 > 419	0.02	6	14	25
13C5-PFNA	IDA	468 > 423	0.02	6	14	25
PFOS	Perfluorooctanesulfonate	499 > 80	0.02	9	108	65
13C4-PFOS	IDA	503 > 80	0.02	9	108	65

**Analysis of Per- and Polyfluorinated
Compounds (PFAS) in Water via In Line
Solid Phase Extraction (SPE)**

Table 1C				
Native Compounds	Typical Native RT (minutes)	IDA analog	Typical IDA RT (minutes)	Quantitation Method
PFBS	6.68	13C3-PFBS	6.68	Isotope Dilution
PFHpA	7.77	13C4-PFHpA	7.77	Isotope Dilution
PFHxS	7.76	18O2-PFHxS	7.76	Isotope Dilution
PFOA	8.44	13C4-PFOA	8.44	Isotope Dilution
PFNA	9.10	13C5-PFNA	9.10	Isotope Dilution
PFOS	9.06	13C4-PFOS	9.06	Isotope Dilution

11.2.2. Tune and calibrate the instrument as described in Section 10.

11.2.3. A typical run sequence is as follows:

- Primer (A number of primers are injected for conditioning of the instrument before analysis, especially when the instrument was idled or changed from a different analysis).
- Blank
- Calibration Curve
- ICB
- ICV
- PFOA RT marker (as needed)
- Rinse Blank (RB, not linked to anything)
- MB
- LCS
- LCSD (if applicable)
- Sample 1
- Sample 1 MS (if applicable)
- Sample 1 MSD (if applicable)
- Sample 2 (up to sample 10 before next CCV)
- CCV
- Up to 10 samples.
- End sequence with CCV

12. CALCULATIONS

Refer to Section 12 of the main body of this SOP for calculation information.

13. METHOD PERFORMANCE

Refer to Section 13 of the main body of this SOP for method performance information.

**Analysis of Per- and Polyfluorinated
Compounds (PFAS) in Water via In Line
Solid Phase Extraction (SPE)**

14. POLLUTION PREVENTION

Refer to Section 14 of the main body of this SOP for pollution prevention information.

15. WASTE MANAGEMENT

Refer to Section 15 of the main body of this SOP for waste management information.

16. REFERENCES

Refer to Section 16 of the main body of this SOP for reference information.

17. METHOD MODIFICATIONS

17.1. Refer to Section 17 of the main body of this SOP for modifications from Method 537, except as detailed below:

17.1.1. Water samples are prepared at 1.0 mL, not 250 mL.

17.1.2. Water sample containers are not preserved with Trizma. Holding time has been changed to 28 days for analysis.

17.1.3. The eluents and HPLC configuration differs. As a result the final extract is in 40:60 methanol:water.

18. ATTACHMENTS

There are no attachments to this Appendix.

19. REVISION HISTORY

Revisions prior to 04/10/2017 have been removed and are available in previous versions of this SOP.

19.1. WS-LC-0025, Attachment 1, Revision 3.5, Effective 02/27/2019

19.1.1. No changes to the attachment with this revision.

19.2. WS-LC-0025, Attachment 1, Revision 3.4, Effective 02/13/2019

19.2.1. Removed Section 3.6, "MPFOA: Perfluoro-n-[1,2,3,4-13C4]octanoic acid. Carbon-13 labeled PFOA".

19.2.2. Removed Section 3.7, "MPFOS: Perfluoro-1-[1,2,3,4-13C4]octanesulfonic acid. Carbon-13 labeled PFOS".

19.2.3. Section 7.2.3 removed, "MPFOS".

Analysis of Per- and Polyfluorinated Compounds (PFAS) in Water via In Line Solid Phase Extraction (SPE)

- 19.2.4. Section 7.3 removed, “PFCA and PFSA”.
- 19.2.5. Section 7.3 added “¹³C3-PFBS” entry to table.
- 19.2.6. Section 10.11.3 revised to, “Projects performed under the auspices of the DoD/DOE QSM (Version 5.1) and the state of New Jersey must meet these criteria for the ICV: Analyte concentrations must be within $\pm 30\%$ of their true values for all analytes, IDA and target.”
- 19.2.7. Table 1B, revised PFBS IDA from “¹⁸O2-PFHxS” to “¹³C3-PFBS” and updated entry values.
- 19.2.8. Table 1C, revised “IS Analog” to “IDA Analog”, revised the PFBS IDA from “¹⁸O2-PFHxS” to “¹³C3-PFBS”, and updated entry values.
- 19.2.9. Editorial changes.
- 19.3. WS-LC-0025, Attachment 1, Revision 3.3, Effective 12/03/2018
 - 19.3.1. No changes to the attachment with this revision.
- 19.4. WS-LC-0025, Attachment 1, Revision 3.2, Effective 08/20/2018
 - 19.4.1. No changes to the attachment with this revision.
- 19.5. WS-LC-0025, Attachment 1, Revision 3.1, Effective 06/21/2018
 - 19.5.1. No changes to the attachment with this revision.
- 19.6. WS-LC-0025, Attachment 1, Revision 3.0, Effective 04/13/2018
 - 19.6.1. Updated labeling and formatting of Tables 1A-1C.
 - 19.6.2. Added section 11.2.3, detailing a typical run sequence.
- 19.7. WS-LC-0025, Attachment 1, Revision 2.9, Effective 11/27/2017
 - 19.7.1. No changes to the attachment with this revision.
- 19.8. WS-LC-0025, Attachment 1, Revision 2.8, Effective 11/06/2017
 - 19.8.1. Section 11.2.1, Routine Instrument Operating Conditions table (SCIEX 5500), added “Minimum of 10 scans/peak”.

**Analysis of Per- and Polyfluorinated
Compounds (PFAS) in Water via In Line
Solid Phase Extraction (SPE)**

19.9. WS-LC-0025, Attachment 1, Revision 2.7, Effective 09/22/2017

- 19.9.1. Section 6.5, removed “The 5 items above are to be maintained in the drawer labeled “Segregated Supplies for in line SPE Analysis” in the LC/MS instrument room.”
- 19.9.2. Added Sections 9.1 – 9.3.
- 19.9.3. Updated Section 11.1.
- 19.9.4. Editorial changes.

19.10. WS-LC-0025 Attachment 1, Revision 2.6, Effective 08/11/2017

- 19.10.1. No revisions to this attachment.

19.11. WS-LC-0025 Attachment 1, Revision 2.5, Effective 07/10/2017

- 19.11.1. No revisions to this attachment.

19.12. WS-LC-0025 Attachment 1, Revision 2.4, Effective 04/25/2017

- 19.12.1. No revisions to this attachment.

19.13. WS-LC-0025 Attachment 1, Revision 2.3, Effective 04/10/2017

- 19.13.1. Changed all mentions of “direct aqueous injection (DAI)” to “in line solid phase extraction (SPE).”
- 19.13.2. Inserted Section 17.1, and changed formatting of the modifications to Method 537 to Section 17.2 and subheadings.

Appendix C

Laboratory Reference Data

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
Polychlorinated Biphenyls (PCBs) (GC)	608.3_PCB_PREC	608_Prep_PCB	Aroclor-1016	12674-11-2	0.100	0.0560	ug/L	50	140	30	50	140	36		
			Aroclor-1221	11104-28-2	0.100	0.0570	ug/L								
			Aroclor-1232	11141-16-5	0.100	0.0740	ug/L								
			Aroclor-1242	53469-21-9	0.100	0.0760	ug/L								
			Aroclor-1248	12672-29-6	0.100	0.0500	ug/L								
			Aroclor-1254	11097-69-1	0.100	0.0400	ug/L								
			Aroclor-1260	11096-82-5	0.100	0.0460	ug/L	8	140	30	8	140	38		
			DCB Decachlorobiphenyl	2051-24-3			ug/L							10	114
			Tetrachloro-m-xylene	877-09-8			ug/L							15	131
Semivolatile Organic Compounds (GC/MS)	625.1_PREC	625_Prep	Benzo[a]anthracene	56-55-3	10.0	0.171	ug/L	33	143	35	33	143	53		
			Benzo[a]pyrene	50-32-8	10.0	0.173	ug/L	17	163	35	17	163	72		
			Benzo[b]fluoranthene	205-99-2	10.0	0.154	ug/L	24	159	35	24	159	71		
			Benzo[g,h,i]perylene	191-24-2	10.0	0.178	ug/L	0	219	35	0	219	97		
			Acenaphthene	83-32-9	10.0	0.172	ug/L	47	145	35	47	145	48		
			Acenaphthylene	208-96-8	10.0	0.125	ug/L	33	145	35	33	145	74		
			Anthracene	120-12-7	10.0	0.135	ug/L	27	133	35	27	133	66		
			Benzo[k]fluoranthene	207-08-9	10.0	0.140	ug/L	11	162	35	11	162	63		
			Butyl benzyl phthalate	85-68-7	10.0	0.666	ug/L	0	152	35	0	152	60		
			Bis(2-chloroethoxy)methane	111-91-1	10.0	0.455	ug/L	33	184	35	33	184	54		
			Bis(2-chloroethyl)ether	111-44-4	10.0	0.402	ug/L	12	158	35	12	158	108		
			Bis(2-ethylhexyl) phthalate	117-81-7	10.0	2.22	ug/L	8	158	35	8	158	82		
			bis (2-chloroisopropyl) ether	108-60-1	10.0	0.551	ug/L	36	166	35	36	166	76		
			4-Bromophenyl phenyl ether	101-55-3	10.0	0.499	ug/L	53	127	35	53	127	43		
			2-Chloronaphthalene	91-58-7	10.0	0.483	ug/L	60	120	35	60	120	24		
			4-Chlorophenyl phenyl ether	7005-72-3	10.0	0.551	ug/L	25	158	35	25	158	61		
			Chrysene	218-01-9	10.0	0.186	ug/L	17	168	35	17	168	87		
			Dibenz(a,h)anthracene	53-70-3	10.0	0.151	ug/L	0	227	35	0	227	126		
			Di-n-butyl phthalate	84-74-2	10.0	1.80	ug/L	1	120	35	1	120	47		
			3,3'-Dichlorobenzidine	91-94-1	10.0	1.15	ug/L	0	262	35	0	262	108		
			Diethyl phthalate	84-66-2	10.0	3.82	ug/L	0	120	35	0	120	100		
			Dimethyl phthalate	131-11-3	10.0	0.515	ug/L	0	120	35	0	120	183		
			2,4-Dinitrotoluene	121-14-2	10.0	2.07	ug/L	39	139	35	39	139	42		
			2,6-Dinitrotoluene	606-20-2	10.0	2.13	ug/L	50	158	35	50	158	48		
			Di-n-octyl phthalate	117-84-0	10.0	0.821	ug/L	4	146	35	4	146	69		
			Fluoranthene	206-44-0	10.0	0.160	ug/L	26	137	35	26	137	66		
			Fluorene	86-73-7	10.0	0.169	ug/L	59	121	35	59	121	38		
			Hexachlorobenzene	118-74-1	10.0	0.161	ug/L	0	152	35	0	152	55		
			Hexachlorobutadiene	87-68-3	10.0	0.543	ug/L	24	120	35	24	120	62		
			Hexachloroethane	67-72-1	10.0	0.395	ug/L	40	120	35	40	120	52		
			Indeno[1,2,3-cd]pyrene	193-39-5	10.0	0.135	ug/L	0	171	35	0	171	99		
			Isophorone	78-59-1	10.0	0.324	ug/L	21	196	35	21	196	93		
			Naphthalene	91-20-3	10.0	0.109	ug/L	21	133	35	21	133	65		
			Nitrobenzene	98-95-3	10.0	0.514	ug/L	35	180	35	35	180	62		
			N-Nitrosodi-n-propylamine	621-64-7	10.0	0.253	ug/L	0	230	35	0	230	87		
			Phenanthrene	85-01-8	10.0	0.167	ug/L	54	120	35	54	120	39		
			Pyrene	129-00-0	10.0	0.175	ug/L	52	120	35	52	120	49		
			1,2,4-Trichlorobenzene	120-82-1	10.0	0.427	ug/L	44	142	35	44	142	50		
			4-Chloro-3-methylphenol	59-50-7	10.0	0.296	ug/L	22	147	35	22	147	73		
			2-Chlorophenol	95-57-8	10.0	0.273	ug/L	23	134	35	23	134	61		
			2,4-Dichlorophenol	120-83-2	10.0	0.262	ug/L	39	135	35	39	135	50		
			2,4-Dimethylphenol	105-67-9	10.0	0.518	ug/L	32	120	35	32	120	58		
			2,4-Dinitrophenol	51-28-5	50.0	6.21	ug/L	0	191	35	0	191	132		
			4,6-Dinitro-2-methylphenol	534-52-1	50.0	2.82	ug/L	0	181	35	0	181	203		
			2-Nitrophenol	88-75-5	10.0	0.564	ug/L	29	182	35	29	182	55		
			4-Nitrophenol	100-02-7	50.0	2.17	ug/L	0	132	35	0	132	131		
			Pentachlorophenol	87-86-5	10.0	3.10	ug/L	14	176	35	14	176	86		
			Phenol	108-95-2	10.0	0.128	ug/L	5	120	35	5	120	64		
			2,4,6-Trichlorophenol	88-06-2	10.0	1.80	ug/L	37	144	35	37	144	58		

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
			Benzidine	92-87-5	5.00	1.88	ug/L	5	120	35	5	120	35		
			Hexachlorocyclopentadiene	77-47-4	10.0	1.76	ug/L	19	120	35	10	120	35		
			N-Nitrosodimethylamine	62-75-9	1.00	0.219	ug/L	10	120	35	10	120	35		
			N-Nitrosodiphenylamine	86-30-6	10.0	0.440	ug/L	55	120	35	55	120	35		
			1,2-Diphenylhydrazine	122-66-7	1.00	0.433	ug/L	43	125	35	43	125	35		
			2-Fluorophenol	367-12-4			ug/L			35			35	10	120
			2,4,6-Tribromophenol	118-79-6			ug/L			35			35	28	120
			Nitrobenzene-d5	4165-60-0			ug/L			35			35	32	120
			Phenol-d5	4165-62-2			ug/L			35			35	10	120
			Terphenyl-d14	1718-51-0			ug/L			35			35	23	127
			2-Fluorobiphenyl (Surr)	321-60-8			ug/L			35			35	38	120
Volatile Organic Compounds (GC/MS)	624.1_LL_PREC	624_Prep	Benzene	71-43-2	1.00	0.130	ug/L	65	135	35	37	151	61		
			Ethylbenzene	100-41-4	1.00	0.110	ug/L	60	140	35	37	162	63		
			Toluene	108-88-3	1.00	0.140	ug/L	70	130	35	47	150	41		
			Vinyl chloride	75-01-4	1.00	0.200	ug/L	5	195	35	0	251	66		
			Xylenes, Total	1330-20-7	2.00	0.150	ug/L	80	120	35	67	120	25		
			Dichlorobromomethane	75-27-4	1.00	0.170	ug/L	65	135	35	35	155	56		
			Bromoform	75-25-2	1.00	0.760	ug/L	70	130	35	45	169	42		
			Bromomethane	74-83-9	1.00	0.420	ug/L	15	185	35	0	242	61		
			Carbon tetrachloride	56-23-5	1.00	0.260	ug/L	70	130	35	70	140	41		
			Chlorobenzene	108-90-7	1.00	0.140	ug/L	65	135	35	37	160	53		
			Chlorodibromomethane	124-48-1	1.00	0.390	ug/L	70	135	35	53	149	50		
			Chloroethane	75-00-3	1.00	0.830	ug/L	40	160	35	14	230	78		
			2-Chloroethyl vinyl ether	110-75-8	10.0	0.260	ug/L	0	225	35	0	305	71		
			Chloroform	67-66-3	1.00	0.130	ug/L	70	135	35	51	138	54		
			Chloromethane	74-87-3	1.00	0.200	ug/L	0	205	35	0	273	60		
			1,2-Dichlorobenzene	95-50-1	1.00	0.150	ug/L	65	135	35	18	190	57		
			1,3-Dichlorobenzene	541-73-1	1.00	0.150	ug/L	70	130	35	59	156	43		
			1,4-Dichlorobenzene	106-46-7	1.00	0.160	ug/L	65	135	35	18	190	57		
			1,1-Dichloroethane	75-34-3	1.00	0.170	ug/L	70	130	35	59	155	40		
			1,1-Dichloroethene	75-35-4	1.00	0.190	ug/L	50	150	35	0	234	32		
			1,2-Dichloroethane	107-06-2	1.00	0.210	ug/L	70	130	35	49	155	49		
			trans-1,2-Dichloroethene	156-60-5	0.500	0.190	ug/L	70	130	35	54	156	45		
			1,2-Dichloropropane	78-87-5	1.00	0.150	ug/L	35	165	35	0	210	55		
			cis-1,3-Dichloropropene	10061-01-5	1.00	0.610	ug/L	25	127	35	0	227	58		
			trans-1,3-Dichloropropene	10061-02-6	1.00	0.670	ug/L	50	150	35	17	183	86		
			Methylene Chloride	75-09-2	5.00	2.62	ug/L	60	140	35	0	221	28		
			1,1,2,2-Tetrachloroethane	79-34-5	1.00	0.130	ug/L	60	140	35	46	157	61		
			Tetrachloroethene	127-18-4	1.00	0.150	ug/L	70	130	35	64	148	39		
			1,1,1-Trichloroethane	71-55-6	1.00	0.240	ug/L	70	130	35	52	162	36		
			1,1,2-Trichloroethane	79-00-5	1.00	0.0900	ug/L	70	130	35	52	150	45		
			Trichloroethene	79-01-6	1.00	0.100	ug/L	65	135	35	70	157	48		
			m-Xylene & p-Xylene	179601-23-1	2.00	0.0800	ug/L								
			o-Xylene	95-47-6	1.00	0.0900	ug/L								
			Acrolein	107-02-8	20.0	2.07	ug/L	60	140	35	40	160	60		
			Acrylonitrile	107-13-1	20.0	1.13	ug/L	60	140	35	40	160	60		
			1,3-Dichloropropene, Total	542-75-6	2.00	1.29	ug/L	61	128	35	45	124	28		
			4-Bromofluorobenzene (Surr)	460-00-4			ug/L			35				79	120
			1,2-Dichloroethane-d4 (Surr)	17060-07-0			ug/L			35				70	121
			Toluene-d8 (Surr)	2037-26-5			ug/L			35				70	123
Organochlorine Pesticides in Water	608.3_Pest_PREC	608_CLLE_Prep	Aldrin	309-00-2	0.0500	0.00240	ug/L	42	140	35	42	140	35		
			alpha-BHC	319-84-6	0.0500	0.00200	ug/L	37	140	35	37	140	36		
			beta-BHC	319-85-7	0.0500	0.00460	ug/L	17	147	35	17	147	44		
			delta-BHC	319-86-8	0.0500	0.00430	ug/L	19	140	35	19	140	52		
			gamma-BHC (Lindane)	58-89-9	0.0500	0.00250	ug/L	32	140	35	32	140	39		
			Chlordane (technical)	12789-03-6	0.500	0.0465	ug/L								
			4,4'-DDD	72-54-8	0.0500	0.00530	ug/L	31	141	35	31	141	39		

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
			4,4'-DDE	72-55-9	0.0500	0.00430	ug/L	30	145	35	30	145	35		
			4,4'-DDT	50-29-3	0.0500	0.00480	ug/L	25	160	35	25	160	42		
			Dieldrin	60-57-1	0.0500	0.00230	ug/L	36	146	35	36	146	49		
			Endosulfan I	959-98-8	0.0500	0.00370	ug/L	45	153	35	45	153	28		
			Endosulfan II	33213-65-9	0.0500	0.00230	ug/L	0	202	35	10	202	53		
			Endosulfan sulfate	1031-07-8	0.0500	0.00370	ug/L	26	144	35	26	144	38		
			Endrin	72-20-8	0.0500	0.00250	ug/L	30	147	35	30	147	48		
			Endrin aldehyde	7421-93-4	0.0500	0.00460	ug/L	47	120	35	47	120	35		
			Heptachlor	76-44-8	0.0500	0.00330	ug/L	34	140	35	34	140	43		
			Heptachlor epoxide	1024-57-3	0.0500	0.00260	ug/L	37	142	35	37	142	26		
			Toxaphene	8001-35-2	2.00	0.0581	ug/L								
			Chlordane (technical) Peak 1	STL00379	0.500	0.0465	ug/L								
			Chlordane (technical) Peak 2	STL00380	0.500	0.0465	ug/L								
			Chlordane (technical) Peak 3	STL00084	0.500	0.0465	ug/L								
			Chlordane (technical) Peak 4	STL00065	0.500	0.0465	ug/L								
			Toxaphene Peak 1	STL00100	2.00	0.0581	ug/L								
			Toxaphene Peak 2	STL00109	2.00	0.0581	ug/L								
			Toxaphene Peak 3	STL00220	2.00	0.0581	ug/L								
			Toxaphene Peak 4	STL00083	2.00	0.0581	ug/L								
			Toxaphene Peak 5	STL00051	2.00	0.0581	ug/L								
			DCB Decachlorobiphenyl	2051-24-3			ug/L			35			35	10	120
			Tetrachloro-m-xylene	877-09-8			ug/L			35			35	33	120
Mercury (CVAA)	245.1	245.1_Prep	Mercury	7439-97-6	0.000200	0.000130	mg/L	85	115	20	70	130	20		
Metals (ICP)	200.7	200.7_P_TR	Chromium	7440-47-3	0.0500	0.000625	mg/L	85	115	20	75	125	20		
			Nickel	7440-02-0	0.0100	0.00220	mg/L	85	115	20	75	125	20		
			Lead	7439-92-1	0.0500	0.00277	mg/L	85	115	20	75	125	20		
			Zinc	7440-66-6	0.0200	0.00967	mg/L	85	115	20	75	125	20		
Solids, Total Suspended (TSS)	2540D		Total Suspended Solids	STL00161	4.00	2.22	mg/L	64	120	20					
Chromium, Trivalent	3500_CR3_B		Chromium, trivalent	16065-83-1	calc		mg/L								
Chromium, Hexavalent	3500_CR_B		Chromium, hexavalent	18540-29-9	0.00500	0.00300	mg/L	80	123	20	31	151	20		
Dioxin Screen (GC/MS SIM)	625DioxinScreen	3510C	2,3,7,8-TCDD	1746-01-6			NONE								
HEM and SGT-HEM	1664A_NP		HEM	STL00181	5.00	1.02	mg/L	78	114	11	78	114	18		
Anions, Ion Chromatography	9056A_28D		Sulfate	14808-79-8	1.00	0.348	mg/L	90	110	20	80	120	15		
Sulfide, Acid soluble and Insoluble (Titrimetric)	9034_Calc	9030B	Sulfide	18496-25-8	3.00	1.41	mg/L	70	120	20	32	130	30		
Hardness, Total (mg/l as CaCO3)	2340C		Hardness as calcium carbonate	STL00009	5.00	2.39	mg/L	90	110	20	80	120	10		
Alkalinity	2320B		Alkalinity	STL00171	5.00	2.60	mg/L	86	123	20	10	190	35		
Volatile Organic Compounds (GC/MS)	8260B	5030B	Acetone	67-64-1	10.0	5.41	ug/L	21	162	35	10	168	35		
			Benzene	71-43-2	1.00	0.130	ug/L	80	123	35	71	122	22		
			Bromodichloromethane	75-27-4	1.00	0.170	ug/L	77	125	35	64	125	27		
			Bromoform	75-25-2	1.00	0.760	ug/L	49	141	35	44	129	28		
			Bromomethane	74-83-9	1.00	0.420	ug/L	41	175	35	19	187	35		
			2-Butanone (MEK)	78-93-3	10.0	1.16	ug/L	39	163	35	37	156	35		
			Carbon disulfide	75-15-0	5.00	0.280	ug/L	60	138	35	43	144	33		
			Carbon tetrachloride	56-23-5	1.00	0.260	ug/L	63	140	35	41	143	30		
			Chlorobenzene	108-90-7	1.00	0.140	ug/L	80	121	35	70	123	23		
			Chloroethane	75-00-3	1.00	0.830	ug/L	33	173	35	11	189	35		
			Chloroform	67-66-3	1.00	0.130	ug/L	79	127	35	68	130	23		
			Chloromethane	74-87-3	1.00	0.200	ug/L	54	143	35	31	154	35		

Limits for Project - 12607, RACER Eckles Rd

Method Description	Method Code	Prep Method	Analyte Description	CAS Number	RL	MDL	Units	LCS - Low	LCS - High	LCS - RPD %	MS - Low	MS - High	MS - RPD %	Surrogate Low	Surrogate High
			1,1-Dichloroethane	75-34-3	1.00	0.170	ug/L	75	133	35	63	136	23		
			1,2-Dichloroethane	107-06-2	1.00	0.210	ug/L	71	135	35	65	135	24		
			1,1-Dichloroethene	75-35-4	1.00	0.190	ug/L	65	139	35	53	140	35		
			1,2-Dichloropropane	78-87-5	1.00	0.150	ug/L	78	133	35	70	132	26		
			cis-1,3-Dichloropropene	10061-01-5	1.00	0.610	ug/L	64	132	35	48	127	30		
			trans-1,3-Dichloropropene	10061-02-6	1.00	0.670	ug/L	55	128	35	40	125	27		
			Ethylbenzene	100-41-4	1.00	0.110	ug/L	80	120	35	66	120	24		
			2-Hexanone	591-78-6	10.0	0.540	ug/L	43	148	35	42	150	35		
			Methylene Chloride	75-09-2	5.00	2.62	ug/L	70	134	35	61	130	29		
			4-Methyl-2-pentanone (MIBK)	108-10-1	10.0	0.420	ug/L	49	143	35	44	143	35		
			Styrene	100-42-5	1.00	0.100	ug/L	79	120	35	68	120	26		
			1,1,2,2-Tetrachloroethane	79-34-5	1.00	0.130	ug/L	65	139	35	60	137	31		
			Tetrachloroethene	127-18-4	1.00	0.150	ug/L	74	130	35	51	136	23		
			Toluene	108-88-3	1.00	0.140	ug/L	78	129	35	62	132	23		
			Trichloroethene	79-01-6	1.00	0.100	ug/L	76	125	35	55	131	23		
			Vinyl chloride	75-01-4	1.00	0.200	ug/L	58	143	35	43	154	29		
			Xylenes, Total	1330-20-7	2.00	0.150	ug/L	80	120	35	67	120	25		
			1,1,1-Trichloroethane	71-55-6	1.00	0.240	ug/L	69	134	35	51	138	27		
			1,1,2-Trichloroethane	79-00-5	1.00	0.0900	ug/L	78	133	35	76	132	25		
			Cyclohexane	110-82-7	1.00	0.240	ug/L	58	145	35	42	135	35		
			1,2-Dibromo-3-Chloropropane	96-12-8	1.00	0.910	ug/L	46	132	35	38	124	35		
			1,2-Dibromoethane	106-93-4	1.00	0.120	ug/L	77	123	35	71	123	27		
			Dichlorodifluoromethane	75-71-8	1.00	0.350	ug/L	29	148	35	28	136	35		
			cis-1,2-Dichloroethene	156-59-2	1.00	0.160	ug/L	76	128	35	64	130	21		
			trans-1,2-Dichloroethene	156-60-5	1.00	0.190	ug/L	78	133	35	68	133	24		
			Isopropylbenzene	98-82-8	1.00	0.0900	ug/L	74	120	35	59	120	31		
			Methyl acetate	79-20-9	10.0	1.72	ug/L	52	145	35	41	142	35		
			Methyl tert-butyl ether	1634-04-4	1.00	0.0700	ug/L	51	133	35	41	136	29		
			1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	1.00	0.410	ug/L	50	156	35	31	156	35		
			1,2,4-Trichlorobenzene	120-82-1	1.00	0.260	ug/L	42	133	35	30	126	35		
			1,2-Dichlorobenzene	95-50-1	1.00	0.150	ug/L	78	120	35	64	120	30		
			1,3-Dichlorobenzene	541-73-1	1.00	0.150	ug/L	78	120	35	62	120	31		
			1,4-Dichlorobenzene	106-46-7	1.00	0.160	ug/L	78	120	35	63	120	28		
			Trichlorofluoromethane	75-69-4	1.00	0.450	ug/L	51	164	35	37	174	35		
			Dibromochloromethane	124-48-1	1.00	0.390	ug/L	70	132	35	60	129	26		
			Methylcyclohexane	108-87-2	1.00	0.330	ug/L	60	125	35	37	123	35		
			m-Xylene & p-Xylene	179601-23-1	2.00	0.0800	ug/L								
			o-Xylene	95-47-6	1.00	0.0900	ug/L								
			1,2-Dichloroethane-d4 (Surr)	17060-07-0	1.00		ug/L			35				70	121
			4-Bromofluorobenzene (Surr)	460-00-4	1.00		ug/L			35				59	120
			Toluene-d8 (Surr)	2037-26-5	1.00		ug/L			35				70	123
			Dibromofluoromethane (Surr)	1868-53-7	1.00		ug/L			35				75	128

Appendix D

Field Analytical and Sampling Standard Operating Procedures

Appendix D Field Analytical and Sampling SOPs

<i>Title</i>	<i>SOP No.</i>
Procedures for Measuring pH	Field S.O.P. No. 1
Procedures for Measuring Conductivity	Field S.O.P. No. 2
Procedures for Measuring Temperature	Field S.O.P. No. 3
Procedures for Measuring Dissolved Oxygen	Field S.O.P. No. 4
Procedures for Measuring Turbidity	Field S.O.P. No. 5
Procedures for Measuring OEP (Eh)	Field S.O.P. No. 6
Soil Headspace VOC Screening	Field S.O.P. No. 7
General Field Activities	Field S.O.P. No. 8
Water Sampling (Groundwater, Residential and Surface Water)	Field S.O.P. No. 9
PFAS Water Sampling Guidelines and Considerations	Field S.O.P. No. 10
Soil Sampling	Field S.O.P. No. 11

Field S.O.P. No. 1

Procedures for Measuring pH

1. Calibration Procedure

The pH meter will be calibrated daily.

1. Switch the unit on by pressing the ON/OFF key.
2. Immerse the electrode in a pH 7 buffer. Stir gently and wait for approximately 20 seconds.
3. Press "CAL" button, display will blink.
4. When reading stabilizes, press "HOLD/CON" button. This will calibrate meter to pH 7.0. Display will stop blinking.
5. If an error message appears, the calibration was not performed correctly. Try using fresh pH solution, changing batteries, or replacing pH sensor, if applicable.
6. Rinse electrode in water and repeat steps for pH 4.0 and/or pH 10.0 buffer solutions.
7. Rinse electrode in distilled/deionized water and then immerse probe in pH 7.0 solution again to check calibration.
8. Rinse electrode with distilled/deionized water. The meter is calibrated and ready for use.

2. Operation Procedure

- 1 Calibrate pH meter.
- 2 Rinse probe in distilled/deionized water.
- 3 Fill plastic disposable beaker with water from the sample.
- 4 Insert probe into sample beaker. Stir gently and wait for approximately 20 seconds and obtain a reading. The meter will read between 0 and 14, in 0.1 increments.
- 5 Log results in field notebook.
- 6 Rinse probe off in distilled/deionized water.
- 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. Rinse probe free of white crystals or dirt with water.
2. Replace batteries on a regular basis.
3. When batteries are low, the unit will display an error message. Remove the cover with its O-ring and replace all batteries paying attention to their polarity. Reinsert the cover with the O-ring and close. Recalibrate the instrument.
4. Keep records of usage, maintenance, calibration, problems, and repairs.

5. A replacement meter will be available onsite or ready for overnight shipment.
6. Store electrode in wet, protective cap.
7. pH meter will be sent back to manufacturer for service when needed.

4. Quality Control

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be ± 0.2 pH units.

If the results are outside of the control limits, rinse electrodes and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis. If the results are still outside of the control limits, check calibration and recalibrate if necessary (see item 2, below). If drift is suspected to be the cause of the problem, clean the electrode and recalibrate. If drift is still apparent, replace electrode.

2. Calibration check results must be ± 0.1 pH unit of the true value. If the result is outside of ± 0.1 pH unit, rinse electrodes and check solution again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in-control calibration.

Field S.O.P. No. 2

Procedures for Measuring Conductivity

Conductivity is the ability of a solution to pass an electric current. This current is carried by inorganic dissolved solids. The measure of conductivity is useful to relate the chemical purity of the water and the amount of dissolved solids in a solution.

1. Calibration Procedure

The conductivity meter will be calibrated daily.

1. Immerse tip in calibration solution for 20 seconds or until reading stabilizes.
2. Turn adjusting screw until proper reading is displayed.
3. Remove from calibration solution, rinse, and cap meter.
4. Always used pre-approved calibration solution.

2. Operation Procedure

1. Calibrate meter.
2. Rinse probe in distilled/deionized water.
3. Fill plastic disposable beaker with water from the sample.
4. Insert probe into sample beaker. Stir gently and wait for approximately 20 seconds and obtain a reading.
5. Log results in field notebook.
6. Rinse probe off in distilled/deionized water.
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. Conductivity meter will be sent back to manufacturer for service when needed.

4. Quality Control

1. The quality control calibration check standard must be analyzed daily. The standard must be within $\pm 10\%$ of the true value or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standard in the field logbook.
2. Duplicate a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicate values are to be within $\pm 15\%$ of each other. If outside of 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. 3

Procedures for Measuring Temperature

Temperature readings will be taken at each water sampling location to assist in pH and conductivity measurement. It will also assist in chemical and biological interpretations.

1. Calibration Procedure

1. There is no calibration procedure for this piece of equipment

2. Operation Procedure

1. Rinse thermometer in distilled/deionized water.
2. Immerse thermometer in the water sample and read it to the nearest degree Celsius (°C) or Fahrenheit (°F).
3. Record reading in the field notebook or relevant log.

3. Preventative Maintenance

1. Replace batteries on a regular basis.
2. Store in protective casing when not in use.
3. Keep records of usage, maintenance, calibration, problems, and repairs.
4. A replacement meter will be available onsite or ready for overnight shipment.
5. Annually, check instrument against thermometer that has been manufactured to a National Standard or equivalent. Temperature reading should be within $\pm 3^{\circ}\text{C}$ or $\pm 5.4^{\circ}\text{F}$.

4. Quality Control

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be $\pm 1^{\circ}\text{Celsius}$.

If the results are outside of the control limits, rinse electrode and repeat analysis. If results are still outside of the control limits, recollect samples and repeat analysis. If the results are still outside of the control limits, check calibration and recalibrate if necessary.

If drift is suspected to be the cause of the problem, clean the electrode and recalibrate. If drift is still apparent, replace electrode.

Field S.O.P. No. 4

Procedures for Measuring Dissolved Oxygen

Conductivity is the ability of a solution to pass an electric current. This current is carried by inorganic dissolved solids. The measure of conductivity is useful to relate the chemical purity of the water and the amount of dissolved solids in a solution.

1. Calibration Procedure - Dissolved Oxygen (DO)

The DO meter will be calibrated daily.

1. Ensure sponge inside instrument's calibration chamber is wet. Insert probe into the calibration chamber.
2. Switch the unit on by pressing the ON/OFF key.
3. Use two fingers to press and release the up and down arrow keys at the same time.
4. Enter the local altitude in hundreds of feet. Use arrow keys to increase or decrease the altitude (ex: 12 indicates 1200 feet). Then press ENTER.
5. Enter the salinity of the water you are about to analyze. The salinity can vary from 0 to 40 parts per thousand (PPT). Use the arrow keys to increase or decrease the number. (Fresh water has a salinity of 0) Then, press ENTER.
6. If the instrument is turned off, it may be necessary to re-calibrate before taking measurements.

2. Operation Procedure

1. Calibrate DO meter.
2. Rinse probe in distilled/deionized water.
3. Insert probe into sample. Allow reading to stabilize and then obtain a reading.
4. Log results in field notebook.
5. Rinse probe off in distilled/deionized water.
6. Replace probe in protective chamber.

3. Maintenance Procedure

1. Rinse probe free of white crystals or dirt with water.
2. Replace batteries on a regular basis or when "LO BAT" message is displayed
3. Replace O₂ probe solution and membrane on a regular basis. Replace membrane per instruction manual.
4. Recalibrate the instrument after replacing batteries, O₂ solution, or membrane.
5. Keep records of usage, maintenance, calibration, problems, and repairs.
6. A replacement meter will be available onsite or ready for overnight shipment.

7. Store electrode in wet, protective chamber.

4. Quality Control

1. Duplicate 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be ± 0.5 mg/L DO and ± 1 degree Celsius.

If the results are outside of the control limits, rinse probe and repeat measurement. If results are still outside of the control limits, recalibrate and repeat measurements of all samples since last in-control duplicate.

Field S.O.P. No. 5

Procedures for Measuring Turbidity

1. Calibration Procedure

The turbidity meter will be calibrated daily.

1. Select a standard in the range of the samples to be tested (ex: 1.0 NTU or 10.0 NTU).
2. Wipe the calibration tube clean with a lint-free cloth.
3. Open the lid of the meter, align the indexing arrow mark on the tube with the arrow on the meter, and insert the tube into the chamber.
4. Close the lid and push the READ button. If the displayed value is not within the limits of the standard, continue with calibration. If reading is within the calibration tolerances, the meter is calibrated and the meter is ready to analyze samples.
5. Push the CAL button for 5 seconds until CAL is displayed. Adjust the display with the up and down arrows until the value of the standard is displayed.
6. Push the CAL button again to set the calibration. The calibration is complete.

2. Operation Procedure

1. Push the READ button. The instrument is now ready to read sample turbidity.
2. Fill a sample tube with sample, wipe tube clean and insert into meter with both arrows aligning (on tube 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 tube 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 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicates must be $\pm 5\%$.

If the results are outside of the control limits, wipe off sample tube, 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 samples since last calibration.

2. Calibration check results must be $\pm 5\%$ of the true value. If the result is outside, refill sample tube, wipe clean, and check again. If still outside the control limit, recalibrate the meter and reanalyze all samples analyzed since the last in-control calibration.

Field S.O.P. No. 6

Procedures for Measuring ORP (Eh)

1. Calibration Procedure

The ORP meter calibration will be checked daily. The ORP meter cannot be calibrated; it can only be checked for accuracy using a known solution.

1. Turn the meter on to ensure that the LCD displays are working.
2. Rinse probe with distilled water and verify that the correct probe is connected to the instrument (red probe for ORP).
3. Insert probe into calibration check solution.
4. If ORP probe does not measure within the accuracy specified in the instruction manual, check/replace batteries and/or prepare a fresh calibration solution. If this does not work, probe should be replaced.

2. Operation Procedure

1. Turn meter on. The instrument is now ready to read ORP.
2. Rinse probe with distilled water in between samples.

3. Maintenance Procedure

1. Replace batteries when necessary.
2. Replace probe when necessary.
3. Keep records of usage, maintenance, calibration, problems, and repairs.

4. Quality Control

1. The quality control calibration check standard must be analyzed daily. The standard must be within $\pm 10\%$ of the true value or the samples run after the last acceptable check standard are to be reanalyzed. Record the calibration standard in the field logbook.
2. Duplicate a minimum of 1 out of 10 samples. If less than 10 samples are analyzed, a duplicate is still required. Duplicate values are to be within $\pm 15\%$ of each other. If outside of 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. 7

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 $\pm 10\%$ of the true value. If the result is outside of $\pm 10\%$, 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.



GHD Field Training Manual

Section 2.0

General Field Activities Standard Operating Procedures

(T100)

July 2015



Please adhere to the following Quality System training requirements:

- Employees who are required to conduct a specific field activity must be properly certified to do the work.
- This involves reviewing the SOP and completing the online training course and exam.
- Employees must also conduct this field work under supervised conditions on at least three occasions, and must be certified by a qualified mentor. Only then can an employee conduct a specific field activity on their own. This is documented on a Field Method Training Record (QSF 021).
- A QSF 021 is not required for this SOP.



Table of Contents

2.	General Field Activities Standard Operating Procedures	1
2.1	Purpose	1
2.2	Safety	1
2.3	Compliance with Governing Codes, Rules, and Regulations	2
2.4	GHD as Waste Generator	2
2.5	Short Service Employee Training, Medical Surveillance, Substance Abuse, and Respirator Fit Tests	3
2.6	GHD - Client Relations	4
2.7	GHD - Contractor Relations	4
2.8	GHD - On-Site Regulatory Agency Representative Relations	5
2.9	GHD - Public Relations	5
2.10	Field Notes	5
2.11	Spill Reporting	6
2.12	Property Access	7
2.13	Utility Clearance	7
2.14	Shipment, Transportation, and Handling of Chemicals and Gases - GHD Personnel	10
2.15	Closing	10

Table Index

Table 2.1 International Color Code System for Utility Marking

Quality System Forms Index

QSF-019	Property Access/Utility Clearance Data Sheet
QSF-020	New Employee Training Requirements
QSF-200, 400, and 500 Series D	Field Data Record Forms



2. General Field Activities Standard Operating Procedures

2.1 Purpose

The purpose of this section of the Field Training Manual is to outline the policies that GHD has developed with regards to personnel who conduct field activities.

2.2 Safety

Safety takes precedence over all other aspects of every project. GHD's safety program is known as the Safety Means Awareness Responsibility and Teamwork (SMART) based on the following principles:

- Preventing injuries, illnesses, and incidents is a valued business practice.
- All injuries and illnesses are preventable by anticipation, recognition, evaluation, and control of causative factors.
- Management at all levels is personally responsible for providing leadership, accountability, and resources to prevent injuries, illnesses, and incidents.
- Adherence to safety policies is a condition of employment for all employees.

No task is to be initiated until the health and safety aspects of that task are understood and appropriate precautions have been implemented. For each site, a Site-Specific Health and Safety Plan (HASP), which includes task-specific Job Safety Analysis (JSA), will have been developed which addresses the tasks to be performed and establishes the methods and procedures to be implemented to safely conduct each task. It is your responsibility to carefully read the HASP, understand its contents, and perform the field tasks in accordance with the methods and procedures outlined. Any areas of uncertainty should be discussed with the Safety and Health Officer (SHO), Site Supervisor, or your Supervisor for that particular task until you fully comprehend the intent of the HASP, the dangers involved, and the proper means to safely proceed. **Do not proceed until all of these aspects are understood.**

The HASP is developed in accordance with all OSHA regulations, provincial regulations, and the site owner's requirements. Copies of the OSHA regulations and provincial regulations are available on the agencies' web sites. You must familiarize yourself with the sections of these regulations that are applicable to your area of service. Each GHD employee has access to the electronic versions (Canadian and United States) Safety and Health Policy Manual on MyPortal. The Safety and Health Manuals serve as the standard vehicle by which we sustain awareness of the importance and requirements for safety and health management in our daily activities. The Safety and Health Policy Statement is posted at the entrance of each GHD building.

New employees that work in the field are part of the Short Service Employee (SSE) program for minimum of 6 months unless they are approved under the variance process. The SSE program sets



the standard for safety training, employee identification, mentoring, and client-specific requirements. The SSE program is on MyPortal.

When you are on a job site where a situation develops with which you are uncertain, you observe work being done by others that does not appear to be consistent with the HASP, or within the bounds of good judgment, immediately implement a Stop Work Authority and report your observations immediately to a senior site representative (i.e., SHO, GHD Project Coordinator, Manager, or Principal). Stop Work Authority is essentially the stopping of your own work or the work of others if you reasonably believe that you or they or the environment is in danger. Most Stop Work issues are resolved informally, but some require more in-depth evaluation to ensure the work can be completed in a safe manner.

If an incident occurs where someone is injured, there is property or motor vehicle damage immediately address any first aid or safety issues. Second, report the situation to the senior site representatives and then all the GHD Incident Hotline (1-866-529-4886). You will be asked to provide information regarding the incident including location, people involved, description of the incident, and injuries and a telephone number for return call.

General or site-specific health and safety inquiries may also be directed to the GHD Regional Health and Safety Manager.

2.3 Compliance with Governing Codes, Rules, and Regulations

All GHD personnel will comply with all governing codes, rules, and regulations at all times. Any questions that arise should be discussed and resolved with the Project Manager.

When you observe work being done by others that does not appear to be consistent with the governing codes, rules, or regulations or within the bounds of good judgment, report your observations immediately to a senior site representative (i.e., GHD Project Coordinator, Manager, or Principal). If necessary, report directly to the other workers if no one else is on site and make sure that appropriate corrective measures are taken promptly.

2.4 GHD as Waste Generator

GHD is not and cannot be a waste generator. GHD cannot sign waste manifests, hazardous or otherwise. Therefore, you cannot sign any manifests. (In isolated cases, where GHD's client provides proper documentation and indemnification, GHD does have the authority to sign as an agent for GHD's client. However, please note that these cases are very rare and you will be made aware of them when this applies.)

In no case is your name or GHD's name to appear on any drum or waste shipment. All arrangements for waste handling are to be coordinated with the client and will be the client's responsibility. All sample records, cuttings, and excess soils (including geologic soil record samples) **must** remain on site or in the client's possession.

Unless instructed by the Project Coordinator, every attempt should be made to avoid the purchase of chemicals by GHD for field use. Pre-work planning should include coordination such that all chemicals to be used by GHD personnel are purchased by the client or the site general contractor.



Sample preservatives should be supplied by the laboratory. After sampling activities are completed, unused preservatives should be returned to the laboratory. At the end of the work, unused and used chemicals must be properly disposed of by the client or the site general contractor.

If chemicals for use by GHD personnel are to be used for a period of time, they should be temporarily stored by the site general contractor or client. If it becomes necessary to bring chemicals back to the offices of GHD, they must be properly stored in approved containers and areas.

2.5 Short Service Employee Training, Medical Surveillance, Substance Abuse, and Respirator Fit Tests

All GHD personnel involved in field activities at environmental sites must participate in GHD's Short Service Employee program, safety training and medical surveillance program.

Short Service Employee (SSE) Program

The SSE Program is intended to ensure new employees are identified, appropriately supervised, trained, and managed in order to prevent incidents such as a personal injury, injury to others, environmental damage, or property damage. The SSE Program is documented on the GHD Portal under the Safety & Health tab.

Training

Each new GHD employee must complete the New Employee Training Requirements Form (QSF-020) with his or her supervisor; this includes safety, quality, and field methods training. The QSF-020 will define all the mandatory training, including attendance and certification at a 40-hour OSHA hazards compliance program (except for those personnel that were grandfathered into the program) for all field personnel who have the potential to be exposed to chemicals at or above their published exposure limits. In addition, field personnel and managers must attend an approved 8-hour refresher course annually. An employee shall coordinate with their supervisor to complete all safety training.

Medical Surveillance & Substance Abuse Program

The GHD medical surveillance program defines the type and frequency of medical exams and substance abuse testing (drug and alcohol) in accordance with the applicable regulations. The GHD Safety & Health Group coordinates the medical surveillance program.

All GHD personnel involved in field activities at environmental sites require an annual medical exam. The Safety & Health Group Administrator will contact you with regards to the process of completing your annual medical exam. An independent Third Party Administrator (TPA) manages all medical exams and related medical records. It is your responsibility to attend and follow up with any required actions. Failure to participate will eliminate your eligibility for work at such sites and may result in no work being available for you.

All GHD personnel involved in field activities are required to participate in annual drug and alcohol testing as allowed by law. Some clients also require GHD employees to participate in random substance abuse testing. To the extent that participation is required of GHD, those personnel



involved at these sites will also be required to participate in, or provide proof of compliance with, GHD's Substance Abuse Testing program. The Safety & Health Group Administrator, the Project Manager, or your supervisor will contact you regarding drug and alcohol testing. The Substance Abuse Policy is documented in the GHD Employee Manual and the GHD Safety & Health Policy Manual; both documents are available on the GHD Portal.

Respirator Fit Tests

Once medically cleared to wear a respirator you will be trained and fit tested annually as part of the GHD Respirator Protection Program, as defined in the GHD Safety & Health Policy Manual.

2.6 GHD - Client Relations

GHD expects all GHD personnel to treat all clients courteously and with respect. It is also expected that you keep them fully informed of project status, problems encountered, and resolutions implemented. However, each client employee may not be associated with the office or division of the client company which is contracting and responsible for the work. The specifics of our purpose and findings must be considered confidential to our contractual contact with the client, not every employee of the client. Know to whom you are talking, and do not release information to anyone unless you are sure they have a right to know.

While the client needs our services, the client also has a business to run. Wherever we are working, our field work is definitely NOT the primary profit-generating activity of the client. Accordingly, be **very** sensitive to minimizing disruption to the normal work flow at the site and to scheduling disruptive activities at the least inconvenient time for the client. This requires that GHD personnel review the on-site activities with the client and coordinate the sequence of work with the on-site contact.

There is no doubt that over time friendships will develop between certain GHD employees and clients. All GHD asks is that you keep these relationships on a professional level. From time to time, it is anticipated that it will be appropriate for you to take clients out for lunch or dinner, for which GHD will reimburse you. It is expected that you will not abuse this responsibility. It is not considered appropriate to either accept gifts from clients or to purchase gifts for them.

2.7 GHD - Contractor Relations

Whenever a GHD employee has been placed in an oversight position with a contractor, it is paramount to remember that you are providing this oversight on behalf of GHD's client and they are entitled to the best service possible. You are expected to administer the contract fairly and at the same time also ensure that all of the rights and privileges afforded GHD's client by the terms and conditions of the contract are taken into consideration. Any improprieties or failures on the part of the contractor are to be reported immediately to senior GHD staff.

There is no doubt that over time friendships will develop between certain GHD employees and contractors. All GHD asks is that you keep these relationships on a professional level. It is not considered appropriate to either accept gifts from contractors or to purchase gifts for them.



2.8 GHD - On-Site Regulatory Agency Representative Relations

GHD personnel are expected to develop a good working relationship with all personnel from the regulatory agencies. This relationship is imperative to ensure prompt resolution of field issues and to ensure that the job receives the approval of the regulatory agencies upon completion. If a field resolution cannot be reached, inform the GHD Project Manager and further discussions will be held with the agencies' field staff supervisors.

While you are expected to be courteous and respectful of the on-site representatives, do not offer any unsolicited information regarding the project unless so instructed by the client.

In the event that an OSHA inspector visits the site and requests information from you, answer all of the questions about which you are knowledgeable. For any areas of uncertainty, simply tell the OSHA inspector that you will get the answer immediately by looking it up in the HASP or contact one of GHD's industrial hygienists for assistance. All other information (e.g., Material Safety Data Sheets, Medical Records, etc.) is available at the GHD office or through one of GHD's industrial hygienists.

2.9 GHD - Public Relations

In the field, whenever you are approached by a member of the community, media, or unknown site personnel, respond courteously as follows:

"These activities are being conducted in conjunction with the program at Site X and I would suggest that you get in touch with Person Y (Project Manager at Company X) for any specific information."

Do not answer any specific questions regarding the site or your activities. Following such an encounter, immediately notify Person Y and provide them with the details of your encounter and the tasks you were performing.

2.10 Field Notes

All activities undertaken in the field must be correctly and completely recorded in bound field books, Quality System Field Data Record Forms (QSF-200, QSF-400, and QSF-500 Series D), or in some other GHD-approved format (i.e., electronically, loose paper). All records will be kept in the GHD-approved format specified for the activities undertaken. The formats have been established to ensure completeness and to provide consistency amongst the field staff regardless of which office they are from. Refer to Section 7.6 (Control of Monitoring and Measuring Equipment) of the GHD Quality System Manual.

These field notes may be called as evidence in a court of law.

In addition to the formal field notes, you are expected to keep running tables that summarize the field activities so that when questioned at any time during the program you can provide a detailed status of the work completed and that which is yet to be done. These lists are also anticipated to serve as check lists to confirm that the correct number and sequence of samples, wells, boreholes,



etc. have been collected or completed. Section 3.4.1 provides additional guidance with respect to documenting field notes.

Upon completion of each project, all of the field documentation is to be brought back and suitably stored at the GHD office in which the field staff who performed the field work are located.

GHD demands that all field note entries be factual and accurate. Everyone recognizes that errors and omissions will be made on occasion. While GHD does not condone a level of effort that is incomplete or inaccurate, it is recognized that it may happen and most of our clients will understand these situations. However, anyone who is caught falsifying any record, no matter how small, will be immediately dismissed.

2.11 Spill Reporting

All spills must be recorded in the field book and reported to the Project Manager as soon as is practicable. The requirements for reporting spills to the regulatory authorities are different in the United States and in Canada. These requirements are presented below.

GHD personnel should make reasonable efforts to stop and contain a spill. These efforts should not include measures which put the individual at risk of injury. If the chemical composition of the spill is unknown, Level B or A personal protective equipment is required. Where possible, the source of the spilled material should be isolated and ditching or berms should be used to contain spilled material. Follow-up actions will depend upon the nature of the material spilled and the size of the spills. If necessary, local emergency response personnel (fire, emergency planning) should be contacted. If possible, decisions to call emergency response personnel should be made in consultation with the Project Manager.

United States

GHD works on construction projects at which the potential for spills is present. These projects are normally conducted within the scope of an agency-approved Work Plan and an order or similar legal document. The Work Plan and the order usually compel GHD and its client to report spills and incidents to the agency.

In all cases of a spill, after efforts have been made to stop and contain a spill and, if necessary, a decision has been made to call emergency response personnel, GHD site personnel must contact the Project Manager immediately. If the Project Manager is not available, then it is imperative that a Principal or Associate be contacted.

Once the Project Manager (or Principal/Associate) is apprised of the situation, appropriate agency notification can be made. If at all possible, the client should be made aware of the requirement and client personnel perform the actual notifications. If necessary, the National Response Center, Environmental Protection Agency (EPA), and state agencies will be notified.

GHD's clients may also have internal notification requirements. These requirements must be confirmed to have been met by the Project Manager before outside agencies are notified.



Canada

In general, a "spill" is subjectively defined in Canada as a discharge of a substance that threatens health, life, property, or the environment. The decision as to whether a discharge is a spill that should be reported to a provincial ministry or Environment Canada must be made by the Project Manager (or a Principal or Associate) in consultation with GHD's client.

The internal notification procedures for GHD's field personnel in Canada are the same as those identified above for the United States.

2.12 Property Access

Prior to commencing any field activity, GHD personnel must ensure that access to the lands under investigation has been granted from the respective landowners. Typically, this task is accomplished by the Project Coordinator who instructs the field staff accordingly, providing the field office with copies of the access agreements/access permission. This documentation must be readily available for examination should local authorities or adjacent landowners request proof of access permission. Field personnel must confirm that this task has been completed before conducting field activities.

To assist GHD personnel in documentation and coordination of property access/utility clearance checking, a data sheet is available for general use. The Property Access/Utility Clearance Data Sheet (QSF-019) must be used to record that access and utility clearances have been obtained. The Property Access/Utility Clearance Data Sheets are available electronically on the Quality System tab of MyPortal.

2.13 Utility Clearance

Field activities which penetrate the ground surface (i.e., test pits, boreholes, well installations, and new construction) **must have a utility clearance performed in advance of any subsurface work**. The utility clearance process is a logistical requirement performed to identify utility presence, utility location, and special hazards that may exist when working in close proximity to these services. The utility check itself does not prevent all incidents but is one component of many activities that if all performed correctly will minimize the potential for utility conflicts. Typically, GHD field personnel are responsible for coordinating utility clearances and documenting completion of utility checks. GHD personnel cannot approve utility clearances; all utility clearance approvals must originate from a client, its authorized agent, or an outside utility group.

On public or private property the following must occur:

- GHD must carefully select the proposed drill or excavation site.
- Site selection must be conducted after a careful review of **all** available utility plans.
- Site selection must involve a physical examination of the proposed work area, checking for utility indicators (this cannot be performed from an office).



Note: The site selection process is one of the most important and difficult tasks for field personnel. Personnel selecting proposed drilling or excavation locations must draw on all source information and use physical evidence to identify potential conflicts and select successful activity locations.

- Site selection must be well marked in the field using wooden stakes and/or white paint such that the proposed location is easily identified (the attached Table 2.1 shows the International Color Code System for Utility Marking).
- Site selection must be documented in writing (i.e., field book sketches), noting field ties to the proposed location such that the location can be reproduced/laid out again if the marker is lost or moved.
- Site utility clearance (by landowner and One-Call Service) should be performed in the presence of GHD personnel and contractor personnel, which will enable GHD/contractor personnel to hear and see first hand the utility concerns present; and lastly.
- Site utility clearance results should be documented by GHD for future reference.

A number of utility clearance documentation methods exist such as:

- Written field book reference - recording date of clearance check, group conducting clearance, sketch of utilities present, and record of clearance confirmation code/information number.
- Written utility clearance documentation from land owner (i.e., Private or Public) showing service checks completed and a sign-off of who conducted the checks.
- Completion of the GHD Property Access/Utility Clearance Data Sheet (QSF-019) by the landowner, with contractor sign-off.

Fact: Utility checking groups/private facility utility checking groups and One-Call-Systems may provide written sign-off that a check was conducted (but under no circumstances do any of these groups accept liability in the event of utility damage or personal injury). In fact a disclaimer usually accompanies any written documentation provided that states that the utility clearance service is a check only, utilities may or may not be positioned as marked and that the contractor breaking ground is ultimately responsible for damaged utilities.

The Property Access/Utility Clearance Data Sheet (QSF-019) is typically required when the client or property owner does not have their own utility clearance form or documentation procedure.

The Property Access/Utility Clearance Data Sheet (QSF-019) will permit the client to identify individual utility clearances or conflicts by initialing the appropriate services checked. Once complete, a sign-off is required to identify the person(s) assuming responsibility for the accurate completion of the utility checking and concurrence that the contractor is aware of the utilities present. Clients or contractor personnel reluctant to sign-off should be made aware that this is not a "liability release" but an indication that the checks were completed. If a utility is damaged and repair and/or liability costs are assigned this will likely be allocated to those that were negligent.



In all areas of the U.S. and Canada the "One-Call System" (or local equivalent) utility clearance services are available and must be contacted before excavation work occurs. **This is the law** in most areas, and certainly GHD's policy.

The "One-Call System" is a safety program designed to prevent utility damage and diminish the potential hazards posed to workers/public during subsurface activities. GHD personnel must be warned that not all utilities participate in these services and the level of service varies from area to area. Laws concerning utility participation within "One-Call Systems" are changing; many areas now are mandatory that all service/utility groups must participate, other areas are voluntary.

Further it should be noted that this service may be performed by "third" party private companies that have competitively bid for this work. Utility service personnel can only rely on the plans provided within their system and the equipment available. Subsequently, these services can and do make mistakes or may misinterpret the information available/data collected. Utility locates are considered an "art not a science"; consequently GHD personnel should be in attendance during location checks to observe and feel comfortable with the service being provided. It is not good practice to mark proposed work locations then complete a utility check without meeting the utility locator face to face to discuss the construction elements.

If a high comfort level is not achieved or other uncertainties exist, GHD can initiate extra activities, at minimal cost, to solve utility clearance concerns. The extra effort options may include one or more of the following:

1. Hand digging to expose utilities of concern (i.e., confirm exact utility position in one or more locations).
2. Hand augering at proposed drill or excavation location to "confirm the absence" of services at the proposed location (in northern climates this may require hand augering to depths beyond the frost line; also beware of utilities at excessive depth beyond hand methods).
3. Detection device screening at proposed activity location (i.e., surface detection equipment can be used to locate area service positions but can also indicate a lack of service presence in the proposed work area), have the utility locate service screen the proposed work area.
4. Hire a private utility locate service to conduct a utility clearance.

Private utility locate groups are a growing industry that has organized an association of membership: National Utility Locate Contractors Association (NULCA). This group can be contacted at 715-635-6004.

In the event of a utility "hit" or "near loss", the GHD Accident/Incident Reporting Form must be completed and submitted to the GHD Health and Safety group through the GHD Incident Hotline (1-866-529-4886).



2.14 Shipment, Transportation, and Handling of Chemicals and Gases - GHD Personnel

Field activities many require the use of chemicals and gases that are required by the Canadian Transportation of Dangerous Goods (TDG) Regulation or the United States Department of Transportation (USDOT) Regulations.

In order to insure that GHD employees understand and adhere to these complex regulations and GHD policy. **No GHD employee may transport a chemical or gas without completing the appropriate training for that country.**

The training covers: definitions of hazardous substances and hazard classes; identification of proper shipping names; proper packaging, labeling, placarding, shipping papers and manifests; emergency response and reporting, and security awareness as required by law. Training is required every 3 years.

In addition, GHD employees may not transport chemicals or gases requiring shipping papers in their personal vehicles.

Chemicals or gases proposed for use at a site may be shipped by the Vendor directly to the site. This eliminates the concern of having to handle and transport regulated hazardous materials. For additional guidance on the transportation of chemicals and gases, please contact a GHD Regional Safety & Health Manager.

At the completion of the job it is warranted, where possible, to dispose of waste chemicals and gases through the proper waste disposal activities at the site. Waste materials **may not be** returned to the GHD office; contact the GHD Waste Services group for guidance. Unused chemicals and gases may potentially be returned to the GHD office as governed by transportation, safety, and environmental regulations; please contact a GHD Regional Safety & Health Manager for guidance.

2.15 Closing

In closing, completion of field activities properly is an important component of our business. The data collected during these activities are used to form conclusions of the projects and to prepare reports that are provided to our client. If the data are not correct, then the conclusions may be incorrect. Although, it is very important to complete field activities properly and to collect correct data, there are key items to remember:

- Mistakes do happen
- Learn from your mistakes
- Think about what you are doing
- Be observant
- Call daily



GHD Field Training Manual

Section 7.0

Water Sampling Standard Operating Procedures

- A. Groundwater
- B. Residential
- C. Surface Water

(T104)

July 2015

Please Adhere to the Following Quality System Training Requirements:

- Employees who are required to conduct a specific field activity must be properly certified to do the work.
- This involves reviewing the SOP and completing the online training course and exam.
- Employees must also conduct this field work under supervised conditions on at least three occasions, and must be certified by a qualified mentor. Only then can an employee conduct a specific field activity on their own. This is documented on a Field Method Training Record (QSF-021).
- Complete the QSF-021 and forward it to trainingrecords-northamerica@ghd.com.
- Please note that three topics are discussed in this SOP. A separate QSF-021 is required for each topic:
 - Groundwater Sampling
 - Residential Water Sampling
 - Surface Water Sampling

Table of Contents

7.	Water Sampling (Groundwater, Residential, and Surface Water)	
	Standard Operating Procedures	1
7.1	Introduction	1
7.2	Background	2
7.3	Planning and Preparation	3
7.4	Safety and Health	4
7.5	Quality Assurance/Quality Control	5
7.6	Equipment Decontamination	6
7.6.1	Purge Water and Decontamination Fluid Disposal	6
7.7	Field Procedures for Groundwater Sampling	7
7.7.1	Well Identification and Inspection	7
7.7.2	Air Monitoring	8
7.7.3	Water Level Monitoring/Well Depth Sounding	8
7.7.4	Well Volume Calculation	9
7.7.5	Well Purging and Stabilization Monitoring	10
7.7.5.1	Typical Method	10
7.7.5.2	Purging Entire Water Column	11
7.7.5.3	Low-Flow Purging (LFP) Technique	12
7.7.5.4	Sampling Techniques	14
7.7.5.5	Order of Sample Collection	14
7.7.6	Sample Acquisition and Transfer	15
7.7.6.1	Sample Labels/Sample Identification	16
7.7.7	Purging/Sampling Equipment	16
7.7.7.1	Peristaltic Pumps	16
7.7.7.2	Suction Pumps	17
7.7.7.3	Submersible Pumps	18
7.7.7.4	Air Lift Pumps	19
7.7.7.5	Bladder Pumps	19
7.7.7.6	Inertia Pumps	20
7.7.7.7	Bailers	20
7.7.7.8	Passive Diffusion Bags	21
7.7.8	Filtering of Groundwater Samples	22
7.8	Field Procedures for Residential Sampling	22
7.8.1	General	22
7.8.2	Field Procedures	22
7.8.3	Field Notes for Residential Sampling	23
7.9	Field Procedures for Surface Water Sampling	24
7.9.1	General	24
7.9.2	Surface Water Sample Location Selection	24
7.9.2.1	Rivers, Streams, and Creeks	25
7.9.2.2	Lakes, Ponds, and Impoundments	25
7.9.3	Sampling Equipment and Techniques	26
7.9.4	Field Notes for Surface Water Sampling	27

Table of Contents

7.10 Follow-Up Activities.....	28
7.11 References.....	29

Figure Index

Figure 3.8 Typical Groundwater/Residential Water Sample Log Entry

Forms Index

SP-02	Project Planning, Completion and Follow-Up Checklist
SP-05	Groundwater Sampling Equipment and Supply Checklist
SP-06	Well Development, Purging, and Sampling Form
SP-08	Sample Collection Data Sheet - Groundwater Sampling Program
SP-09	Monitoring Well Record for Low-Flow Purging
SP-17	Equipment and Supply Checklist - Surface Water Sampling, Sediment Sampling, and Flow Measurement

Quality System Forms Index

QSF-012	Vendor Evaluation Form
QSF-014	Field Equipment Requisition Form
QSF-019	Property Access/Utility Clearance Data Sheet
QSF-021	Field Method Training Record
QSF-030	Safety and Health Schedule (Canada)
QSF-031	Safety and Health Schedule (U.S.)

7. Water Sampling (Groundwater, Residential, and Surface Water) Standard Operating Procedures

7.1 Introduction

Groundwater, residential, and surface water sampling are conducted in order to characterize the groundwater and surface water quality at a site. Standard Operating Procedures (SOPs) are presented herein for the collection of groundwater and surface water samples from:

- Monitoring wells
- Residential wells
- Surface water bodies

This guideline is not intended to provide the basis for designing a groundwater or surface water monitoring program, but instead assumes that a groundwater and/or surface water monitoring program has already been designed. It is also assumed that a site-specific Work Plan has been established and that a GHD representative is preparing to mobilize to the site.

Groundwater and surface water sampling procedures vary from project to project due to:

- Different chemicals of concern.
- Different guidance provided by local, provincial/state, and/or federal regulatory agencies with jurisdiction at the site.
- The specific objectives of the project.

It is essential that all groundwater, residential, and surface water sampling activities conform to local, state/provincial, and federal regulations. Therefore, it is essential that the GHD representative carefully reviews the Work Plan requirements. The primary goal of groundwater, residential, and surface water sampling is the collection of samples representative of the hydrostratigraphic unit and/or surface water body. It is necessary to use appropriate sampling techniques to collect representative samples that provide reliable and reproducible results in accordance with the Work Plan and all relevant regulations.

The remainder of this section is organized as follows:

- Section 7.2 Background
- Section 7.3 Planning and Preparation
- Section 7.4 Safety and Health
- Section 7.5 Quality Assurance/Quality Control
- Section 7.6 Equipment Decontamination
- Section 7.7 Field Procedures for Groundwater Sampling

- Section 7.8 Field Procedures for Residential Sampling
- Section 7.9 Field Procedures for Surface Water Sampling
- Section 7.10 Follow-Up Activities
- Section 7.11 References

7.2 Background

The objective of a groundwater and residential monitoring program is to obtain samples that are representative of existing groundwater conditions, or samples that retain the physical and chemical properties of groundwater in the hydrostratigraphic unit. Surface water sampling is performed to collect samples that are representative of physical and chemical properties of surface water bodies. Improper sampling and transport practices will cause compounds of interest to be removed or added to a sample prior to analysis. The importance of proper and consistent field sampling methods cannot be over emphasized. It is equally important that proper documentation occurs throughout the sampling program.

The most important aspect of groundwater sampling is the collection of groundwater samples that are free of suspended silt, sediment, or other fine-grained material. Fine-grained material has a variety of chemical compounds sorbed to the particles or has the ability to sorb chemicals from the aqueous phase. This causes a bias in the subsequent analytical results. Reproducible and reliable analytical data are invaluable to a groundwater monitoring program. GHD frequently criticizes the sampling activities completed by others due to the collection and analyses of turbid samples. This SOP discusses sampling protocols that typically achieve sediment-free samples.

When sampling for monitored natural attenuation (MNA) parameters, more stringent protocols are followed to ensure sediment-free samples that are representative of the total mobile load (i.e., dissolved and naturally suspended particles). Low-flow purging (LFP) techniques are strongly recommended, if not mandated, when collecting groundwater samples for MNA parameters. The LFP techniques detailed in Section 7.7.5.3 are in accordance with United States Environmental Protection Agency (USEPA) LFP procedures (Puls and Barcelona, 1996).

Groundwater sampling is required for various reasons, including:

- Investigating potable or industrial water supplies
- Tracking contaminant plumes
- Investigating a site with suspected groundwater contamination

Groundwater is usually sampled from in-place wells, installed either temporarily or permanently. Municipal, industrial, or residential wells may also be sampled during an investigation. When completing residential well sampling it is important that representative samples are collected. Poor or incorrect sampling techniques will result in erroneous results. Incorrect results disclosed to the public will create a false impression, making it difficult to change the perception when correct results are reported.

Groundwater and residential sample collection are performed from non-impacted to most impacted locations. This eliminates the potential for cross-contamination. A review of all historical analytical data is performed to ensure the exact sampling sequence.

Surface water sampling locations are selected based on many factors including:

- The study objectives
- The location of point source discharges
- The location of no-point source discharges and tributaries
- The presence of structures (e.g., bridges, dams)
- Accessibility

Surface water sampling should be performed from downstream to upstream locations. This ensures that surface water sampling activities do not cause suspended sediments to bias samples collected downstream.

7.3 Planning and Preparation

Prior to groundwater, residential, and surface water sampling:

1. Review the Work Plan, project documents, and Site-Specific Health and Safety Plan (HASP) with the Project Manager/Coordinator.
2. Review the Quality Assurance Project Plan (QAPP) with the Project Coordinator and Project Chemist to determine Quality Assurance/Quality Control (QA/QC) and decontamination requirements.
3. Complete a Field Equipment Requisition Form (QSF-014). Assemble all sampling equipment and supplies required per the Groundwater Sampling Equipment and Supply Checklist (Form SP-05). The Project Planning, Completion, and Follow-Up Checklist (Form SP-02) should be used for guidance throughout the project.
4. Assemble the site plan, well logs, and previous sampling/purging data required for the sampling event. Determine the exact number and locations of wells to be sampled.
5. Obtain all forms to record purging and sampling activities (Forms SP-06, SP-08, and SP-09).
6. Confirm with the Project Manager/Coordinator that a Property Access/Utility Clearance Data Sheet (QSF-019) has been completed. For residential sampling, ensure that homeowners have been notified of the intended sampling event. Confirm the presence of any dogs on site, modify the site-specific Job Safety Analysis, if there is a dog.
7. Arrange access to the site. Obtain all well and site keys. Consider site access conditions (e.g., snow).
8. For surface water sampling consider if hazards exist due to deep/fast moving water, difficult access, and if additional GHD personnel are required for safety and health reasons.

9. For residential sampling contact homeowners to make arrangements for a site visit, arrange for site dog to be removed from all areas where a GHD employee will be working. The client or another party may be responsible for making arrangements.
10. Complete a Vendor Evaluation Form (QSF-012) and file in the Project file for any Vendors that do not have full approval status or are not listed on the Approved Vendor List (QSL-004). Completion of a Safety and Health Schedule (QSF-030 for Canadian work; QSF-031 for U.S. work) is necessary for all Vendors who complete field services. Prior to mobilization on site, the Vendor must submit the form to the Regional Safety and Health Manager for review and approval (if not already posted on QSL-004).
11. Contact the GHD Chemistry group to arrange:
 - SSOW (Simplified Scope of Work)
 - Laboratory
 - Sample containers delivery
 - Preservatives if required
 - Filtration information if required
 - Coolers
 - Shipping details
 - Sample starting date
 - Expected duration of sampling program
12. If several sampling events are planned, evaluate with the client the benefit of purchasing and installing dedicated sampling equipment. Dedicated purging and sampling equipment reduces potential cross-contamination and reduces decontamination requirements. At a minimum, sample tubing is dedicated to each well and is left secured in the well for future use. For LFP it is recommended that each well is dedicated with a bladder pump and tubing to eliminate well disturbance.
13. Evaluate sample notification needs with the Project Coordinator. Have the regulatory groups, client, landowner, GHD personnel, and laboratory been notified of the sampling activities?
14. Evaluate containment and disposal requirements for purge waters.
15. Plan sampling activities to ensure that wells that historically go dry or have poor recharge fit into the sampling program. This will reduce the time required for sample collection.
16. Plan the sequence of sampling activities to reduce the potential for cross-contamination. For groundwater sampling, start with clean wells and progress to impacted wells. For surface water sampling, start downstream and progress upstream.

7.4 Safety and Health

GHD is committed to conducting field activities in accordance with sound safety and health practices. GHD adheres to high safety standards to protect the safety and health of all employees,

subcontractors, customers, and communities in which they work. The safety and health of our employees takes precedence over cost and schedule implications.

Field personnel are required to implement the Safety Means Responsibility Awareness Teamwork (SMART) program as follows:

- Assure the HASP is specific to the job and approved by a Regional Safety & Health Manager.
- Confirm that all HASP elements have been implemented for the job.
- A Job Safety Analysis (JSA) for each task has been reviewed, modified for the specific site conditions, and communicated to all appropriate site personnel. The JSAs are a component of the HASP.
- Incorporate Stop Work Authority; Stop, Think, Act, Review (STAR) process; Safe Task Evaluation Process (STEP); Observations process; Near Loss and Incident Management process in the day-to-day operations of the job.
- Review and implement applicable sections of the GHD Safety & Health Policy Manual.
- Confirm that all site personnel have the required training and medical surveillance as defined in the HASP.
- Be prepared for emergency situations, locating safety showers, fire protection equipment, evacuation route, rally point, and first aid equipment before you begin working, and make sure that the equipment is in good working order.
- Maintain all required Personal Protective Equipment (PPE), safety equipment, and instrumentation necessary to perform the work effectively, efficiently, and safely.
- Be prepared to call the GHD Incident Hotline at 1-866-529-4886 for all involving injury/illness, property damage, vehicle incident, and/or significant Near Loss.

It is the responsibility of the Project Manager to:

- Ensure that all GHD field personnel have received the appropriate health and safety and field training and are qualified to complete the work.
- Provide subcontractors with a Job Hazard Analysis to enable them to develop their own HASP.
- Ensure that all subcontractors meet GHD's (and the Client's) safety requirements.

7.5 Quality Assurance/Quality Control

A well-designed QA/QC program will:

- Ensure that data of sufficient quality are obtained, for proper site management decisions or remediation design.
- Allow for monitoring of staff and contractor performance.
- Verify the quality of the data for the regulatory agency.

It is important to note that a QA/QC program should be developed on a site-specific basis. QA/QC requirements are discussed in Section 3.9.

7.6 Equipment Decontamination

Equipment decontamination procedures for a groundwater, residential, or surface water monitoring program will be described in detail in the site-specific Work Plan or in the QAPP.

Equipment is decontaminated between sampling locations and prior to leaving the site. Upon completion of the sampling program, all equipment is decontaminated at the site and then returned clean to the appropriate field equipment manager.

For most groundwater, residential, and surface water sampling programs, sampling equipment (e.g., pumps, bailers, water level indicators) is typically cleaned as follows:

1. Wash with clean potable water and laboratory detergent, using a brush as necessary to remove particulates.
2. Rinse with tap water.
3. Rinse with deionized water.
4. Air dry for as long as possible.

If required, the following steps may be added when sampling for Volatile Organic Compounds (VOCs) and metals:

1. Rinse with 10 percent nitric acid (only if samples are to be analyzed for metals).
2. Rinse with deionized water.
3. Rinse with appropriate solvent (pesticide grade isopropanol, methanol, acetone, hexane, if required).
4. Rinse again with deionized water.
5. Air dry for as long as possible.
6. Wrap samplers in aluminum foil to prevent contamination.

Caution: Check the QAPP to confirm the cleaning protocol. Use of incorrect cleaning protocol could invalidate chemical data.

7.6.1 Purge Water and Decontamination Fluid Disposal

Project-specific disposal methods for purged groundwater and decontamination fluids are determined by the Project Manager during the sampling program's planning and preparation stage (see Section 7.3), but may include:

1. Off-site treatment at private treatment/disposal facility or publicly owned treatment facilities (sanitary sewer).
2. On-site treatment at a client-operated facility.
3. Direct discharge to the surrounding ground surface, allowing infiltration to the underlying subsurface.
4. Direct discharge to an impervious pavement surface allowing for evaporation.

Options 3 and 4 are permitted only after careful review of these practices and the anticipated site conditions. Under no circumstances shall GHD personnel aggravate an existing condition or spread contamination into clean areas.

Decontamination fluids (specifically cleaning solvents/acids) are segregated and collected separately from wash water and purge water. Often small volumes of solvents used during the course of a groundwater, residential, or surface water sampling program will evaporate if left in an open pail. If evaporation is not possible, off-site disposal need to be arranged.

7.7 Field Procedures for Groundwater Sampling

The typical series of events that takes place for a groundwater sampling program is:

1. Well identification and inspection
2. Air monitoring
3. Water level monitoring
4. Well depth sounding
5. Well volume calculation
6. Purging and sampling equipment installation
7. Well purging and stabilization monitoring
8. Sample collection, sample preparation, completion of chain-of-custody, (COC) sample packaging
9. Final water level monitoring (if required), purging, sampling equipment removal, secure the well
10. Equipment decontamination
11. Field note completion and review
12. Sample shipment and COC distribution
13. Purged groundwater and decontamination fluid disposal
14. Sample record documentation, equipment return
15. Completion and distribution of appropriate forms

It is recommended that new plastic sheeting be placed on the ground around the well to prevent contamination of purging and sampling equipment and accessories (e.g., pumps, hoses, rope.).

7.7.1 Well Identification and Inspection

At sites with numerous wells or wells nests, misidentification of wells has occurred. The GHD representative must be alert to the possibility of potential cap switching, mislabeled wells, or unlabeled well locations.

Determine proper well location and identification by comparing the well log details to the measured well depths (i.e., total well depth, casing diameter, casing stick-up, or stick-down distances), field tie-ins, and site plan.

Once well identification has been established, complete a thorough well inspection:

1. Determine if the well cap and lock are secure, and check for vandalism.
2. If no lock is present, dedicate a new lock to the well location.
3. Examine the integrity of the surface seal.
4. Check for cracks, evidence of frost heave, or subsidence in the vicinity of the well.
5. Examine the integrity of the protective casing. Ensure that the casing can be closed and locked.
6. If required, re-label the well to assist in future identification.
7. If the well is installed with dedicated sampling equipment, check for cracks or leaks in tubing, and worn or frayed rope.
8. Record all the well inspection details in the field book to document well conditions and suitability for groundwater sampling activities.
9. Forward the well inspection results to the Project Coordinator, especially if repairs are required.

7.7.2 Air Monitoring

Prior to removing a well cap, measure the breathing space above the well with a photoionization detector (PID) to establish background of undifferentiated organic vapor levels. Repeat this process once the well cap has been removed. If either of the PID levels exceed the air quality criteria established in the HASP, air-purifying respiratory (APR) protection or a supplied air system is required. Also take a PID reading inside the riser pipe. This PID reading is a good indication of elevated chemical or non-aqueous phase liquids (NAPL) presence. Report all elevated PID levels to the Project Coordinator immediately to determine if additional health and safety and personnel protective equipment is required. The HASP will provide the required action levels and PPE.

7.7.3 Water Level Monitoring/Well Depth Sounding

Prior to commencing well purging and groundwater sampling, the water level is measured for hydraulic monitoring and to determine the well volume. Typically, a complete round of water level measurements is taken at a site to establish groundwater conditions prior to initiating well purging or groundwater sampling activities.

A watertight cap provides an airtight seal on the casing and the water level positioned in the casing area. The cap creates a vacuum or pressurized condition in the casing section which can support or depress the water column in the well casing. This can produce an artificially high or low water level in the well casing. This effect can cause a few inches or feet of error in the static water level. Once the cap is removed, allow the pressure to stabilize for about a half hour. Measure the water level

frequently to ensure that stabilization of the water level has occurred. Once the water level has stabilized (i.e., is static) the correct water level may be measured.

A number of instruments are available to measure groundwater levels. GHD typically uses:

- Battery-operated water level indicators (i.e., audible and/or visual identification of water level)
- Battery-operated oil/water interface probes (i.e., audible and/or visual identification of water levels and presence of NAPL)
- Electronic transducers (numerous manufacturers) and recording devices for long-term hydraulic monitoring
- Stevens™ recorders (both float and electronic instrumentation) for long-term hydraulic monitoring

Section 8.0 describes in detail the equipment and monitoring techniques for water level measurements.

Well depth sounding is often required to confirm well identification, evaluate the accumulation of sediment in the well bottom, or assist in determining the standing well volume. Sounding is performed using a water level indicator or a measuring tape with a weighted end. The water level indicator or weighted tape is lowered to the bottom of the well and a comparison is made of the installed well depth versus the measured well depth. The presence of excessive sediment or drill cuttings may warrant redevelopment of the well prior to well purging and groundwater sampling activities.

The total well depth is compared to the original installed total well depth. If the well screen is more than 50 percent blocked by accumulated sediment, the well is redeveloped prior to the next groundwater sampling event. Report all wells requiring redevelopment to the Project Coordinator. Well depth sounding is performed on an annual or biannual basis if the well is equipped with a dedicated pump.

For LFP, well depth measurement is performed to ensure proper pump intake placement. The use of a wide-based probe, such as a weighted tape, is necessary to minimize penetration and disturbance of accumulated sediment. The measuring device is lowered slowly through the water column to the well bottom to minimize mixing of the stagnant well casing water and disturbance of sediment.

Note: Don't forget that decontamination procedures apply to the water level monitoring equipment as well as the groundwater sampling equipment. If well sounding is performed, the entire measuring device must be thoroughly decontaminated prior to re-use. Measuring the well depth with certain water level indicators may damage the probe seal. Therefore, a tape with a weighted end should be used to measure well depth.

7.7.4 Well Volume Calculation

Prior to commencing well purging, the volume of water in the well must be known to determine the volume of groundwater to be removed. A well volume is defined as the volume of water contained in

the well screen and casing (and in the case of an open bedrock hole, the volume of water in the open corehole and possibly in the well casing). To determine the standing water volume in a well:

1. Calculate the distance from the bottom of the well to the static water level.
2. Measure the inside diameter of the well or casing. Obtain the volume of standing water in the well using the following formula:

$$V = \pi r^2 h \text{ (7.48 U.S. gallons/cubic feet) (1 liter/1,000 cubic centimeters)}$$

Where:

V = volume of water in gallons or liters

π = 3.142

r = radius of well casing (feet or meters)

h = depth of water column in the well (feet or meters)

Typical 1 - Foot Casing Volumes	
Diameter (inches)	Gallons (U.S.) of Water Per Foot of Casing
1.5	0.09
2	0.16
3	0.37
4	0.65
6	1.47

Typical 1 Meter Casing Volumes		
Diameter		Litres per Meter of Casing
(inches)	6 (cm)	
1.5	3	1.14
2	5	2.02
3	8	4.56
4	10	8.11
6	15	18.24

7.7.5 Well Purging and Stabilization Monitoring

7.7.5.1 Typical Method

Prior to initiating groundwater sample collection, the wells is purged of the standing stagnant groundwater volume. This volume is not representative of the groundwater in the hydrostratigraphic unit. Purging is performed until the water in the well is representative of the actual conditions in the hydrostratigraphic unit. Stabilization is usually achieved by the removal of three to five times the volume of standing water in the well (USEPA convention). Purging is considered complete once purged groundwater is free of sediment and field parameters including specific conductance, temperature, and turbidity are stable. Stabilization is achieved when field measurements for specific conductance and temperature are within a range of plus or minus 10 percent of the average for the

last three readings. Field measurement for pH should be within a range of plus or minus 0.1 pH unit of the average for the last three readings, and groundwater turbidity values should be less than 5 nephelometric turbidity units (NTU) (guidance value only). Once the number of well volumes required to achieve stabilization is established, the volume required to reach stabilization for future sampling events is reduced or eliminated. Extended purging of a well will generally result in achieving sediment-free groundwater conditions.

During purging, if stabilization has not occurred after removal of five well volumes, purging is continued until ten well volumes have been removed. If stabilization still has not been achieved, stabilization may be dropped as a pre-condition to groundwater sampling. The Project Coordinator should be notified that stabilization has not occurred after the removal of ten well volumes.

At high yielding wells, removing three to five well volumes is usually sufficient prior to initiating groundwater sampling. For low yield wells (i.e., wells that pump dry after one well volume) it is necessary to purge the well dry on three successive days, unless the well recovers to full static conditions in a shorter time. If the recharge is relatively high, groundwater sampling will be initiated once the well has fully recovered to static groundwater conditions, or to a level that is sufficient to collect the necessary groundwater sample volume.

Note: Purging of dry wells should be scheduled to begin on Monday or Tuesday, to reduce weekend requirements.

Turbidity of purged groundwater is evaluated by a visual examination for sediment/silt presence or by using a nephelometer which physically measures groundwater turbidity in NTUs. Generally, a turbidity value of 50 NTU or less is acceptable, although some regulatory agencies have established lower criteria (i.e., less than 5 NTU). If 50 NTU is not achieved, filtration of samples may be required. LFP can generally result in turbidity values less than 5 NTU.

Note: Agitation of the water column within the well will increase turbidity. Therefore, bailers and inertia pumps (Waterra™) are of limited use for collecting sediment-free samples. The tubing of peristaltic pumps must be secured to prevent movement of the tubing within the water column which would disturb sediment. The best method to reduce sediment disturbance is low-volume non-agitation pumping (i.e., bladder pump).

Well purging is accomplished using dedicated equipment or by using either peristaltic, bladder, or other approved purging methods. Purging and sampling equipment are dependent on the total well depth. Bailing can be used for well purging but this method stirs up sediment and increases the purging effort required before stabilization is achieved. Equipment available for well purging is discussed in Section 7.7.7. Monitoring equipment used during well purging includes a water level indicator, pH meter, thermometer, conductivity meter, and turbidity meter.

7.7.5.2 Purging Entire Water Column

The purging equipment is lowered into the top of the standing water column. Well purging is completed from as close to the top of the water column as possible, not from the well bottom, unless poor well recovery occurs. Purging from the top of the water column moves water from the formation through the well screen of the well and into the well casing. This allows for the entire

static volume to be removed. Purging at depth in the water column does not remove water above the pump intake and results in the collection of unrepresentative samples.

If required, the pump intake can be adjusted. If the recovery rate is greater than the pumping rate, the pump should remain suspended until the required purged volume has been removed. If the recovery rate is less than the pumping rate, the pump should be lowered to ensure the removal of the required well volume.

7.7.5.3 Low-Flow Purging (LFP) Technique

LFP purging results in minimal drawdown during well purging, so less purging is required before formation water is removed. The volume required for purging using LFP is significantly reduced. LFP results in less agitation and mobilization of sediments compared to traditional sampling techniques.

A pre-cleaned stainless steel bladder pump equipped with a Teflon™ bladder is strongly recommended for LFP. The discharge line should be polyethylene or Teflon™ lined tubing with an inside diameter of 1/4 or 3/8 inch (6 or 10 mm). Check the Work Plan or QAPP to ascertain the proper bladder and discharge tubing. Smaller discharge tubing ensures that the tubing remains filled with water and reduces air bubbles at low purging rates. The airline to the pump is generally 1/4-inch (6 mm) inside diameter polyethylene tubing. The pump is secured to nylon rope and positioned in the well so that the pump intake is set at the mid-point of the well screen, or a minimum of 2 feet (0.6 m) above the bottom of the well or accumulated sediment level. It is important that the rope, airline, and discharge tubing are measured prior to installation in the well. The bladder pump and tubing are lowered very slowly through the water column to minimize mixing of the stagnant well casing water and to minimize the agitation of sediment into suspension, which would increase the purging time. It is recommended, and in some instances regulated, that pump installation occurs at least 24 hours prior to initiating LFP. It is recommended that a bladder pump be dedicated to the well for regular monitoring events.

During LFP, the pumping rate should be between 100 and 500 milliliters per minute (mL/min). It is recommended that initial pumping be conducted at a lower rate to limit drawdown in the well. During purging, groundwater levels are measured to maintain a maximum 0.4 foot (0.1 m) of drawdown. The pumping rate can be gradually increased during LFP. Pumping rate increases will be dependent on the drawdown and the stabilization of field parameters discussed below. Pumping rate adjustments should occur in the first 15 minutes of purging. After this time the pumping rate should remain constant and flow rate adjustments should be avoided. During purging, the pumping rate and groundwater level should be measured at least every 10 minutes. It is recommended that water level measurements occur at 5-minute intervals.

During LFP, stabilization of the purged groundwater is required to ensure the collection of representative groundwater samples from the formation and not from the stagnant water in the well casing. Field parameters including pH, temperature, specific conductance, oxidation-reduction potential (ORP), dissolved oxygen (DO), and turbidity should be monitored during LFP. The measurement of these field parameters is used to evaluate if stabilization of the purged groundwater has occurred prior to the collection of groundwater samples. The field measurements should be measured and recorded at 5-minute intervals. Groundwater stabilization is considered

achieved when three consecutive readings for each of the field parameters, taken at 5-minute intervals, are within the following limits:

pH	±0.1 pH units of the average value of the three readings
Temperature	±3 percent of the average value of the three readings
Conductivity	±0.005 milliSiemen per centimeter (mS/cm) of the average value of the three readings for conductivity <1 mS/cm and ±0.01 mS/cm of the average value of the three readings for conductivity >1 mS/cm
ORP	±10 millivolts (mV) of the average value of the three readings
DO	±10 percent of the average value of the three readings
Turbidity	±10 percent of the average value of the three readings, or a final value of less than 5 NTU

During LFP, field parameters are measured using a flow-through cell apparatus. At the start of LFP the purge water is visually inspected for clarity prior to connecting to the flow-through cell. If the purge water is turbid, LFP continues until the purge water is visually less turbid prior to connecting to the flow-through cell. Field parameters may be obtained using individual meters or a multiple meter unit; however, the use of a flow-through cell is highly recommended. All meters must be calibrated daily in accordance with the manufacturer's and GHD's calibration instructions, and a calibration record maintained in a standard GHD field book.

During LFP the meter readings are monitored for evidence of meter malfunction. The following are common indicators of meter malfunctions:

- DO above solubility (e.g., oxygen solubility is approximately 11 milligrams per liter (mg/L) at 10°C) may indicate a DO meter malfunction.
- Negative ORP and DO less than 1 to 2 mg/L may indicate either an ORP or a DO meter malfunction (i.e., should have positive ORP and DO less than 1 to 2 mg/L under oxidizing conditions).
- Positive ORP and DO less than 1 mg/L may indicate either an ORP or a DO meter malfunction (i.e., should have a negative ORP and DO less than 1 mg/L under reducing conditions).

Meter calibration fluids should be available for meter recalibration in the field. Spare meters should also be available for meter replacement if necessary.

Note: DO levels exceeding the solubility of oxygen in water are erroneous and are indicative of meter malfunction or poor sampling techniques causing turbulence and aeration. DO concentrations cannot exceed:

9 mg/L at 20°C

10 mg/L at 15°C

11 mg/L at 10°C

14 mg/L at 1°C

Stabilization will be considered complete when the field parameters have stabilized as indicated in the above table. Purging will continue if stabilization does not occur, until a maximum of 20 screen volumes has been removed. LFP causes groundwater to be drawn from a significant distance above or below the pump intake. Therefore, the screen volume is based on a 5-foot (1.5 m) screen length. After the removal of 20 screen volumes, purging will continue if the purged water remains

visually turbid and appears to be clearing. Also purging will continue if the field parameters vary only slightly outside of the stabilization criteria and appear to be approaching stabilization.

If the recharge to the well is insufficient to conduct LFP, the well should be pumped dry and allowed to recharge sufficiently for the collection of the groundwater sample volume. Wells purged dry are required to meet the stabilization criteria detailed above.

7.7.5.4 Sampling Techniques

Upon completion of purging, with groundwater stabilization and clarity meeting the applicable protocol described above, groundwater sample collection can proceed. Generally the field parameters of pH, temperature, and specific conductance are monitored first, then any other required field measurements.

Samples are collected directly from the purging pump, when possible, or an alternate device (i.e., pump or bailer) may be installed or used. If new sampling equipment is installed, the first few bails or discharge volumes should be discarded to allow acclimation of the sampling equipment with the groundwater.

Samples are typically collected from the pump or bailer with the discharged groundwater collected directly in the appropriate sample containers. The interior of the bottle or cap must not be touched or handled in anyway. New gloves (i.e., disposable nitrile gloves or equivalent) should be worn for the collection of each sample. Caps from sample bottles must not be placed on the ground or in pockets to eliminate the possibility of cross-contamination.

Descriptions of the various equipment and sampling methods for the collection of groundwater samples are contained in Section 7.7.7.

The following describes the main activities involved in the collection of groundwater samples.

7.7.5.5 Order of Sample Collection

Groundwater samples are collected and containerized in the order following volatilization sensitivity:

1. VOCs
2. Semi-volatile organic compounds (SVOCs)
3. Total organic carbon
4. Total organic halides
5. Extractable organics
6. Total metals
7. Dissolved metals
8. Phenols
9. Cyanide
10. Sulfate and chloride

11. Nitrate and ammonia
12. Microbiological parameters
13. Radionuclides

QA/QC requirements for groundwater sampling are described in detail in Section 3.9.

7.7.6 Sample Acquisition and Transfer

If groundwater sample collection is performed using a pump, the flow rate must not exceed 100 mL/min during the collection of groundwater samples for VOCs. The low flow rate will reduce the possibility of degassing samples. During the collection of groundwater into the sample container or filtration device, minimize agitation and aeration of the sample. Groundwater samples are transferred directly into the sample container for submittal to the laboratory. Groundwater samples should not be collected in larger containers and subsequently transferred to smaller sample containers; however, on occasion this will be required for filtration or sample composting. During VOC sample collection, samples must not be collected, handled, or containerized near or in the vicinity of a running motor or exhaust which may contaminate the samples.

Groundwater samples for VOCs are collected in laboratory supplied 40 mL glass vials. The vials are filled to the top until a meniscus is formed, then topped with a Teflon™-lined cap. To prevent the loss of volatiles, it is important that no air bubbles or headspace are present in the sample container. Inverting and tapping the vial will check for the presence of air bubbles. If air bubbles are present, the sample should be topped off again and resealed. This process may only be performed a maximum of twice, at which time the sample must be discarded and the sample retaken. If preservatives were present in the bottle from the laboratory, a new sample vial must be used.

Note: Gas bubbles that appear in VOC containers after sample collection may be a result of degassing or reaction with preservative. If this occurs, note this occurrence on the chain-of-custody. Re-sampling is not required in most cases.

During sample collection ensure groundwater samples are preserved according to laboratory requirements. If required and supplied by the laboratory, preserve the samples in accordance with the QAPP. Some laboratories pre-preserve bottles so that once the groundwater sample is added the preservation is completed. In either case, it is advisable to check sample preservation using litmus paper. Using litmus paper ensures that groundwater sample preservation has been completed to the proper pH as required by the QAPP. If preservation of a sample does not meet the requirements of the QAPP, it may be necessary to add additional preservative, or note on the chain-of-custody that incomplete sample preservation has occurred.

Once sample collection is complete, samples are placed in a cooler on ice to maintain a sample temperature no more than 4°C.

7.7.6.1 Sample Labels/Sample Identification

Label all groundwater samples with the following, written in indelible ink:

1. A unique sample number (see Section 3.9 for guidance)
2. Date and time
3. Parameters to be analyzed
4. Job number
5. Sampler's initial

Secure the label to the bottle. It is recommended that bottle labels be covered with wide clear tape to protect the label during sample packing and shipment. Pack glassware in appropriate packing material to deter breakage during sample packing and shipment. Sample labels can be prepared in advance in GHD offices that have label-generating programs.

An example of a groundwater sample log entry is provided on Figure 3.8.

Section 3.9 details sample labeling requirements for environmental sampling programs. Section 3.9 also details COC requirements and sample shipment requirements.

7.7.7 Purging/Sampling Equipment

GHD maintains a wide variety of purging and sampling equipment for well purging and groundwater sample collection. The groundwater sampler should be familiar with purging and sampling equipment and understand equipment limitations and proper use. Some equipment is very useful for well purging (i.e., high flow rates) but is not permissible for LFP or for sampling sensitive parameters (e.g., VOCs cannot be collected with a submersible (turbine) or suction pump). If the groundwater sampler understands the various equipment operation and limitations, the proper selection of purging and sampling equipment is made, which will minimize the purging and sampling duration and maximize productivity.

Caution: Gas powered equipment requires special attention to ensure that staff hauling these units do not cause equipment or sample contamination. Frequent changes of disposable glove as well strict separation of sampling crew tasks (i.e., those handling pumps and hoses do not contact generator or are involved in any refueling activities) are required.

The following subsections describe the equipment available for groundwater sampling, the equipment use, approximate flow rates, and advantages and disadvantages of the equipment.

7.7.7.1 Peristaltic Pumps

A peristaltic pump is acceptable for purging wells and for most groundwater sample analytes. The groundwater sampler must ensure that a peristaltic pump is acceptable to regulatory agencies with local jurisdiction for VOC and SVOC sample collection. The QAPP will provide sampling requirements.

A peristaltic pump is capable of lifting water from a maximum depth of 25 feet (7.6 m) below ground surface or the pump, whichever is greater. A peristaltic pump is a self-priming, low volume, suction pump which consists of a rotor with ball bearing rollers. Flexible silicon tubing is inserted around or in the pump rotor and squeezed in place by the heads as they revolve in a circular pattern. The section of silicon tubing must not exceed 3 feet (0.9 m) in length. Additional rigid polyethylene or Teflon™ tubing is attached to the flexible tubing and placed in the well. Another piece of rigid tubing is attached to the discharge end of the flexible silicon tubing to facilitate sample collection. The entire length of rigid and flexible silicon tubing is dedicated to the well for future use. The tubing is typically tied and suspended in the well. The flexible or rigid tubing is not reused in other wells because cross-contamination will occur.

Note: Often a length of tubing is accidentally dropped into a well and can be difficult to retrieve. Retrieval can be accomplished by sending another piece of tubing down the well overlapping the lost section of tubing. Once in place, rotate the tubing, essentially wrapping or corkscrewing the lost tubing and new tubing together. After a number of turns are completed pull the tubing, hopefully with the lost section wound around the new piece. Repeat the procedure until successful.

Liquid is pulled into the tubing by the peristaltic pump through the creation of a vacuum as the rotor head turns. An advantage of using a peristaltic pump is that no pump parts come in direct contact with the sample. A peristaltic pump is capable of providing low flow sampling rates (i.e., typically less than 500 mL/min) with less agitation than other suction pumps. However, it is important that the tubing is secured during pumping to prevent the tubing from moving and causing agitation. A peristaltic pump also allows for regulation of the flow rate by increasing or decreasing the rotor head speed.

Peristaltic pumps are small and easily mobilized to remote sample locations. They require minimal setup, and do not require decontamination between sample locations. The disadvantages of a peristaltic pump are its limited lift and flow capabilities and the limited ability to collect VOC and SVOC samples. If VOC or SVOC sampling, check the QAPP to see if sampling with a peristaltic pump is allowed. Also check with regulatory agencies with local jurisdiction to see if the use of a peristaltic pump for collection of VOC and SVOC samples is acceptable. If using a peristaltic pump for purging, and the collection of VOCs and SVOC samples with the peristaltic pump is not acceptable, it is common to collect the initial VOC and SVOC analytes with a stainless steel bottom loading bailer. The peristaltic pump can then be used to collect the remaining sample analytes.

Peristaltic pumps are becoming more popular for LFP. However, it should be noted that a peristaltic pump may cause degassing, pH modification, and possible VOC loss.

7.7.7.2 Suction Pumps

A number of suction pumps (e.g., centrifugal) exist that can be used for purging applications only. A suction pump draws water through a suction line by creating a vacuum in the suction line or hose. Once drawn into the pump, the groundwater comes into direct contact with the pump rotor/pumping chamber area and it is therefore undesirable for groundwater sampling due to high groundwater agitation. Decontamination of suction pumps is extremely difficult. As with peristaltic pumps, most suction pumps have a limited lift capability of about 25 feet (7.6 m). Larger suction pumps, like

2-inch (5 cm) trash pumps, can achieve high flow rates under low hydraulic head. Flow rates of 15 to 20 U.S. gallons per minute (USgpm) (57 to 76 liters per minute [L/min]) can be achieved. This high flow rate minimizes purging time. New or dedicated suction line should be used at each well if a suction pump is used for purging.

Large suction pumps are also useful for well development, in conjunction with agitation and surging.

Large suction pumps are not suited for LFP due to degassing, pH modifications, VOC loss, and lack of flow adjustment.

Caution: The groundwater sampler must prevent the siphoning of purged water from a bulk container back into the well. For example, the following scenario is possible: Joe Sampler has completed purging well 'xyz' and has turned off the 2-inch trash pump. The trash pump discharge line is inserted into a wastewater tank and is submerged below the tank water level. As Joe prepares his glassware and sample pump, the wastewater tank contents are siphoned back into the well. This can result in cross contamination with water from other sites/wells which have been purged either:

- into the tank
- through the pump
- through the discharge line

All discharge lines/groundwater purge pumps must be provided with a check valve to prevent this situation.

Drilling rig pumps including Moyno, progressive cavity, bean, and mud pumps can be used for well purging and well development.

Suction pumps are a useful tool for high rate purging and well development. They require no additional equipment other than a suction line and discharge line for each well. They are mobile and easily transported around and between sites. Suction pumps are limited to use in wells with less than 25 feet (7.6 m) of lift, are difficult to decontaminate, and are unsuitable for sample collection. Large suction pumps are not suitable for LFP.

7.7.7.3 Submersible Pumps

A submersible pump generally provides high discharge rates for purging at depths beyond the capabilities of a suction pump. Based on its size, a submersible pump can pump water from substantial depths at very high pumping rates and can provide higher groundwater extraction rates than other methods. At high pumping rates, a submersible pump can cause agitation and aeration. This results in some submersible pumps not being suitable for the collection of groundwater samples for VOC and SVOC analysis.

Adjustable rate submersible pumps, constructed of stainless steel or Teflon™, are suitable and approved for LFP provided low flow rates are maintained.

The submersible pump, including the electrical cable and lowering cable, must be decontaminated between wells in accordance with the Work Plan or QAPP.

A submersible pump installed in bedrock or in a deep well should be attached to rigid piping (i.e., 3/4-inch (1.9 cm) steel) to allow for pulling or pushing of the pump. The pump may need to be pushed or pulled to the appropriate installation depth, past tight spots in the well, and when affixing the electrical cable and lowering the cable/safety line. Even when rigid piping is used, a safety line must be attached to the pump in case the piping becomes unthreaded or the pump connection is lost.

Submersible pumps can provide high flow rates that are useful for deep well or large diameter well purging activities. They tend to be labor intensive because of decontamination problems, power supply, and discharge piping size. Some submersible pumps are not suitable for some sample analytes. Small submersible pumps (i.e., 2-inch (5 cm) Grundfos™) have the proper construction and have adjustable flow rates, making them suitable for LFP.

7.7.7.4 Air Lift Pumps

An air lift pump operates using compressed air or nitrogen. The compressed air or nitrogen comes into direct contact with the groundwater and forces groundwater from the pump chamber through a series of check balls into the discharge line. An air lift pump operates on alternate pump discharge and pump recharge cycles. The pump and recharge cycles are controlled using a control box at ground surface. Air lifting is possible from deep depths with moderate to low flow rates (2 to 3 USgpm [7.6 to 11.5 L/min]) depending on the pump installation depth, static head, discharge tubing diameter, and air supply pressure.

Since the air or nitrogen comes in direct contact with the groundwater, an air lift pump should not be used for the collection of groundwater samples for VOC and SVOC analysis.

An air lift pump is a good tool for deep well purging and development. If an air lift pump is used for purging, an alternate sampling method will be required (e.g., bailers or bladder pump) for the collection of VOC and SVOC groundwater samples.

7.7.7.5 Bladder Pumps

Bladder pumps, as with air lift pumps, are driven by compressed air or nitrogen but the air or nitrogen does not come in contact with the groundwater. The contact between the air or nitrogen and the groundwater is eliminated by the presence of a Teflon™, polyethylene, or natural rubber bladder. The pump operation, as with the air lift pump, is cyclic and is controlled using a control box at ground surface. The control box controls the pump filling and discharge time. Because the air or nitrogen does not come in direct contact with the groundwater, and there is limited groundwater agitation and degassing, a bladder pump is the best sampling equipment for the collection of groundwater samples for VOC and SVOC analysis.

Bladder pump operation is very quiescent, causing little formation and well disturbance. By using a bladder pump, collecting a sediment-free groundwater sample is easily achieved. An adjustable rate bladder pump should be used for LFP. Bladder pumps generally are only able to achieve a maximum pumping rate of 1.5 USgpm (5.7 L/min). It is important to note that flow rates should be reduced in deep well applications.

Well purging and sampling can be performed using a bladder pump. Once sampling is completed, the pump should be disassembled and decontaminated in accordance with the Work Plan or QAPP prior to use in other wells. The sample tubing is generally 1/4- or 3/8-inch (6 or 10 mm) diameter polyethylene or Teflon™ lined polyethylene tubing. The air line is generally 1/4-inch (6 mm) polyethylene tubing. The sample and air line tubing are typically suspended in the well for future use (dedicated). At some sites a complete sampling system (bladder pump, discharge tubing, and air line) is dedicated to each well.

Bladder pumps provide excellent sample quality and are useful in deeper sampling applications. There are no analyte restrictions. Bladder pumps are strongly recommended for LFP applications.

Bladder pumps require additional equipment including control box, compressed air or nitrogen, and tubing. The setup of a bladder pump is quite labor intensive unless a dedicated system is in place. Decontamination of a bladder pump requires pump disassembly and re-assembly. Finally, bladder pumps are not capable of high flow rates, thus purging times tend to be increased slightly.

7.7.7.6 Inertia Pumps

An Inertia pump or Waterra™ pump is a manually operated or mechanically driven pump which uses only a foot valve on the sample/purge tubing. "Jerking" the sample/purge tubing with the attached foot valve removes groundwater from the well. The rapid lifting and lowering action of the tubing imparts an inertia to the water column within the sample/purge tubing. This causes the water column to rise to ground surface and discharge from the end of the sample/purge tubing. The foot valve holds the water column in the tubing during the lifting process and allows groundwater to enter the sample/purge tubing during the lowering, or down stroke.

GHD owns both manual and mechanical gas-powered inertia systems. Flow rates with inertia pumps are variable and are dependent on cycle speed, tubing size, foot valve size, well depth, and depth to groundwater. The inertia pump is a useful method for purging and for collection of most groundwater sample analytes. Acceptability of VOC and SVOC sampling with inertia pumps is gaining approval in selected areas. Prior to using an inertia pump as a sampling device, check the sampling requirements in the QAPP, or obtain approval from the Project Coordinator.

Inertia pumps are useful for the extraction of dense non-aqueous phase liquids (DNAPL). The only equipment that is exposed to the gross contamination is the foot valve and a small section of the sample/purge tubing. On most projects, the foot valve and sample/purge tubing are dedicated to the well.

Inertia pumps tend to cause extensive disturbance to the water column. The vigorous lifting and lowering of the inertia pump tends to make it difficult to collect sediment-free groundwater samples. Therefore, inertia pumps are not suitable for LFP.

7.7.7.7 Bailers

A bailer is a manual sampling device consisting generally of a hollow tube (e.g., Teflon™, PVC, or stainless steel) with a lower check ball that permits water entry and prevents water loss. The bailer is lowered slowly into the well. This allows water to enter the bailer through the bottom, and the weight of the water inside the bailer closes the check ball when the bailer is retrieved from the well.

A rope or cable is affixed to the bailer to allow the lowering and retrieval of the bailer from the well. Bailing tends to be disruptive to the water column and formation. Obtaining sediment-free groundwater samples using a bailer tends to be difficult, if not impossible. VOCs and SVOCs, as well as other analytes can be collected using a bailer, but it is important that these analytes be as sediment-free as possible. The compatibility of the bailer material and groundwater analytes should be reviewed and approved prior to using a bailer for the collection of groundwater samples. Generally, Teflon™ bailers are acceptable for the collection of most analytes.

Power winches with overhead tripods are available to assist in purging and sampling deep or large volume wells.

Flow rates attained using a bailer is a function of the bailer size and retrieval frequency. Retrieval frequency is dependent on well depth, water depth, and well recharge rate. Bailing is not practical for deep wells or for the removal of large well volumes.

A bailer is a useful tool for well development as the surging action from the bailer insertion and removal from the well promotes sediment suspension and subsequent removal. However, obtaining completely sediment-free samples, or samples below 50 NTU, is difficult if not impossible using a bailer.

A bailer provides representative samples once the well has been adequately developed and purged. A bailer is not suitable for LFP. Rope used for bailing must be kept off the ground and free of other contaminating material that could be introduced to the well. Rope can either be dedicated to the well for future use or discarded.

7.7.7.8 Passive Diffusion Bags

When sampling with diffusion bags the well must be fully developed using an alternate method.

A diffusion bag is a polyethylene bag that contains deionized water. The bag is attached to an appropriate length of rope or cable in order to be submerged to the appropriate depth (indicated in the Work Plan, QAPP, or as instructed by the Project Coordinator). Cable or rope used to suspend diffusion bags can be dedicated to the well for future use or discarded.

Once submerged to the appropriate depth, the diffusion bag is left in the well for an extended period of time, usually 14 days, to allow the bag to equilibrate with the water in the well. The use of diffusion bags eliminates well purging prior to sampling. Placement of multiple diffusion bags in a well allows for vertical groundwater profiling.

Diffusion bags are a low cost method for the collection of groundwater samples. Advantages include:

- No purge water to dispose of.
- No equipment decontamination between wells.
- Simple logistics and operation.
- Reduction in personnel and exposure times.
- Samples collected are representative of formation water adjacent to well.

- Allow for vertical profiling of water column.
- Appropriate for long-term monitoring programs.

The disadvantage of diffusion bags is the length of equilibrium time, generally 14 days. Currently, there are membranes available for diffusion bags suitable for the collection of groundwater samples for select SVOC, and metals analyses. However, there are no membranes currently available for polychlorinated biphenyls (PCBs).

Note: Handle diffusion bags only when wearing clean nitrile or surgical gloves.

7.7.8 Filtering of Groundwater Samples

Filtering is an important process to remove suspended particulate that affect sample results. Filtration of groundwater samples is generally limited to metals analysis.

Filtering can be completed in the field using in-line filters or a vacuum filter kit. Filtering of samples can also be completed by the laboratory, in which case the samples must not be preserved and must be at the laboratory in at least 24 hours of sample collection.

7.8 Field Procedures for Residential Sampling

7.8.1 General

When sampling potable water supply wells it is important to ensure that the samples collected are representative of the aquifer being sampled. Poor or incorrect sampling techniques will result in erroneous sample results that can be disclosed to the public. Incorrect sample results may make any changes in the public perception hard to accomplish when correct results are reported.

7.8.2 Field Procedures

The requirements of a residential well sampling program should be reviewed with the Project Coordinator prior to initiating sampling activities. While similar field procedures used in groundwater sampling (including documentation, sample identification, date, time, etc.) are required in residential well sampling, additional procedures are also required.

Prior to collection of groundwater samples from a residential well, the well must be purged to ensure that samples collected are representative of the formation. Purging removes standing water from the well casing, pipes, and pressure or holding tank. Purging of a residential well requires the removal of one well volume. If access to the well is not available to determine the well volume, purging for a period of 15 to 30 minutes is generally sufficient. Field measurements for pH, conductivity, and temperature are recorded during purging activities until the readings indicate that stabilization has occurred.

Sampling of residential wells is generally performed using the existing pumping system. However, GHD purging and sampling equipment can be used. It is important that only designated **clean** purging and sampling equipment be used for residential well sampling. The use of the existing pumping system is preferred, as this is more representative of the water quality provided to the

residence. Using the existing pumping system also minimizes the possibility of damaging the well and existing pumping system when installing additional purging and sampling equipment.

If GHD equipment is used for residential well sampling, it must be cleaned prior to and between use with a bleach and deionized water solution wash followed by a thorough deionized water rinse.

Note: In addition to the special technical procedures noted, GHD personnel must be aware of this unique situation of conducting sampling at private residences. Special care must be taken to be polite and courteous at all times. Offer only necessary information and maintain a clean work area that is returned to pre-sampling conditions. Personnel should have proper identification available, and only remain in areas long enough to complete the required tasks.

Taps selected for residential well sampling should be located as close to the well as possible. Locate the taps before any treatment systems and, if possible, the pressure tank. It is important to note, if possible, all water treatment devices in operation at the residence including:

- Water softeners
- Filtration units
- Ultraviolet light
- Reverse osmosis
- Distillers
- Chlorinators

Leaking taps that allow water to flow from the stem of the valve handle and around the tap should not be used as sampling locations. Aerators, strainers, and hose attachments should be removed prior to sampling. Maintain a steady flow of water during sampling activities to avoid pressure fluctuations that may cause sheets of microbial growth lodged in the pipes to break loose. Open the cold water tap for a period of 15 to 30 minutes to allow for the complete purging of the pumping system. Maintain a smooth-flaring water stream at a low to moderate pressure without splashing. Do not change the flow rate. Changes in the flow could dislodge particles in the pipes or faucet.

When sampling for microbiological parameters, the end of the faucet must be flame sterilized. During residential well sample, never place caps from sample containers on the ground or in a pocket. Instead, hold the sample container in one hand and the sample container cap in the other. Be very careful not to touch the inside of the sample container cap. Wear new disposable gloves at each sampling location and following contact with a potential contaminant source. The inside of the sample bottle must not be touched with bare hands or allowed to contact the surface of the faucet.

7.8.3 Field Notes for Residential Sampling

Full documentation of each residential well is required and includes:

1. Well depth
2. Casing construction and diameter

3. Well installation date if known
4. Pumping system configuration
5. Piping system construction (e.g., copper, lead-joint, ABS)
6. Presence of treatment devices

Obtain the name and exact mailing address for all residence or well owners, as well as home and work telephone numbers. This information is required to inform the residence or well owner of the results of the sampling activities.

Document residential well sampling activities in a standard GHD field book. Figure 3.8 provides typical residential well sampling field note requirements. Note that additional documentation of well details, treatment devices, piping system, and special circumstances are required in the field book in addition to the sample log entry.

7.9 Field Procedures for Surface Water Sampling

7.9.1 General

Surface water sampling is performed to obtain samples for surface water bodies that are representative of existing surface water conditions.

Surface water sampling locations for surface water quality and groundwater interaction studies are selected based on the following:

1. Study objectives
2. Location of point surface discharges
3. Non-point source discharges and tributaries
4. Presence of structures (e.g., bridge, dam)
5. Accessibility

During surface water sampling it is important to obtain samples that are not impacted by the re-suspension of sediment produced because of improper or poor surface water sampling techniques.

7.9.2 Surface Water Sample Location Selection

Prior to conducting surface water sampling activities, the first requirement is the consideration and development of surface water sampling locations. It is important that all surface water sampling locations be selected in accordance with the Work Plan and described to and discussed with the Project Coordinator.

Bridges and piers are good locations for surface water sampling locations since they provide easy access and permit water sampling across the entire width of the surface water body. The JSA for sampling from bridges must include a traffic management plan to assure the employee has considered using a spotter, signage, cones, and flags to warn car traffic of the work adjacent to the

roadway. Wading for surface water samples increases the chances of disturbance of sediments from the floor of the surface water body.

When wading for surface water samples in lakes, ponds, streams, and slow moving rivers be aware of potential safety and health risks. A life vest and safety line must be worn at all times where footing is unstable or when sampling in fast moving or more than 3 feet (0.9 m) deep. A two-person team is required for most surface water sampling activities, a Project Manager must approve a one person sampling team. If the site conditions require the use of the life vest and safety line, the two people involved in the sampling must be competent swimmers.

Surface water samples must be collected with no suspended sediments. Surface water samples are collected commencing with the furthest downstream location to avoid sediment interference with upstream locations.

7.9.2.1 Rivers, Streams, and Creeks

Surface water samples are generally collected in areas of surface water bodies that are representative of the surface water body conditions. Representative surface water samples will usually be collected in sections of surface water bodies that have a uniform cross section and flow rate. Mixing is influenced by turbulence and water velocity, therefore the selection of surface water sampling locations immediately downstream of a riffle area (i.e., fast flow zone) will ensure good vertical mixing. These locations are also likely areas for deposition of sediment since this occurs in areas of decreased flow velocity.

Surface water sampling locations should not be established in areas near point source discharges including tributaries, industrial effluents, and municipal effluents. Surface water sampling of these source discharge points can be performed to assess the impact of these source areas on overall surface water quality.

Sample tributaries as close to the mouth as possible. It is important to select surface water sample locations considering the impact downstream, including tributary flow and sediment.

In all instances, properly document all surface water sampling locations in a standard GHD field book. Documentation may include photographs and tie-ins to known structures.

7.9.2.2 Lakes, Ponds, and Impoundments

The surface water in lakes, ponds, and impoundments has a greater tendency to be stratified than water in rivers and streams. Lack of mixing in these surface water bodies may require additional surface water sample collection. Extreme turbidity variances may occur where highly turbid surface water courses enter a lake or pond. Therefore, each layer of the stratified surface water column may need to be considered separately. Stratification is generally a result of water temperature differences, with cooler heavier water being trapped below warmer water.

Surface water sample locations for lakes, ponds, and impoundments should adequately represent the conditions of the surface water body. All intakes and outflows that may provide biased surface water representation should be identified and documented. Surface water sample locations with adjacent structures (e.g., banks, piers) may also provide biased samples, as the potential for boundary flow and eddies exists.

The number of surface water sample locations on lakes, ponds, or impoundments will vary depending on the purpose of the investigation, as well as the size and shape of the surface water body. In ponds and small impoundments a single surface water sample should be collected at the deepest point. In naturally formed ponds, the deepest point is usually near the center of the surface water body. In impoundments the point is usually near the dam.

In lakes and larger impoundments, several sub-samples should be taken to form a single composite sample. These vertical surface water sampling locations are collected along a pre-determined grid.

In irregular shaped lakes with several bays and covers that are protected from the wind, additional surface water samples are required to properly represent surface water quality at various locations in the lake. Additional surface water samples should be taken at discharges, tributaries, and other factors or sources that are suspected of affecting the surface water quality.

In all instances, properly document all surface water sampling locations in a standard GHD field book. Documentation may include photographs and tie-ins to known structures.

7.9.3 Sampling Equipment and Techniques

When collecting surface water samples, direct dipping of the sample container into the stream or water is acceptable unless the sample container contains preservatives. If preserved, a pre-cleaned unpreserved sample container should be used to collect the surface water sample. The surface water sample is then transferred to the appropriate preserved sample container. When collecting surface water samples, submerge the inverted bottle to the desired sample depth and tilt the opening of the sample container upstream to fill. During surface water sample collection, wading or movement may cause sediment deposits to be re-suspended and can result in biased samples. Wading is acceptable if the stream has a noticeable current and the samples are collected directly in the sample container when faced upstream. If the stream is too deep to wade in or if additional samples must be collected at various depths, additional sampling equipment will be required. Surface water samples should be collected about 6 inches (15 cm) below the surface, with the sample bottles being completely submerged. Taking the surface water sample at this depth eliminates the collection of floating debris in the sample container.

Surface water sample collection where the flow depth is less than 1 inch (<2.5 cm) requires the use of special equipment to eliminate sediment disturbance. Surface water sampling may be conducted with a container then transferred to the appropriate sample container, or collection may be performed using a peristaltic pump. A small excavation in the stream bed to create a sump for sample collection can also be considered but should be prepared in advance to allow all the sediment to settle prior to surface water sampling activities.

Teflon™ bailers can be used for surface water sampling if it is not necessary to collect surface water samples at specific depths. A bottom loading bailer with a check ball is sufficient. When the bailer is lowered through the water, the water is continually displaced through the bailer until the desired depth is reached. The bailer is retrieved and the check ball prohibits the release of the collected surface water sample. Bailers are not suitable in surface water bodies with strong currents, or where depth-specific sampling is required.

For discrete and specified depth surface water sampling, and the parameters to be monitored do not require a Teflon™ coated sampling device, a standard Kemmerer or Van Dorn sampler can be used. The Kemmerer sampler is a brass cylinder with rubber stoppers that leave the sampler ends open while the sampler is being lowered. The sampler is lowered in a vertical position to allow water to pass through. The Van Dorn sampler is plastic and is lowered in a horizontal position. For both samplers, a messenger is sent down a rope when the sampler has reached the required depth. The messenger causes the stopper on the sampler to close. The sampler is then retrieved and the surface water sample can be collected through a valve. DO sample bottles can be filled by allowing overflow using a rubber tube attached to the valve. During depth-specific surface water sampling, take care not to disturb bottom sediments.

Glass beakers or stainless steel cups may also be used to collect surface water samples if parameter interference does not occur. The beaker or cup must be rinsed at least three times with the surface water sample prior to sample collection.

All equipment must be thoroughly decontaminated as outlined in Section 7.6.

7.9.4 Field Notes for Surface Water Sampling

Use a standard GHD field book to record daily surface sampling activities, describe surface water sampling locations, sampling techniques, and, if applicable, provide a description of photographs taken. Visual observations are important and provide valuable information when interpreting surface water quality results. Observations include:

1. Weather conditions
2. Stream flow directions
3. Stream physical conditions (width, depth, etc.)
4. Tributaries
5. Effluent discharges
6. Impoundments
7. Bridges
8. Railway trestles
9. Oil sheens
10. Odors
11. Buried debris
12. Vegetation
13. Algae
14. Fish and other aquatic life
15. Surrounding industrial areas

The following factors should be considered for surface water sampling:

1. **Predominant Surrounding Land Use:** Observe the prevalent land use type in the vicinity and note any other land uses in the area which, although not dominant, may potentially affect surface water quality.
2. **Local Watershed Erosion:** Note the existing or potential erosion of soil in the local watershed and its movement into the stream. Erosion can be rated through visual observation of watershed stream characteristics including increases or decreases in turbidity.
3. **Local Watershed Non-Point Source Pollution:** This refers to problems or potential problems other than erosion and sedimentation. Nonpoint source pollution can be diffuse agricultural and urban runoff. Other factors may include feed lots, wetlands, septic systems, dams, impoundments, and mine seepage.
4. **Estimated Stream Width:** The estimated distance from shore at a transect representative of the stream width in the area.
5. **Estimated Stream Depth:** Riffle (rocky area), run (steady flow area), and pool (still area). Estimate the vertical distance from the water surface to the bottom of the surface water body at a representative depth at three locations.
6. **High Water Mark:** Estimate the vertical distance from the bank of the surface water body to the peak overflow level, as indicated by debris hanging in bank or flood plain vegetation, and deposition of silt. In instances where bank flow is rare, high water marks may not be evident.
7. **Velocity:** Record or measure the stream velocity in a representative run area.
8. **Dam Present:** Indicate the presence or absence of a dam upstream or downstream of the surface water sampling location. If a dam is present, include specific information detailing the alteration of the surface water flow.
9. **Channelized:** Indicate if the area surrounding the surface water sampling location is channelized.
10. **Canopy Cover:** Note the general proportion of open to shaded areas which best describes the amount of cover at the surface water sampling location.

7.10 Follow-Up Activities

The following should be performed once groundwater, residential, and surface water sampling is completed:

1. Double check the Work Plan and QAPP to ensure all samples and QA/QC samples have been collected and confirm with the Project Coordinator.
2. Decontaminate all equipment at the site then return clean to the appropriate office equipment manager.
3. Dispose of purge water and cleaning fluid as specified in the Work Plan.
4. Notify the contract laboratory when the samples should arrive. Enclose a completed chain-of-custody in each cooler.

5. Complete and file the appropriate forms and data sheets. Also file the field notes. For groundwater, residential, and surface water sampling these forms include:
 - Project Planning, Completion, and Follow-Up Checklist (Form SP-02)
 - Well Development, Purging, and Sampling Form (Form SP-06)
 - Sample Collection Data Sheet - Groundwater Sampling Program (Form SP-08)
 - Monitoring Well Record for Low-Flow Purging (if performed) (Form SP-09)
6. Return site and well keys.

7.11 References

For additional information pertaining to groundwater sampling activities the user of this manual may reference the following:

ASTM D5474	Guide for Selection of Data Elements for Groundwater Investigations
ASTM D4696	Guide for Pore-Liquid Sampling from the Vadose Zone
ASTM D5979	Guide for Conceptualization and Characterization of Groundwater Systems
ASTM D5903	Guide for Planning and Preparing for a Groundwater Sampling Event
ASTM D4448	Standard Guide for Sampling Groundwater Wells
ASTM D6001	Standard Guide for Direct-Push Water Sampling for Geoenvironmental Investigations.

For additional information pertaining to surface water sampling, the user of this manual may reference the following:

ASTM D5358	Practice for Sampling with a Dipper or Pond Sampler
ASTM D4489	Practices for Sampling of Waterborne Oils
ASTM D3325	Practice for the Preservation of Waterborne Oil Samples
ASTM D4841	Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
ASTM D4411	Guide for Sampling Fluvial Sediment in Motion
ASTM D4823	Guide for Core-Sampling Submerged, Unconsolidated Sediments
ASTM D3213	Practice for Handling, Storing, and Preparing Soft Undisturbed Marine Soil
ASTM D3976	Practice for Preparation of Sediment Samples for Chemical Analysis
ASTM E1391	Guide for Collection, Storage, Characterization, and Manipulation of Sediments for Toxicological Testing
ASTM D4581	Guide for Measurement of Morphologic Characteristics of Surface Water Bodies
ASTM D5906	Guide for Measuring Horizontal Positioning During Measurements of Surface Water Depths
ASTM D5073	Practice for Depth Measurement of Surface Water



GHD Field Training Manual

Draft Addendum to Section 7.0 for PFAS Considerations Water Sampling Standard Operating Procedures

(T120)

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Please Adhere to the Following Quality System Training Requirements:

- Employees who are required to conduct a specific field activity must be properly certified to do the work.
- This involves reviewing the SOP and completing the online training course and exam.
- Employees must also conduct this field work under supervised conditions on at least three occasions, and must be certified by a qualified mentor. Only then can an employee conduct a specific field activity on their own. This is documented on a Field Method Training Record (QSF-021).
- Complete the QSF-021 and forward it to trainingrecords-northamerica@ghd.com.



Table of Contents

7.	PFAS Water Sampling Guidelines and Considerations (Groundwater, Residential, and Surface Water)	
	Standard Operating Procedures	1
7.1	Introduction	1
7.2	General Field Procedures	1
7.3	Decontamination Procedures	2
7.4	Sampling Precautions	3
7.5	Equipment/Materials	4
7.6	References.....	6

Quality System Forms Index

QSF-012	Vendor Evaluation Form
QSF-014	Field Equipment Requisition Form
QSF-019	Property Access/Utility Clearance Data Sheet
QSF-021	Field Method Training Record
QSF-030	Safety and Health Schedule (Canada)
QSF-031	Safety and Health Schedule (U.S.)



7. PFAS Water Sampling Guidelines and Considerations (Groundwater, Residential, and Surface Water) Standard Operating Procedures

7.1 Introduction

Sampling for per- and polyfluoroalkyl substances (PFAS) in drinking water, groundwater, and surface water can be a challenge if proper quality assurance and project planning (QAPP) are not developed and followed. The following sections provide guidelines and considerations for successful PFAS sampling events. These guidelines are meant to be used as a general addendum to Section 7.0 in regards to sample collections for laboratory analysis. Due to the changing nature in PFAS regulations and available best practices, this addendum will be updated as more research is performed on sampling materials and techniques.

7.2 General Field Procedures

Field team members must wash their hands with PFAS-free water and Alconox® or Liquinox® prior to handling any sampling equipment or bottles, touching the sampling ports, or putting on nitrile gloves. If liquids or food are consumed during the course of sampling, which is not to occur in the area of sampling activities at the Site, the field team member must wash their hands with PFAS-free water and Alconox® or Liquinox® afterwards, before putting on a new pair of nitrile gloves. It has been noted that Alconox® and/or Liquinox® may cause irritation to the skin. An acceptable alternative for hand washing is Seventh Generation® hand soap.

During sampling, never place caps from sample containers on the ground or in a pocket. The protocol is to hold the sample container in one hand and the sample container cap in the other. It is important to not touch the inside of the sample container cap or the inside of the sample container to any ports or with your hands. New disposable nitrile gloves at each sampling location and following contact with a potential contaminant source. Nitrile gloves must be changed prior to and after collecting samples for volatile organic compounds (VOC) analysis in order to circumvent potential contamination issues due to the Teflon®-lined caps of the VOC vials. Nitrile gloves also need to be worn when labelling bottles and preparing coolers for shipment in order to avoid contact with adhesives that are necessary to perform these procedures, which could lead to contamination of the PFAS samples.

The following represents a general PFAS sampling approach:



1. Sampler must wash hands with certified PFAS free water before wearing initial pair of nitrile gloves to limit contamination during sampling from activities undertaken prior to arrival at the site.
2. Samples for PFAS analysis should be collected in laboratory supplied polypropylene or high-density polyethylene (HDPE) bottles with unlined non-Teflon polypropylene or HDPE screw cap.
3. PFAS samples should be filled to the bottom of the neck of the bottle and not to the very top to ensure that the preservative (Trizma® - for Drinking Water samples only) is not flushed out if the bottle is preserved.
4. After filling and securely capping, the bottles should be inverted at least 5 times to distribute the preservative and must be placed on ice in coolers (samples cannot exceed 10°C).
5. Samples should be placed in zip-lock bags that will be packed in a cooler using regular ice doubled-bagged in zip-lock bags.
6. PFAS Field Blanks should be collected by opening the bottle of PFAS-free water (provided by the lab) and leaving it exposed to air in the vicinity of the sampling port.
7. Following the collection of all PFAS samples, the laboratory provided PFAS-free water will be poured from the container into the preserved bottles from the lab.
8. The now empty Field Blank water bottle used should be returned to the lab with the filled sample containers.

Field quality control samples will be used as a means of assessing quality from the point of sample collection. Such quality control samples will include field reagent blanks, equipment rinse blanks, and sample duplicates. The collection and analysis of QC samples are imperative for PFAS analyses due to low detection limits and widespread commercial use of PFAS containing products. The frequency of quality control sample collection will be defined in the project specific QAPP.

7.3 Decontamination Procedures

Field sampling equipment used at each sample location will require cleaning between uses. The Safety Data Sheets (SDSs) of commonly used detergents or soaps used in decontamination procedures will be reviewed to assure that fluoro-containing chemicals are not in the ingredients list. Laboratory-certified PFAS-free water for the final rinse during decontamination of sampling equipment will be used. Decontaminate larger equipment (for example, drill rigs and large downhole drilling and sampling equipment) with potable water using a high-pressure washer or steam. To the extent practical, rinse parts of equipment coming in direct contact with samples with PFAS-free water. Heavy equipment is best cleaned within a decontamination facility or other means of containment (for example, a bermed, lined pad and sump, or a portable, self-contained decontamination booth). Potable water sources should be analyzed in advance for PFAS. Wherever possible, rinse equipment with PFAS-free water immediately before use.



7.4 Sampling Precautions

Standard sampling procedures can be used at most PFAS sites with exceptions and additional considerations related to the chemical nature PFAS and issues associated with potential use of PFAS-containing or adsorbing sampling equipment and supplies. The following are sampling precautions for various environmental matrices that are defined in the Interstate Technology and Regulatory Council's Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods PFAS fact sheet:

7.4.1 Groundwater

The most inert material (for example, stainless steel, silicone, and HDPE), with respect to known or anticipated contaminants in wells should be used whenever possible. Dedicated sampling equipment installed in existing wells prior to investigation should be thoroughly checked to ensure that the equipment is PFAS-free. For long-term investigations, samples may be collected in duplicate with and without existing dedicated equipment. If PFAS analyses show that the equipment does not affect results, the equipment may be kept and used long term. This determination depends on project-specific requirements, however, and should only be used by a project team with full disclosure to all stakeholders.

7.4.2 Surface water

To avoid cross-contamination from sampling materials to sample media, the outside of all capped sample containers should be rinsed multiple times with the surface water being sampled before filling the containers. When site conditions require, remote sampling into sample containers can be accomplished by clamping the container onto the end of a clean extension rod. The extension rod must be made of PFAS-free material and have been decontaminated. Within the context of sample collection objectives, the sample location in the water column should consider the potential stratification of PFAS in solution and their tendency to accumulate at the air/water interface.

7.4.3 Pore water

Peristaltic pumps with silicone and HDPE tubing are typically used for porewater sample collection, along with push point samplers, porewater observation devices (PODs), or drive point piezometers. Push point samples and drive point piezometers are made of stainless steel, while PODs consist of slotted PVC pipe and silicone tubing. These samplers should be dedicated and not reused across a site or multiple sites.



7.4.4 Pit water (e.g. excavation dewatering pit)

Peristaltic pumps with silicone and HDPE tubing, bailers, and buckets are typically used for pit water sample collection. Tubing and bailers should be dedicated and not reused across a site or multiple sites. Buckets should be purchased new for each sampling event and deconned with Aloconox® or Liquinox® and water, followed by a rinse with certified PFAS free water from the laboratory. Decon should occur immediately prior to collecting the sample of interest.

7.4.5 Influent/Effluent water (e.g. treatment system)

Water treatment system influent/effluent water is typically sampled using small buckets, beakers, or other containers, or collected directly into a laboratory supplied sample container. Sampling supplies should be purchased new for each sampling event and deconned with Aloconox® or Liquinox® and water, followed by a rinse with certified PFAS free water from the laboratory. Decon should occur immediately prior to collecting the sample of interest.

Many gaskets, piping, hosing, pumps, and filters used in water treatment have the potential to contain Teflon or other sources of PFAS; therefore, the influent samples should be taken before they reach gaskets, piping, pumps, or filters in the water treatment assembly. Effluent samples should be taken at the point of discharge from the treatment system (after water is in contact with all gaskets, pumps, filter, etc.). To ensure the collection of a representative sample through treatment, the system should be purged or flushed to limit potential leaching from equipment materials.

7.5 Equipment/Materials

At this point, many materials used during the course of common environmental investigations can potentially contain PFAS. Due to the limited available published literature and/or guidance on which materials affect sampling results, a conservative approach will be used to rigorously exclude materials known to contain PFAS. Safety Data Sheets (SDSs) will be reviewed prior to use during PFAS sampling.

Materials to avoid during sampling events include:

- Teflon, polytetrafluoroethylene (PTFE)
- Waterproof coatings containing PFAS
- Food containers
- Chemicals with “fluoro” on the SDS
- Fluorinated ethylene propylene (FEP)
- Ethylene tetrafluoroethylene (ETFE)
- Low density polyethylene (LDPE), polyvinylidene fluoride (PVDF)

The following represents a list of prohibited items vs. acceptable items for PFAS sampling:

Prohibited Items	Acceptable Items
Field Equipment	



Teflon® containing materials (caps, o-rings, tubing)	High-density polyethylene (HDPE) materials
Low density polyethylene (LDPE) materials	Acetate Liners
	Silicon Tubing
Waterproof field books	Loose paper (non-waterproof)
Plastic clipboards, binders, or spiral hard cover notebooks	Metal field clipboards or with Masonite
Post-It Notes®	Sharpies®, pens
Chemical (blue) ice packs	Regular ice
Field Clothing and PPE	
New cotton clothing or synthetic water resistant, waterproof, or stain-treated clothing, clothing containing Gore-Tex™	Well-laundered clothing made of natural fibers (preferable cotton) washed at least 6 times since purchased
Clothing laundered using fabric softener	No fabric softener
Boots containing Gore-Tex™	Boots made with polyurethane and PVC and leather steel-toe safety boots
Tyvek®	Powder-free nitrile gloves
No cosmetics, moisturizers, hand cream, or other related products as part of personal cleaning/showering routine on the morning of sampling	Sunscreens - Alba Organics Natural Sunscreen, Yes To Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my face, Baby sunscreens that are “free” or “natural” Insect Repellents - Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus Insect repellent, Herbal Armor, California Baby Natural Bug Spray, BabyGanics Sunscreen and insect repellent - Avon Skin So Soft Bug Guard Plus – SPF 30 Lotion
Sample Containers	
LDPE or glass containers	HDPE or polypropylene
Teflon-lined caps	Unlined polypropylene caps
Rain Events	
Waterproof or water-resistant rain gear	Gazebo tent that is only touched or moved prior to and following sampling activities and not touched with sampling gloves
Equipment Decontamination	
Decon 90®	Alconox® and/or Liquinox®
Water from an on-site well or any other potable water supply system	Deionized and deionized demonstrated PFAS-free water from an analytical laboratory or certified vendor
Food Considerations	
All food and drink, with exceptions noted on right	Bottled water and hydration fluids (i.e, Gatorade® and Powerade®) to be brought and consumed only in the staging areas and not touched with sampling gloves



In certain cases, it may be impossible to eliminate materials that affect PFAS results in samples. An example would be specific personal protective equipment (PPE) that are needed at hazardous sites where PFAS are the secondary or co-contaminant and the primary contaminant requires specific materials for proper sampling. In this case, increasing the equipment rinse blank samples will more thoroughly document PFAS concentrations.

7.6 References

For additional information pertaining to PFAS sampling activities the user of this manual may reference the following:

Government of Western Australia Department of Environmental Regulation. 2016. Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS), Contaminated Sites Guidelines. February 2016. Accessed November 22, 2017:

<https://www.der.wa.gov.au/images/documents/your-environment/contaminated-sites/guidelines/Guideline-on-Assessment-and-Management-of-PFAS-.pdf>

Interstate Technology and Regulatory Council. 2018. Site Characterization Considerations, Sampling Precautions, and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS).

Shoemaker, J. A., P. E. Grimmett, and B. K. Boutin. 2009. Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). USEPA Method 537, Rev 1.1, EPA 600-R-08-092, 50 pp.

USDOD EDQW (Environmental Data Quality Workgroup). 2017a. "Department of Defense (DoD) Quality Systems Manual (QSM) for Environmental Laboratories," Version 5.1, 2017. <http://www.denix.osd.mil/edqw/home/>

USDOD EDQW. 2017b. "Bottle Selection and other Sampling Considerations When Sampling for Per- and Poly-Fluoroalkyl Substances (PFASs)," Revision 1.2, July. <http://www.denix.osd.mil/edqw/home/>



GHD Field Training Manual

Section 5.0

Soil Sampling Standard Operating Procedures

Part 1 - Surficial Soil Sampling, Borehole Installation and Sample Collection, and Test Pit Excavation and Sampling
(T102A)

Part 2 - GHD Approach for Soil Materials Description and Classification
(T100)

July 2015



Please adhere to the following Quality System training requirements:

- Employees who are required to conduct a specific field activity must be properly certified to do the work.
- This involves reviewing the SOP and completing the online training course and exam.
- Employees must also conduct this field work under supervised conditions on at least three occasions, and must be certified by a qualified mentor. Only then can an employee conduct a specific field activity on their own. This is documented on a Field Method Training Record (QSF-021).
- Complete the QSF-021 and forward it to trainingrecords-northamerica@ghd.com.
- Please note that four topics are discussed in this SOP. A separate QSF-021 is required for each topic:
 - Surficial Soil Sampling
 - Borehole Installation and Sample Collection
 - Test Pit Excavation and Sampling
 - GHD Approach for Soil Materials Description and Classification



Table of Contents

5.	Soil Sampling Standard Operating Procedures	1
5.1	Introduction	1
5.2	Sampling Methods	2
5.2.1	Surficial Soil Sampling	2
5.2.2	Borehole Installation and Sampling	2
5.2.3	Test Pit Excavation and Sampling	2
5.2.4	Grab Versus Composite Samples	3
5.3	Planning and Preparation	3
5.4	Safety and Health	4
5.5	Quality Assurance/Quality Control	5
5.6	Equipment Decontamination	5
5.7	Procedures for Soil Classification	6
5.7.1	Coarse Grained Soils	9
5.7.2	Fine-Grained Soil	10
5.8	Procedures for Surficial Soil Sampling	13
5.8.1	Background	13
5.8.2	Random, Biased, and Grid-Based Sampling	13
5.8.3	Sample Interval	13
5.8.4	Procedures for Surficial Sampling	14
5.9	Procedures for Borehole Installation and Sampling	17
5.9.1	Location and Marking of Drill Sites/Final Visual Check	17
5.9.2	Sample Collection	18
5.9.2.1	Split-Spoon Samplers	20
5.9.2.2	Shelby Tube Samplers	23
5.9.2.3	Direct-Push Sampling Systems	24
5.9.3	Field Sample Screening	25
5.9.4	Chemical Description	26
5.9.5	Chemical Sample Preparation and Packaging	27
5.9.6	Physical Sample Preparation and Packaging	27
5.9.6.1	Split-Spoon Samples	28
5.9.6.2	Shelby Tube Samples	28
5.9.6.3	Direct-Push Soil Samples	29
5.9.7	Communication of Field Findings	30
5.9.8	Borehole Abandonment	30
5.9.9	Borehole Tie-In/Surveying	30
5.9.10	Field Notes	31
5.10	Procedures for Test Pit Excavation and Sampling	32
5.10.1	Location and Marking of Test Pits/Final Visual Check	32
5.10.2	Test Pit Location Setup	33
5.10.3	Sample Collection	33
5.10.4	Field Sample Screening	35
5.10.5	Sample Description and Logging of Test Pits	35
5.10.6	Chemical Description	36



Table of Contents

5.10.7	Chemical Sample Preparation and Packaging	37
5.10.8	Documentation.....	38
5.10.9	Test Pit Abandonment	38
5.10.10	Restoration	38
5.11	Follow-up Activities	38
5.12	References.....	39

Figure Index

- Figure 3.12 Typical Test Pit Log Entry
- Figure 5.1 Typical Overburden Log
- Figure 5.2 Split-Spoon Sample Selection Details

Forms Index

- SP-02 Project Planning, Completion, and Follow-Up Checklist
- SP-03 Test Pit Stratigraphy Log
- SP-12 Borehole Installation/Soil Sampling Equipment and Supply Checklist
- SP-13 Drilling/Well Construction Checklist
- SP-14 Stratigraphy Log (Overburden)

Quality System Forms Index

- QSF-012 Vendor Evaluation Form
- QSF-014 Field Equipment Requisition Form
- QSF-019 Property Access/Utility Clearance Data Sheet
- QSF-021 Field Method Training Record
- QSF-030 Safety and Health Schedule (Canada)
- QSF-031 Safety and Health Schedule (U.S.)



5. Soil Sampling Standard Operating Procedures

5.1 Introduction

Soil sampling is conducted to characterize the physical and/or chemical conditions at a site. Standard Operating Procedures (SOPs) are presented herein for obtaining a variety of soil samples for physical and chemical analyses, including:

- Surficial soil samples (soil between ground surface and 6 to 12 inches (15 to 30 cm) below ground surface)
- Subsurface samples that require borehole installation
- Test pit excavations

This guideline is not intended to provide the basis for designing a soil sampling program, but instead assumes that a soil sampling program has been designed, a Work Plan has been established, and the sampling team is preparing to mobilize to the field.

Soil sampling procedures vary from project to project due to different parameters of concern, different guidance provided by the state/province where the site is located, or the specific objectives for the project. Therefore, it is essential that the sampling team members carefully review the Work Plan. The primary goal of surface soil sampling is to collect representative samples for examination and chemical analysis (if required).

The remainder of this section is organized as follows:

- Section 5.2 Sampling Methods
- Section 5.3 Planning and Preparation
- Section 5.4 Safety and Health
- Section 5.5 Quality Assurance/Quality Control
- Section 5.6 Equipment Decontamination
- Section 5.7 Procedures for Soil Classification
- Section 5.8 Procedures for Surficial Soil Sampling
- Section 5.9 Procedures for Borehole Installation and Sampling
- Section 5.10 Procedures for Test Pit Excavation and Sampling
- Section 5.11 Follow-up Activities
- Section 5.12 References



5.2 Sampling Methods

5.2.1 Surficial Soil Sampling

Surficial soil sampling is less frequently used than subsurface soil sampling (which involves borehole installation). Typically, surficial soil sampling is used when a large site is being assessed and the extent of contamination is unknown. In this case, surficial sampling is helpful in identifying the location of surface releases (e.g., historical spills of hydrocarbons) that may have contributed to subsurface contamination. A surficial soil sampling program is also recommended for sites with suspected atmospheric deposition of contaminants (e.g., stacks), areas of surface spills, or recent spills.

Surficial soil sampling is used when contamination is known to be restricted to the surficial region of the soil stratum. Thus, surficial sampling can be useful at brownfield sites, where it is necessary to determine if soils are contaminated with specific contaminants of concern (e.g., metals) as part of a purchaser's due diligence. Surficial soil sampling can also be required when obtaining data in order to perform a site-specific risk assessment.

For the purposes of this section, the surficial soil is considered to be the 0- to 6-inch (0 to 15 cm) soil horizon.

Samples are collected from areas where surficial soil contamination is known or suspected. Samples from a particular depth increment must not be mixed with soil from other depths. Soil horizons displaying different properties should be sampled separately, since they may behave very differently with respect to contaminant accumulation and movement.

5.2.2 Borehole Installation and Sampling

A significant portion of GHD's field activities involve borehole installation.

Several manual methods are available for the collection of shallow subsurface soil samples (e.g., hand augers, post-hole augers). However, the most common methods used by GHD to advance boreholes are a drill rig equipped with continuous flight hollow-stem augers (HSAs) and split-spoon samplers, or a direct-push drilling unit equipped with solid tube soil samplers.

5.2.3 Test Pit Excavation and Sampling

Test pits are typically excavated to explore and define geologic conditions (or buried waste/debris) and to allow the collection of subsurface soil samples for geotechnical or chemical analysis. Test pits give a more complete view of the subsurface soil conditions than soil borings. Test pits are excavated using either a rubber-tired backhoe or track-mounted excavator, and can extend 10 to 15 feet (3.0 to 4.6 m) below ground surface.

The use of test pits for investigation is determined on a site-specific basis. Experience from past projects has identified the following issues:

1. The nature and extent of contamination which may be encountered may be unknown. The Site-specific Health and Safety Plan (HASP) and Job Safety Analysis (JSA) must be specific to the level of Personal Protective Equipment (PPE); this may be Level A or B.



2. Waste materials, including drums, may be encountered. A plan must be in place specifying how this material will be handled.
3. Air emissions of some compounds may occur. A plan must be in place to ensure that employees and the public are adequately protected.
4. Community relations concerns may exist (e.g., workers in chemically protective "moon suits"). A notification plan may be required.
5. All underground utilities must be located utilizing documentation using the GHD Subsurface Clearance Protocol.

5.2.4 Grab Versus Composite Samples

A grab sample is collected to identify and quantify compounds at a specific location or interval. The sample is comprised of no more than the minimum amount of soil necessary to make up the volume of sample dictated by the required sample analyses. Composite samples are a mixture of a given number of sub-samples and are collected to characterize the average composition in a given surface area.

Samples to be analyzed for volatile organic compounds (VOCs) are always collected as grab samples. Mixing of soil samples to create a composite is not performed. Mixing of soil samples results in partial volatilization of VOCs from the soil, and thus compromises the integrity of the composite soil sample.

5.3 Planning and Preparation

The following activities are required prior to undertaking a soil sampling program:

1. Review the Work Plan, project documents, and health and safety requirements with the Project Coordinator.
2. Complete a Field Equipment Requisition Form (QSF-014) and assemble all equipment, materials, log books, and forms. Form SP-02 (Project Planning, Completion, and Follow-Up Checklist) should be used for guidance throughout the project. Borehole Installation/Soil Sampling Equipment and Supply Checklist (Form SP-12) provides a summary of the typical equipment/materials required for soil sampling. Drilling/Well Construction Checklist (Form SP-13) provides a listing of pre-planning and site activities that is designed as an aid to preparing and completing the project.
3. Obtain a site plan and any previous stratigraphic logs. Determine the exact number, location, and depths of samples to be collected.
4. Complete a Vendor Evaluation Form (QSF-012) and file in the project file for any vendors that do not have full approval status or are not listed on the Approved Vendor List (QSL-004). Completion of a Safety and Health Schedule (QSF-030 for Canadian work; QSF-031 for U.S. work) is necessary for all vendors who complete field services. Prior to mobilization on site, the vendor must submit the form to the Regional Safety and Health Manager for review and approval (if not already posted on QSL-004).



5. Contact GHD's Chemistry Group to arrange/determine:
 - SSOW (simplified Scope of Work)
 - Glassware/sample jars
 - Cooler
 - Shipping details
 - Start date
 - Laboratory
 - Expected sampling duration
6. Initiate a Property Access/Utility Clearance Data Sheet (QSF-019), if necessary. In most instances, surface sampling activities do not require utility clearances.
7. Determine notification needs with the Project Coordinator. Have the regulatory groups, client, landowner, GHD personnel, and laboratory been informed of the sampling event?
8. Determine the methods for handling and disposal of wash waters and spent decontamination fluids.

In addition to the above, the following may be required when conducting a borehole or test pit program:

1. Establish a water source for drilling and decontamination activities. Pre-plan the methods for handling and disposal of drill cuttings, wash waters, and spent decontamination fluids.
2. Arrange with driller to provide paraffin wax, melting pot, and heat source (if required).

5.4 Safety and Health

GHD is committed to conducting field activities in accordance with sound safety and health practices. GHD adheres to high safety standards to protect the safety and health of all employees, subcontractors, customers, and communities in which they work. The safety and health of our employees takes precedence over cost and schedule implications.

Field personnel are required to implement the Safety Means Awareness Responsibility Teamwork (SMART) program as follows:

- Assure the HASP is specific to the job and approved by a Regional Safety and Health Manager.
- Confirm that all HASP elements have been implemented for the job.
- A JSA for each task has been reviewed, modified for the specific site conditions and communicated to all appropriate site personnel. The JSAs are a component of the HASP.
- Incorporate Stop Work Authority; Stop, Think, Act, Review (STAR) process; Safe Task Evaluation Process (STEP); Observations process; Near Loss and Incident Management process in the day-to-day operations of the job.
- Review and implement applicable sections of the GHD Safety and Health Policy Manual.



- Confirm that all site personnel have the required training and medical surveillance, as defined in the HASP.
- Be prepared for emergency situations, locating safety showers, fire protection equipment, evacuation route, rally point, and first aid equipment before you begin working, and make sure the equipment is in good working order.
- Maintain all required PPE, safety equipment, and instrumentation necessary to perform the work effectively, efficiently, and safely.
- Be prepared to call the GHD Incident Hotline at 1-866-529-4886 for all incidents involving injury/illness, property damage, and vehicle incident and/or significant Near Loss.

It is the responsibility of the Project Manager to:

- Ensure that all GHD field personnel have received the appropriate health and safety and field training and are qualified to complete the work.
- Provide subcontractors with a Job Hazard Analysis to enable them to develop their own HASP.
- Ensure that all subcontractors meet GHD's (and the client's) safety requirements.

5.5 Quality Assurance/Quality Control

A well-designed Quality Assurance/Quality Control (QA/QC) program will:

- Ensure that data of sufficient quality are obtained in order to facilitate good site management.
- Allow for monitoring of staff and contractor performance.
- Verify the quality of the data for the regulatory agency.

The QA/QC program is developed on a site-specific basis. QA/QC requirements are discussed in detail in Section 3.9.

5.6 Equipment Decontamination

Borehole Installation and Sampling

Prior to use and between each borehole location at an environmental site, the drilling and sampling equipment must be decontaminated in accordance with the Work Plan or the methods presented in this section.

The minimum wash procedures for decontamination of drilling or excavating equipment are:

1. High pressure hot water detergent wash (brushing as necessary to remove particulate matter).
2. Potable, hot water, high pressure rinse.

Cover the clean augers with clean plastic sheeting to prevent contact with foreign materials. For geotechnical, geologic, or hydrogeologic studies where contaminants are not present, it is sufficient to clean the drilling or excavating equipment simply by removing the excess soils.



On environmental sites, the soil sampler equipment (split spoons, trowel, spoons, shovels, bowls) are typically cleaned as follows:

1. Wash with clean potable water and laboratory detergent, using a brush as necessary to remove particulates.
2. Rinse with tap water.
3. Rinse with deionized water.
4. Air dry for as long as possible.

In addition, the following steps may be added when sampling for VOCs and metals:

1. Rinse with 10 percent nitric acid (only if samples are to be analyzed for metals).
2. Rinse with deionized water.
3. Rinse with appropriate solvent (pesticide grade isopropanol, methanol, acetone, hexane, if required).
4. Rinse again with deionized water.
5. Air dry for as long as possible.
6. Wrap split-spoon samplers in aluminum foil to prevent contamination.

Caution: Check the Quality Assurance Project Plan (QAPP) to confirm the cleaning protocol.
Use of incorrect cleaning protocol could invalidate chemical data.

5.7 Procedures for Soil Classification

This SOP for Soil Classification is not intended to provide complete training in soil classification. Soil Classification will require additional training and experience.

Criteria and procedures for soil classification and description include:

1. A standard method of describing the soil by name and group symbol.
2. Standard field identification methods based on visual examination and manual tests on representative soil samples by a qualified GHD representative for interpretation of subsurface conditions at the site.
3. Verifying field description descriptions through the inspection.
4. Confirming descriptive information by laboratory determination of selected soil characteristics if required in the Work Plan.
5. Factual overburden stratigraphic logs completed by GHD personnel responsible for interpreting the subsurface conditions at the site and review/confirmation of soil descriptions by the Project Coordinator.

The overburden stratigraphic log is the factual description of the soil at each borehole location and will be relied on to interpret soil characteristics at the site. The overburden stratigraphic log will also be used to interpret the soil characteristics' influence and significance on the subsurface



environment. GHD personnel responsible for interpreting the subsurface conditions at the site will also verify overburden stratigraphic log accuracy. If practical, the Project Coordinator, Geologist, or Geotechnical Engineer should confirm the soil descriptions and examine representative soil samples.

Describing and classifying soils is a skill that is learned through experience and by systematic training using laboratory results of soil composition in comparison to field descriptions.

Note: Attendance at a soil identification course provided by GHD is mandatory.

Descriptions for natural undisturbed soils are recorded on a Stratigraphy Log (Overburden) (Form SP-14). An example of a completed Stratigraphy Log (Overburden) is presented on Figure 5.1.

Soil descriptions are completed in the following order:

1. Unified Soil Classification System (USCS) group symbol(s) (e.g., SM) of primary soil components or dual or borderline symbols.
2. Name and adjective description of primary, secondary, and minor grain size components.
3. Relative density for non-cohesive soils or consistency for cohesive soils.
4. Gradation and soil structure for non-cohesive soils or structure and plasticity for cohesive soils.
5. Color.
6. Moisture content.
7. Other physical observations including presence of staining and or odors.

Note: When describing observed odors, be as specific as possible to classify general odor category and strength of odor. Odors are generally chemical, petroleum, or septic related, varying from slight to moderate to strong. Identification of specific chemical compounds (i.e., benzene, gasoline) is not necessary and is often inaccurate as detailed chemistry commonly shows an array of chemicals present.

When describing vegetative matter presence in soils, do not use the term organic. The use of the term organic often leads to confusion regarding the presence of organic chemicals (i.e., VOCs, semi-volatile organic compounds [SVOCs]). Similarly, as noted above, use more specific terms for odors than organic.

The description of fill soils is similar to those used to describe native undisturbed soils. Fill soils will be identified as fill (i.e., SP/GP-Sand and Gravel [Fill]). To determine if soils are fill, look for evidence that the soil has been artificially placed (e.g., brick fragments, slag, glass, wood fragments). Relative or inconsistent soil density can also assist in determining if soils are fill, along with irregular soil structure.

Soils are identified and grouped consistently to determine subsurface pattern or changes and non-conformities in the soil stratigraphy. The stratigraphy of each soil boring or test pit is compared



to ensure that patterns or changes in soil stratigraphy are noted and that consistent terminology is used.

Visual examination, physical observation, and manual tests (based on ASTM D2488, Standard Practice for Description and Identification of Soils [Visual-Manual Procedure]) are used to aid in classifying and grouping soil samples in the field. These procedures are described in the following subsection. ASTM D2488 should be reviewed for detailed explanations of the procedures. (Note that the related ASTM D2487 Standard Practice for Classification of Soils for Engineering Purposes [Unified Soil Classification System] uses slightly different percentages of soil components.) Visual-manual procedures used to aid in soil identification and classification include:

1. Visual determination of grain size, soil gradation, and percentage of various soil components to the nearest 5 percent (i.e., gravel, sand, silt, and clay).
2. Dry strength, dilatancy, toughness, and plasticity tests (i.e., thread or ribbon test) for identification of inorganic fine-grained soils (e.g., CL or CH [clays], and ML or MH [silts]).
3. Soil compressive strength and consistency estimates based on thumb indent and or pocket penetrometer (preferred) methods.

The three main soil divisions are:

1. Coarse-grained soils (e.g., sand and gravel)
2. Fine-grained soils (e.g., silts and clays)
3. Soils with high natural organic and vegetative matter content (e.g., peat, marl)

These soil divisions are presented in the table of USCS classifications below.

Major Division			Group Symbol	Typical Description
Coarse grained soils more than 50% retained on No. 200 sieve	Gravel more than 50% of coarse fraction retained on No. 4 sieve	clean gravel <5% fines	GW	well graded gravel, gravel-sand mixtures
			GP	poorly graded gravel, gravel-sand mixtures
		gravel with >15% fines	GM	silty gravel, gravel-sand-silt mixtures
			GC	clayey gravel, gravel-sand-clay mixtures
	Sand more than 50% of coarse fraction passes No. 4 sieve	clean sand <5% fines	SW	well graded sand, fine to coarse sand, gravelly sand
			SP	poorly graded sand
		sand with >15% fines	SM	silty sand, sand-silt mixtures
			SC	clayey sand, sand-clay mixtures
Fine grained soils more than 50%		inorganic	ML	Inorganic silt
			CL	Inorganic clay



Major Division			Group Symbol	Typical Description
passes No. 200 sieve	Silt and Clay liquid limit <50, low plasticity	organic	OL	organic silt, organic clay
				silt of high plasticity, elastic silt
	Silt and Clay liquid limit ≥50, high plasticity	inorganic	MH	clay of high plasticity, fat clay
			CH	organic clay, organic silt, low plasticity
		organic	OL	organic clay, organic silt, high plasticity
			OH	
Highly organic soils			Pt	peat

5.7.1 Coarse Grained Soils

The USCS symbols for coarse-grained soil are primarily based on grain size, grain size distribution (gradation), and percent of fines (silt and clay content).

Grain size classification used for describing soils is in terms of particle size and sieve size (e.g., gravelly sand, trace silt). Coarse-grained soil is composed of more than 50 percent by weight, sand size, or larger (75 µm diameter, No. 200 sieve size). Note that there are other definitions for coarse-grained or coarse textured soil and for sand and for sand size as soil having greater than 70 percent particles equal to or greater than 50 µm diameter (after "Guidelines for Contaminated Sites in Ontario") or 60 µm diameter ("Canadian Foundation Manual").

The percentage descriptors for soil components are different for coarse-grained versus fine-grained soils. The following are the percentage component descriptors for coarse-grained soils:

Noun (e.g., sand, gravel)	Major Component
Adjective (e.g., silty, clayey, sandy, gravelly)	Greater than 15%
With (e.g., with silt, with clay, with sand, with gravel)	5% to 15%
Trace (e.g., trace silt, trace clay, trace sand, trace gravel)	<5%

Grain size distribution of coarse-grained soils includes:

- Poorly graded (i.e., soil having a uniform or predominantly one grain size, SP and GP)
- Well graded (i.e., poorly sorted soils with a wide range of particle sizes with substantial percentage of intermediate sizes, SW and GW)
- Dirty (i.e., soil having greater than 15 percent fines, SM, SC, GM, and GC)

Coarse-grained soils are further classified based on the percentage of fine-grained soils (e.g., silts and clays) they contain. Coarse-grained soils containing greater than 15 percent fine-grained soils are described with an adjective (e.g., silty [SM, GM], clayey [SC, GC]). This description is attributed to soil particles that adhere when the soil sample is rubbed between the hands or adhere to the sides of sample jars after shaking, or rolling in the jar. The jar shake test will also result in the segregation of sand and gravel particles and can be used as a visual aid in determining sand and gravel content percentages.



Examples of the group symbol, name, and adjectives used to describe the primary, secondary, and minor components of soil are:

- GW - Sandy Gravel (e.g., 70 percent gravel and 30 percent sand, well graded)
- GW - Sandy Gravel-trace silt (less than 5 percent silt, well graded)
- SP - Sand (a uniform sand, predominantly one sand grain size)
- SM - Silty Sand, with clay (sand with greater than 15 percent silt, and 5 to 15 percent clay)

Relative density is important in establishing the engineering properties and behavior of coarse-grained soils. Relative density of non-cohesive (coarse-grained) soils is determined using the standard penetration test (SPT) blow counts (N-values) in accordance with ASTM D1586. A detailed discussion of the SPT and N values can be found in Section 5.9.2.1.

The SPT provides reliable indications of the relative density of sand and fine gravel. N-values in coarse-grained soil are influenced by a number of factors that result in overestimated relative densities. For example, in coarse-grained gravel, dilatent silty fine sands, sand below the water table and uniform coarse sand, N-values tend to be conservative and under estimate the relative density. The Project Geotechnical Engineer will assess these effects, if required.

Other methods, such as modified SPT and cone penetration tests, are used on occasion to supplement or replace the SPT method for certain site-specific conditions. All modifications to the SPT or substitute methods must be recorded as required to interpret test results and correlate relative density.

5.7.2 Fine-Grained Soil

A fine-grained soil is made up of more than 50 percent silt and clay (i.e., fines greater than 50 percent by weight passing the 75 μm (No. 200) sieve size). Description of visual-manual field methods and criteria to further characterize and group fine-grained soil (e.g., CL, CH, ML, and MH) are discussed in ASTM D2488.

The percentage descriptors for components is different for fine-grained versus coarse-grained soils. The following are the percentage component descriptors for fine-grained soils:

Noun (e.g., silt, clay)	Major Component
Adjective (e.g., sandy, gravelly, silty, clayey)	Greater than 30%
With (e.g., with sand, with gravel, with silt, with clay)	15% to 30%
Few (e.g., few sand, few gravel, few silt, few clay)	5% to 15%
Trace (e.g., trace silt, trace clay, trace sand, trace gravel)	<5%

Further soil characterization tests include dry strength, dilatency, toughness, and plasticity (thread or ribbon test).

Criteria for Describing Dry Strength

Description	Criteria
None	The dry specimen crumbles into powder with mere pressure of handling.
Low	The dry specimen crumbles into powder with some finger pressure.



Description	Criteria
Medium	The dry specimen breaks into pieces or crumbles with considerable finger pressure.
High	The dry specimen crumbles into powder with finger pressure; specimen will break into pieces between thumb and a hard surface.
Very High	The dry specimen cannot be broken between the thumb and a hard surface.

Criteria for Describing Dilatancy

Description	Criteria
None	No visible change in small wetted specimen when rapidly shaken in palm of hand.
Slow	Water appears slowly on the surface of the specimen during shaking and does not disappear or disappears slowly upon squeezing.
Rapid	Water appears quickly on the surface of the specimen during shaking and disappears quickly upon squeezing or stretching.

Criteria for Describing Toughness

Description	Criteria
Low	Only slight pressure is required to roll the thread near the plastic limit; the thread and the lump are weak and soft.
Medium	Medium pressure is required to roll the thread to near the plastic limit; the thread and the lump have medium stiffness.
High	Considerable pressure is required to roll the thread to near the plastic limit; the thread and the lump have very high stiffness.

Criteria for Describing Plasticity

Description	Criteria
Nonplastic	1/8-inch (3 mm) thread cannot be rolled at any water content.
Low	The thread can barely be rolled and the lump cannot be formed when drier than the plastic limit.
Medium	The thread is easy to roll and not much time is required to reach the plastic limit; the thread cannot be re-rolled after reaching the plastic limit; the lump crumbles when drier than the plastic limit.
High	It takes considerable time rolling and kneading to reach the plastic limit; the thread can be re-rolled several times after reaching the plastic limit; the lump can be formed without crumbling when drier than the plastic limit.

Examples of group symbol identification based on visual-manual procedures and criteria for describing fine grained soil are:

Group Symbol	Dry Strength	Dilatancy	Toughness	Plasticity
ML	None to low	Slow to rapid	Low or thread cannot be formed	Slight
CL	Medium to high	None to slow	Medium	Low
MH	Low to medium	None to slow	Low to medium	Low
CH	High to very high	None	High	High



Positive classification by USCS group symbols as described in ASTM D2487, is through laboratory determination of particle size characteristics, liquid limit, and plasticity index. The need for laboratory testing will be determined by the Project Hydrogeologist, Geologist, or Geotechnical Engineer and will be detailed in the Work Plan. If no laboratory testing is performed to confirm soil classification, a statement of qualification (method used) is required for group symbols.

Examples of terminology that accompany the group symbols are:

- ML - Sandy Silt (e.g., 30 percent sand)
- CL - Clay (lean) with sand (e.g., 15 to 29 percent sand)

The USCS group symbols require the use of lean clay (CL) and fat clay (CH). The use of these symbols is dependent on the plasticity of the soil. Classification such as silty clay can only be used for a very narrow set of conditions, and will only be used if Atterberg Limit results are available. The lean and fat clay designations are not universally used, but adherence to the USCS requires that these symbols be used.

Correlation of N-values and consistency for clays is unreliable. Consistency determinations will be performed using more appropriate static test methods, especially for very soft to stiff clays. N-values are more reliable in hard clays.

Estimates of unconfined compressive strength (S_u) can be obtained by a pocket penetrometer test. To estimate consistency and compressive strength with a pocket penetrometer, cut a minimum 4-inch (10 cm) soil core perpendicular to the soil core length. Hold the core with moderate confining pressure so as not to deform the soil core. Slowly insert the pocket penetrometer tip into the perpendicular face of the soil core until the pocket penetrometer indents the soil core to the mark indicated on the piston of the penetrometer. The pocket penetrometer estimate of the soil compressive strength (S_u) is the direct reading of the value mark on the graduated shaft indicated by the shaft ring marker, or by the graduated piston reading at the shaft body. For average estimates, complete this procedure several times on the ends and middle of the soil core. For Shelby tube samples (or thin wall samplers), perform the pocket penetrometer test at several locations on the exposed ends of the sample.

In situ shear vane tests or other test methods provide better compressive strength estimates for very soft to stiff consistency clay soil.

Describing soil consistency is an important component in evaluating the engineering properties and strength characteristics of fine-grained cohesive soil. Consistency terms like soft and hard are based on the unconfined compressive strength (S_u) and shear strength or cohesion (c_u) of the soil.

Patterns of soil gas and groundwater movement in fine-grained soil are influenced by natural soil structure. Soil structure is dependent on the depositional method and to a lesser extent climate. The identification of fill soil is equally important in determining soil characteristics in fine-grained soils.



5.8 Procedures for Surficial Soil Sampling

This section provides a limited discussion on considerations for the design of a soil sampling program in order to provide the sampling team members with a basic understanding of those considerations.

5.8.1 Background

Soil sampling locations are selected in order to obtain representative soils with the minimum number of samples. Prior to conducting an investigation, a site inspection may eliminate many uncertainties with respect to site characteristics and result in a more complete soil sampling study. The site inspection should identify pertinent features (e.g., rock outcrops, drainage patterns, surface runoff, surface cover characteristics (e.g., grass, gravel, concrete), wet areas, and fill areas) and evaluate the relationship between those features and potential sources of contaminants. An understanding of these relationships and conditions is important in developing a sampling plan.

5.8.2 Random, Biased, and Grid-Based Sampling

Unless there is a strong indication of contaminant presence, such as staining, soil sample locations may be randomly selected from several areas within the site, such as near obvious potential sources of current or historic contamination. Potential sources include large transformers, aboveground storage tanks (ASTs), manholes, outdoor storage racks, and drainage swales.

If an area shows evidence of contamination, such as staining or vegetative stress, biased samples are collected from the area to characterize the contamination. Background and control samples are also biased, since they are collected in locations typical of non-site-impacted conditions.

When a soil sampling investigation involves a large area, grid-based soil sampling is performed. There is no single grid size that is appropriate for all sites. Common grid sizes are developed on 50- and 100-foot (15 to 30 m) centers. It is acceptable to integrate several different grid sizes in a single investigation.

For a surficial soil sampling program, it is also important to consider the presence of structures and drainage pathways that might affect contaminant migration. It is sometimes desirable to select sampling locations in low-lying areas which are capable of retaining some surface water flow since these areas could provide samples which are representative of historic site conditions (worst-case scenario if surface water flow is a concern).

5.8.3 Sample Interval

Surficial soil is generally considered to be soil between ground surface and 6 to 12 inches (15 to 30 cm) below ground surface. However, for risk assessment purposes, regulatory authorities often consider soil from ground surface to 2 feet (0.6 m) below ground surface to be surficial soil.

Note: Ontario regulations state that surficial soils are 0 to 6 inches (0 to 15 cm) below ground surface.



The exact interval to be considered as surficial soil is often a matter of discussion with the regulatory authorities that review the Work Plan. The sample interval is important to the sample collection method and to the manner in which the data are ultimately interpreted. Another important factor is the type of soil. If there are different types of soil present at the site, this may have a bearing on the sample interval. For example, it may be important to separately sample a layer of material with high organic carbon content which overlies a layer of fine-grained soil.

5.8.4 Procedures for Surficial Sampling

Soil sampling methods are dependent upon the sample interval of interest, the type of soil material to be sampled, and the requirements for handling the sample after retrieval. The most common method for collection of surficial soil samples is the use of a stainless steel trowel. Soil samples may also be collected with spoons and push tubes. Often a shovel is required to open a trench such that sampling can be conducted. Soil that has come in contact with the shovel cannot be used as sample material.

In all cases, the sampling device must be constructed of an inert material with smooth surfaces which can be easily decontaminated. The decontamination protocol employs a sequence of cleaning agents and water designed to remove surface contaminants (refer to Section 5.6). All sampling equipment is cleaned between sample locations. A typical surficial soil sampling protocol is outlined below:

1. Collect surficial soil samples using a precleaned stainless steel trowel or other appropriate tool. Each sample consists of soil from the surface (or other starting depth) to the depth specified in the Work Plan. Sample in ditches only when there is no water present.
2. Use a new pair of disposable gloves at each sample location.
3. Prior to use, at each sample location, decontaminate all sampling tools as specified in the Work Plan or as described in Section 5.5.
4. Use a precleaned sampling tool to remove the sample from the layer of exposed soil. Place the collected soil directly into a clean, prelabeled sample jar and seal with a Teflon-lined cap. If a sample is to be split for duplicate analyses, first homogenize the soil in a precleaned stainless steel bowl.
5. After collection, place the samples on ice or cooler packs in a laboratory-supplied cooler.

Surficial debris (e.g., grass cover) should be removed from the area where the sample is to be collected using a separate precleaned device.

In the event that soil conditions are not as described in the Work Plan, or if there are unexpected distinct layers of soil present (e.g., a layer of high organic carbon content overlying a layer of fine-grained soil), sampling personnel should immediately report the conditions to the Project Coordinator for direction. Similarly, if a sampling location is in a gravel or paved area, sampling personnel should confirm with the Project Coordinator whether the surface samples are to be collected from the gravel/pavement subbase material or from the first layer of soil beneath these layers.



Also, sampling team members should immediately report any conditions to the Project Coordinator that they believe may have a negative effect on the quality of the results.

It is generally inadvisable to collect samples containing excessive amounts of large particles such as gravel. Gravel presents difficulties for the laboratory in terms of sample preparation and the results may not be truly representative of contaminant concentrations in nearby soil.

All conditions at the time of sample collection are properly documented in a field log book. This includes a thorough description of the sample characteristics including grain size, color, and general appearance; date/time of sampling; and labeling information. The location of the sampling point is described in words, and three measurements are taken from adjacent permanent structures so that, if necessary, the sample location can be readily identified in the field at a future date. It is often advisable to have a licensed land surveyor accurately survey the locations.

Soil samples are homogenized in a stainless steel bowl prior to filling sample containers. This step can be bypassed if only one sample container is required to be filled, as long as the laboratory will homogenize the sample upon receipt. It is important that soil samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample interval. When using a round bowl, mixing is achieved by stirring the material in a circular motion and occasionally turning the material over. Fill the sample container completely, leaving no headspace.

Do not mix soil for samples for VOC analyses as this promotes the partial volatilization of compounds from the soil.

In 1997, EPA adopted new methods for sampling soils for VOC analysis. Method 5035 calls for collecting soil using a coring device (EnCore). For analysis of low level VOCs (typically 1 to 200 $\mu\text{g}/\text{kg}$), soil is sealed in a specially prepared vial with a solution of sodium bisulfate. For higher levels of VOCs, the soil is placed in a vial with a volume of methanol. This method increases the complexity of collecting soils and makes it imperative that the sampler and laboratory work closely together. For some soil sampling programs, multiple EnCores are required for each sample interval. The number of EnCores required per sample interval should be ascertained during the prior planning and preparation stage.

Discrete Grab Sampling Methodology for Surficial Soils

Discrete grab sampling is employed when the sampling location is considered to be a small area (approximately 1 square foot [0.1 square meter]) that has both a consistent soil type and a consistent level of contaminant impact.

When collecting a discrete grab surficial soil sample, use the following procedure:

1. Using the sampling device (e.g., trowel, spoon, Oakfield sampler) scoop soil from the top 2 inches (5 cm) into the sample container. If the sample is being collected for VOC analyses, perform this step as quickly as possible in order to minimize the loss of volatile compounds from the soil.
2. Collect a field screening sample from the same sampling location as the discrete grab sample and at the same time. Scoop soil into a zip-loc bag until it is no more than one quarter full.



3. Do not mix the soil for samples collected for VOC analyses (for sample homogenization purposes) as this will promote the loss of volatile compounds from the soil. The laboratory will obtain a representative sample from the container by using coring techniques before the laboratory analysis is performed.

Composite Sampling Methodology for Surficial Soils

A composite sample can be obtained directly from the soil surface by combining a number of discrete grab samples from a number of sampling locations on the soil surface. For preparation of a meaningful composite sample, the soils from the sub-samples taken from the different sampling locations should have (by visual observation) similar contaminant concentrations.

When collecting a composite surface soil sample, use the following procedure:

1. Choose a number of discrete sampling locations that will give a representative sample of the defined composite area at each sampling location.
2. Using the sampling device (e.g., trowel, spoon), scoop the soil from the top 2 inches (5 cm) into the sample container. As much as practical, try to put approximately the same volume of soil from each sampling location into the container.
3. Move to the next sampling location and repeat steps 1 and 2.
4. Collect a maximum of five surface samples (to avoid the complete dilution of any hot spots).
5. When the last location has been sampled, ensure the sample container is filled with soil, leaving no headspace.
6. Since composite samples are used for semi-volatile organic compounds (SVOCs) and inorganic parameters, minimizing the sample collection time is not as important as when discrete samples for VOC analyses are being collected. However, the preferred practice is that the sampler take no longer than necessary to obtain the sample.
7. Collect a field screening sample from the same sampling location as the composite sample and at the same time. As much as practical, try to put approximately the same volume of soil from each discrete grab sampling location into a zip-loc bag. The zip-loc bag should be no more than one quarter full after all the sub-samples have been added.

Since composite samples are not analyzed for VOCs, there is no reason to avoid mixing the sub-samples from the various sampling locations in the sample container (homogenization). However, since the laboratory will use coring techniques to ensure that a sample is representative of the entire container, there is no need to perform field homogenization of the soil within the sample container.

During the sampling program, the sampling team leader will stay in contact with the GHD chemist assigned to the project such that the GHD chemist can properly inform the contract laboratory of the progress of the work. This includes submitting sample summaries and/or copies of completed chain-of-custody forms to the GHD chemist.



Finally, some GHD QAPPs require a designation of a QA/QC officer for field activities. The sampling team leader may be required to conduct certain field audit activities and, at minimum, should be familiar with and responsible for completion of all QA/QC sample activities.

5.9 Procedures for Borehole Installation and Sampling

Once the prior planning and preparation activities are completed, the drilling program can proceed. The typical series of events that takes place is:

1. Locating and marking boring locations.
2. Initiation of a Property Access/Utility Clearance Data Sheet (QSF-019), including obtaining appropriate signoffs by the client representative and drilling subcontractor representative.
3. Contractor mobilization; equipment and material check.
4. Site selection of decontamination pad and drum staging area (if applicable); final visual examination of proposed drilling area for utility conflicts.
5. Decontamination of sampling and drilling equipment prior to use in accordance with the Work Plan or as described in Section 5.6.
6. Borehole advancement utilizing the approved method as outlined in the Work Plan.
7. Soil sample collection; descriptions of the soil samples in accordance with GHD protocol.
8. Monitoring well installation (if applicable).
9. Sample preparation and packaging.
10. Abandonment of boreholes or installation of monitoring wells.
11. Collection of groundwater samples (if monitoring wells are installed).
12. Surveying of borehole location and elevations.
13. Field note completion and review.

5.9.1 Location and Marking of Drill Sites/Final Visual Check

The proposed borehole locations marked on the site plan are located in the field and staked. On most sites, this will likely be done several days in advance of the drill rig arriving on site. Unless boreholes are to be installed on a fixed grid, the proposed locations are usually strategically placed to assess site conditions.

Note: Any borehole (and all the records thereof) which is completed with casing as a temporary or permanent monitoring well, will be designated by the monitoring well number only (i.e., MW1-yy). Boreholes drilled strictly as soil test borings in which no casing is set (even if an open-hole groundwater sample is collected) will be designated by the boring number only (i.e., BH1-yy).

Once the final location for the proposed boring has been selected and utility clearances are complete, one last visual check of the immediate area should be performed before drilling proceeds. This should confirm the locations of any adjacent utilities (subsurface or overhead) and verification



of adequate clearance. If gravity sewers or conduits exist in the area, any access manholes or chambers should be opened and the conduit/sewer alignments confirmed. Do not enter manholes unless confined space procedures are followed.

If possible, it is prudent to use a hand auger or post-hole digging equipment to a sufficient depth to confirm that there are no buried utilities or pipelines. Alternatively, a Hydrovac truck can vacuum a large diameter hole to check for utilities, although soils collected this way may require containment on site. This procedure generally clears the area to the full diameter of the drilling equipment which will follow.

Caution: Do not assume site plan details regarding pipe alignments/position are correct. Visually check pipe position when drilling near sewers. Personnel should also be alert to additional piping presence if the plans are outdated.

If it is necessary to relocate a proposed borehole due to terrain, utilities, access, etc., the Project Coordinator must be notified and an alternate location will be selected.

5.9.2 Sample Collection

A boring is advanced incrementally to permit intermittent or continuous sampling. Test intervals and locations are normally stipulated by the Project Coordinator or Work Plan. Typically, the depth interval for sampling is 2.5 to 5 feet (0.75 to 1.5 m), or less in homogeneous strata, with at least one test and sampling location at every change of stratum. In some cases samples are taken continuously (i.e., 2-foot (0.6 m) long samples at 2-foot (0.6 m) intervals).

Collected soil samples are described in the field using the USCS (visual-manual procedure). The soil description is recorded on a Stratigraphic Log (Overburden) (Form SP-14) or field book in the following order:

1. USCS Soil Symbol of major component
2. Native or fill
3. Secondary and minor soil components
4. Relative densities/consistency
5. Grain-size/plasticity
6. Gradation/structure
7. Color
8. Moisture content
9. Observations of odor or visual chemical presence (i.e., non-aqueous phase liquid [NAPL])
10. Additional descriptions

For environmental sampling, always change gloves between collecting subsequent soil samples to prevent cross-contamination. Decontaminate all tools (e.g., samplers, spatulas) prior to use on each sample to prevent cross-contamination in accordance with the Work Plan or as described in Section 5.6.



Any drilling procedure that provides a suitably clean and stable hole before insertion of the sampler, and assures that the standard penetration test (SPT) or other sampling technique is performed on essentially undisturbed soil, is acceptable. The drilling method is selected based on the subsurface conditions. Each of the following methods has proven to be acceptable for specific subsurface conditions:

- HSA with inside diameter between 2.5 and 6.25 inches (5.7 to 15.9 cm)
- Solid stem auger (SSA) with auger diameter between 2.5 and 6.25 inches (5.7 to 15.9 cm)
- Direct-push (dual tube systems, discrete soil sample systems)
- Open-hole rotary drilling
- Wash boring

Several drilling methods are not acceptable. These include:

- Jetting through an open tube sampler and then sampling when the desired depth is reached.
- SSA use below the groundwater table in non-cohesive soils.
- Casing driven below the sampling depth prior to sampling.
- Advancing a borehole with bottom discharge bits.
- Advancing a boring for subsequent insertion of the sampler solely by means of previous sampling when performing SPT (the open hole must be larger in diameter than the split-spoon sampler).

Discrete Grab Sampling Methodology for Boreholes

When borehole drilling, the split-spoon sample retrieved from the borehole is considered a discrete grab sample that has been taken from one sampling location, as long as both the stratigraphy of the entire sample and the level of contamination are consistent over the length of the split-spoon sample. If a single split-spoon sample contains soils from two different stratigraphic units, the soils from each of these stratigraphic units are considered separate discrete grab samples.

If a single split-spoon sample contains soils from a single stratigraphic unit, but visual observation indicated that some of the soil was heavily impacted with contaminants, while the rest of the soil was only lightly impacted, then the soils representing each of the two levels of contamination are considered two separate discrete grab samples.

Composite Sampling Methodology for Boreholes

A composite sample is obtained by combining a number of discrete grab samples from the same borehole. For preparation of a meaningful composite sample, the soils from the sub-samples taken from the different split-spoon samples should be from a single stratigraphic unit and have (by visual observation) similar contaminant concentrations (or be physically similar for geotechnical testing purposes).



Use the following methodology for preparing a composite sample from these discrete grab split-spoon samples:

1. Prior to collecting a sample of the soil for field vapor screening or chemical analysis, if smearing of soil is apparent on the outside of the soil core, scrape away the outer layer of the soil using a decontaminated putty knife, stainless steel spoon, or similar implement. This should only be performed if the soil core sample is consolidated. Do not use this procedure for unconsolidated soil samples.
2. Split the sample longitudinally along the length of the split-spoon sampler. Use one half of the core sample to prepare a composite sample to be used in soil headspace vapor screening measurements, and the other half to prepare a composite sample to be submitted to the laboratory for chemical analysis or geotechnical testing.
3. Place sub-samples from various sampling locations (i.e., split-spoon samples) into a zip-loc bag for field screening. As much as practical, attempt to place approximately the same volume of soil from each sampling location into the zip-loc bag.
4. For samples where laboratory analysis is also desired, place sub-samples from various sampling locations into the appropriate soil sample containers. As much as practical, attempt to place approximately the same volume of soil from each sampling location into the sample container.

The following subsections describe specific protocols for split-spoon sampling, Shelby tube sampling, and methods for collecting soil samples using a direct-push rig.

5.9.2.1 Split-Spoon Samplers

This method is used to obtain representative samples of subsurface soil materials and to determine a measure of the in situ relative density of the subsurface soils. The test methods described below must be followed to obtain representative samples.

SPT involves the use of split-barrel samplers (also known as split spoons). Split-spoon sampling is performed in accordance with ASTM D1586. The split-spoon sampler consists of an 18- or 24-inch (45 or 60 cm) long, 2-inch (5 cm) outside diameter tube, which comes apart lengthwise into two halves. An example of a split-spoon sampler is presented on Figure 5.2.

Note: A typical 2-inch (5 cm) outside diameter split-spoon is 1 3/8-inch (3.5 cm) diameter at the drive shoe and 1 1/2-inch (3.8 cm) diameter within the barrel of the split spoon. The volume of the soil in a completely filled 24-inch (61 cm) long split-spoon is approximately 19.8 oz (586 mL), thus the sample volume requirements are important if multiple types of parameters requiring differing analytical techniques are required (i.e., VOCs, SVOCs, metals, petroleum hydrocarbon compounds [PHC]). Soil recovery in a split spoon is often less than 24 inches (61 cm), resulting in less available volume.



Once the borehole is advanced to the target depth and cleared of cuttings, representative soil samples are collected in the following manner:

1. The split-spoon sampler is inspected to ensure it is properly cleaned and decontaminated. The driving shoe (tip) should be relatively sharp and free of severe dents and distortions.
2. The cleaned split-spoon sampler is attached to the drill rods and lowered into the borehole. Do not allow the sampler to drop onto the soil in the bottom of the borehole.
3. After the sampler has been lowered to the bottom of the hole, it is given a single blow to seat it and make sure that it is in undisturbed soil. If there still appears to be excessive cuttings in the bottom of the borehole, remove the sampler from the borehole and remove the cuttings.
4. Mark the drill rods in three or four successive 6-inch (15 cm) increments, depending on sampler length, so that the advance of the sampler under the impact of the hammer can be easily observed for each 6-inch (15 cm) increment.

The sampler is then driven continuously for either 18 or 24 inches (45 or 60 cm) by use of a 140-pound (63.5 kg) hammer. The hammer may be lifted and dropped by either the cathead and rope method, or by using a trip, automatic, or semi-automatic drop system. The hammer should free-fall a distance of 30 inches (± 1 inch) (75 cm, ± 25 mm) per blow. Measure the drop at least daily to ensure that the drop is correct. To ensure a free-falling hammer, no more than 2 1/4 turns of the rope may be wound around the cathead (see ASTM D1586). The number of blows applied in each 6-inch (15 cm) increment is counted until one of the following occurs:

1. A total of 50 blows have been applied during any one of the 6-inch (15 cm) increments described above.
2. A total of 100 blows have been applied.
3. There is no advancement of the sampler during the application of ten successive blows of the hammer (i.e., the spoon is 'bouncing' on a stone or bedrock).
4. The sampler has advanced the complete 18 or 24 inches (45 or 60 cm) without the limiting blow counts occurring as described above.

In some cases where the limiting number of blow counts has been exceeded, GHD may direct the driller to attempt to drive the sampler more if collection of a greater sample length is essential, as long as the sampler is still being advanced.

On the field form, record the number of blows required to drive each 6-inch (15 cm) increment of penetration. The first 6 inches (15 cm) is considered to be a seating drive. The sum of the number of blows required for the second and third 6 inches (15 cm) of penetration is termed the "standard penetration resistance" or the "N-value".



Note: If the borehole has sloughed and there is caved material in the bottom, the split spoon may push through this under its own weight, but now the spoon is partially 'pre-filled'. When the spoon is driven the 18 or 24 inches (45 or 60 cm) representing its supposedly empty length, the spoon fills completely before the end of the drive interval. Three problems arise:

1. The top part of the sample is not representative of the in-place soil at that depth.
2. The SPT value will be artificially higher toward the bottom of the drive interval since the spoon was packed full. These conditions should be noted on the field log.
3. The available sample volume is significantly reduced.

The sampler is then removed from the borehole and unthreaded from the drill rods. The open shoe (cutting end) and head of the sampler are partially unthreaded by the drill crew and the sampler is transferred to the geologist/engineer work surface.

Note: A table made out of two sawhorses and a piece of plywood is appropriate, or a drum, both covered with plastic sheeting.

The open shoe and head are removed by hand by the drill crew or GHD representative, and the sampler is tapped so that the tube separates.

Note: Handle each split spoon with clean disposable gloves if environmental samples are being collected from that split-spoon sample.

Measure and record the length of sample recovered making sure to discount any sloughed material that is present on top of the sample core.

Caution must be used when conducting split-spoon sampling below the groundwater table, particularly in sand or silt. These soils tend to heave or "blow back" into the HSA due to the difference in hydraulic pressures between the inside of the HSA and the undisturbed soil. To equalize the hydraulic pressure, it may be necessary to fill the inside of the HSA with potable water from a reliable and pre-tested source. Drilling mud is uncommonly used and presents problems for sample collection and well development. The water level within the boring or HSA needs to be maintained at or above the in situ groundwater level at all times during drilling, removal of drill rods, and sampling. Since heave or blow back is not always obvious to the driller, it is essential that the water level in the borehole always be maintained at or above the groundwater level. Split-spoon sampling below the water table in sands and silt occasionally results in non-representative samples being collected due to the heaving effect disturbing the soil. This is particularly important if the water level in the hole has not been maintained at the in situ water level.

Heaving conditions and the volume of potable water used should be noted on a Stratigraphic Log (Overburden) (Form SP-14). The volume of water added must be removed during well development prior to groundwater sampling. This practice may not be acceptable if environmental samples are to be collected.

Suspected low N-values should be noted on the field logs. If it is critical to have accurate N-values below the water table, other methods can be employed, such as conducting a dynamic cone



penetration test. This quick and easy test involves attaching a cone shaped tip to the end of the drill rods, and driving the tip into the ground similar to the split-spoon method, except that the borehole is not pre-augered. Cones may be driven 20 to 40 feet (6.1 to 12.2 m) through a formation without augering. Blow counts are recorded for each 1 foot (0.3 m) of advancement. Consult the Project Manager if such conditions are unexpectedly encountered.

Note: A 3-inch (7.5 cm) outside diameter split spoon is available in order to obtain larger sample volumes. However, the SPT values from driving this sampler are typically much higher than those for the 2-inch (5 cm) split spoon.

Larger-Diameter Barrels

A variation of split-barrel sampling involves the use of a longer, larger diameter barrel in conjunction with a HSA. The sampling barrel is installed inside the auger with a swivel attachment to limit rotation of the barrel. After completion of a 5-foot (1.5 m) auger penetration, the auger is left in place and the barrel retrieved from the borehole. This method provides a larger diameter core, which may be desirable for bench-scale testing or where a large volume of soil is required for sample analyses. The sampler should be handled and the sample retrieved in the same way as described above for split-spoon sampling.

5.9.2.2 Shelby Tube Samplers

Thin-walled samplers such as Shelby tubes are used to collect relatively undisturbed samples (as compared to split-spoon samples) of soft to stiff clayey soils. The Shelby tube has an outside diameter of 2 or 3 inches (5 to 7.5 cm) and is 3 feet (0.9 m) long. These undisturbed samples are used for certain laboratory tests of structural properties (consolidation, hydraulic conductivity, shear strength) or other tests that might be influenced by sample disturbance. Procedures for conducting thin-walled tube sampling are provided in ASTM D1587, and are briefly described below:

1. The soil deposit being sampled must be cohesive in nature, and relatively free of gravel and cobble materials, as contact with these materials will damage or collapse the sampler.
2. Clean out the borehole to the sampling elevation using whatever method that will ensure the material to be sampled is not disturbed. If groundwater is encountered, maintain the liquid level in the borehole at or above groundwater level during the sampling operation.
3. Bottom discharge bits are not permitted. Side discharge bits may be used, with caution. Jetting through an open-tube sampler to clean out the borehole to sampling elevation is not permitted.
4. Remove loose material from the center of the casing or HSA as carefully as possible to avoid disturbance of the material to be sampled.
5. Place the sample tube so that its bottom rests on the bottom of the hole. Advance the sampler into the formation without rotation by a continuous and relatively rapid motion. Usually hydraulic pressure is applied to the top of the drill rods.
6. Determine the length of advance by the resistance and condition of the formation, but the length shall never exceed 5 to 10 diameters of the tube in sands and 10 to 15 diameters of the tube in clays.



7. In no case should the length of advance be greater than the sample-tube length minus an allowance for the sampler head and a minimum of 3 inches (7.5 cm) for cuttings.
8. The tube may be rotated to shear the bottom of the sample 2 to 3 minutes after pressing in, and prior to retrieval to ensure the sample does not slide out of the tube. Lift the weight of the rods off of the tube prior to rotating.
9. Withdraw the sampler from the formation as carefully as possible in order to minimize disturbance of the sample.
10. Package and transport the sample in accordance with project-specific requirements.

Occasionally, the Project Manager/Coordinator may require extraction of the sample from the tube in the field. Use the following procedure:

1. A sample extruder, which consists of a clamp arrangement to hold the tube and a hydraulic ram to push the sample through the tube, is usually provided by the driller. To prevent cross-contamination, ensure the extruder is field cleaned between each sample.
2. The sample is then extruded into a carrying tray; these are often made from a piece of 4-inch (10 cm) or 6-inch (12.5 cm) diameter polyvinyl chloride (PVC) pipe cut lengthwise. Ensure the carrying tray is field cleaned between each sample. The sample is carried to the work station for geologic description. Trim the potentially cross-contaminated exterior and place it in the appropriate container.
3. The Shelby tube sampler is then thoroughly field cleaned and decontaminated for reuse. Since they are thin-walled, the tubes are easily damaged, crimped, or otherwise distorted during handling or pushing. The Shelby tube should be inspected before use and, if significantly damaged, rejected.

5.9.2.3 Direct-Push Sampling Systems

Direct-push refers to the sampler being 'pushed' into the soil material without the use of rotation to remove the soil. This method relies on the drill unit static weight combined with rapid hammer percussion for advancement of the tool string. Soil samples are continuously obtained. Groundwater and vapor samples can also be collected utilizing this method and appropriate tooling. Subsurface investigations typically sample to depths of 30 feet (9.1 m) or more; however, depth will vary based on the site-specific geology.

Direct-push methods are widely used for underground storage tank (UST) investigations and property investigations. This method is used extensively for initial site screening activities to establish site geology and to delineate vertical and horizontal plume presence. Small diameter wells (3/4 or 1 inch [2 or 2.5 cm]) diameter can be installed using direct-push methods, often using a pre-packed screen. SPT values cannot be obtained when sampling with a direct-push discrete soil sampler.

This method is also popular due to the limited cuttings produced during the drilling and sampling process and the increased sampling process speed, which can be much quicker than the sample description and sample preparation process. (It is often helpful to have two people, depending on the nature of the work program.)



Continuous soil samples are collected in tube samplers (various lengths), affixed with a cutting shoe and internal liner (PVC, Teflon, or acetate are available). The soil sampler may be operated in open-mode (when borehole collapse is not a concern), or closed-mode (when minimization of sample slough is desired). Closed-mode operation involves the placement of a temporary drill-point in the cutting shoe and driving the assembled sampler to depth. Once at the required depth, the temporary drill-point is released (via internal threading) and the sampler is driven to the desired soil interval. The drill-point slides inside the sample liner, riding above the collected soil column. Once driven to depth, the sampler is retrieved to the ground surface and the sample liner with soil, is removed for examination.

Caution: Be careful when opening interval liners with knives, as severe cuts may result from the knife slipping. A special two-blade hooked knife is available for opening the liners. Generally the driller/helper will open the liner for you.

5.9.3 Field Sample Screening

When soil sampling at sites with known or suspected VOC impact, it is often required to measure the soil for the presence of undifferentiated organic vapors. This field screening can be performed using a photoionization detector (PID). Immediately upon the opening of the split-spoon or discrete soil sampler, the soil is screened with a PID (HNU, Microtip, or equivalent) for the presence of undifferentiated organic vapors. This is accomplished by running the PID along the length of the soil sample. Record the highest reading.

Note: The PID measurement must be taken upwind of the drill rig or any running motors so that exhaust fumes will not affect the measurements.

Another method of field screening is head space measurement. This consists of placing a portion of the soil sample in a sealable glass jar, placing aluminum foil over the jar top, and tightening the lid. The jar is only partially filled. The jar is shaken and set aside for at least 30 minutes. After the sample has equilibrated, the lid of the jar is opened, the foil is punctured with the PID probe, and the air (headspace) above the soil sample is monitored. Record this headspace reading on the field form or in the field book. As an alternative, the soil can be placed in a sealable zip-loc bag.

Note: Perform headspace readings in an area that is not subject to wind. Also, in the winter, it is necessary to allow the samples to equilibrate in a warm area to $\pm 70^{\circ}\text{F}$ (20°C) (e.g., site trailer or van, but not direct heat or sunshine). The portion of the sample used for headspace analysis cannot be used for VOCs analysis.

Representative portions of the soil sample must be retained for geologic record following description. Place the soil portions into labeled, sealable sample containers (usually mason jars or zip-loc bags) without destroying any apparent stratification. If a stratigraphic change is observed within the split-spoon sampler, a separate geologic record sample is kept.

All geologic record samples are to be retained by the client. Geologic record samples must not return to or be placed in storage at a GHD office. An example of a properly completed Stratigraphy Log (Overburden) is presented on Figure 5.2.



5.9.4 Chemical Description

During soil examination and logging, carefully check for the presence of light or dense NAPL. NAPL may be present in gross amounts or present in small/minute quantities. The adjectives and corresponding quantities used when describing NAPL within a soil matrix are as follows:

Visual Description	Fraction of Soil Pore Volume Containing NAPL
Saturated	>0.5
Some	0.5 - 0.25
Trace	<0.25

A complete description of NAPL must describe the following:

- Color
- Quantity
- Density (compared to water) (i.e., light/floats or heavy/sinks)
- Odor (if observed)
- Viscosity (i.e., mobile/flowable, non-mobile/highly viscous-tar like)

The presence of an "iridescent sheen" by itself does not constitute "NAPL presence", but may be an indicator that NAPL is close to the area.

NAPL presence within a soil matrix may be confirmed by placing a small soil sample within water, shaking, and observing for NAPL separation (i.e., light or dense) from the soil matrix.

Trace amounts of NAPL are identified/confirmed by a close visual examination of the soil matrix, (i.e., separate soil by hand, wearing disposable gloves) and performing a careful inspection of the soil separation planes/soil grains for NAPL presence.

Often during sample examination with a knife, an iridescent sheen will be noted on the soil surface (i.e., clay/silts) if the knife has passed through an area of NAPL.

There are a number of more complicated tests available to confirm/identify NAPL presence, these are:

- Ultraviolet (UV) fluorescent analysis
- Hydrophobic dyes (use with care, consult the health and safety SOPs as some hydrophobic dyes are potential human carcinogens)
- Centrifugation
- Chemical analysis

GHD typically utilizes organic vapor detection results, visual examination, soil/water shake testing, and chemical analysis, to confirm NAPL presence. The more complex techniques described may be incorporated on sites where clear colorless NAPL is present and its field identification is critical to the program.



5.9.5 Chemical Sample Preparation and Packaging

Subsurface soil samples are usually grab samples, used to characterize the soil at a specific depth or depth interval (e.g., 2 to 4 feet [0.6 to 1.2 m]). On occasion, composite samples are collected from a borehole over a greater depth interval (e.g., 5 to 15 feet [1.5 to 4.1 m]).

The following describes the collection of grab samples for chemical analysis (all soil from one split spoon). Figure 5.2 shows the split-spoon sample selection details.

Clayey Soils

1. Discard upper and lower ends of sample core (3 inches [7.5 cm]).
2. Use a precleaned stainless steel knife.
3. Cut the remaining core longitudinally.
4. With a sample spoon, remove soil from the center portion of the core and place in a precleaned stainless steel bowl.
5. Remove large stones and natural vegetative debris.
6. Homogenize the soil and place directly into sample jars.

Note: Samples for VOC analysis must not be homogenized. Collect soil from the length of the center portion of the core and place in the sample container. Completely fill the container. No air space (headspace) should remain in the sample container.

Sandy Soils

As sandy soils have less cohesion than clayey soils, it is not easy to cut the core longitudinally to remove the center of the sample. Therefore, with a stainless steel spoon, scrape away surface soils which have likely contacted the sampler and then sample the center portion of the soil core.

Note: Place all soil samples collected for chemical analysis immediately into a cooler with ice.

Record all soil samples in the sample log book. Label samples as specified in Section 3.9.1.2.

In 1997, EPA adopted new methods for sampling soils for VOC analysis. Method 5035 calls for collecting soil using a coring device (EnCore). For analysis of low-level VOCs (typically 1 to 200 $\mu\text{g/kg}$) soil is commonly sealed in a specially prepared vial with a solution of sodium bisulfate. For higher levels of VOCs, the soil is placed in a vial with a volume of methanol. This method increases the complexity of collecting soils and makes it imperative that the sampler and laboratory work closely together. For some soil sampling programs, multiple EnCores are required for each sample interval. Holding times for samples in EnCores may be 24 to 48 hours if not field preserved; therefore, the GHD sampler, laboratory, and GHD chemist should discuss sampling and shipping procedures prior to beginning the work program.

5.9.6 Physical Sample Preparation and Packaging

When a sample is collected for geotechnical or hydrogeologic properties, the sample needs to be prepared and packaged in a manner to maintain its physical properties. Soil samples are usually



grab samples, collected from a specific depth or depth interval (e.g., 2 to 4 feet [0.6 to 1.2 m]). On occasion, composite samples are collected from the borehole over a greater depth interval (e.g., 5 to 15 feet [1.5 to 4.6 m]).

The following describes the collection of grab samples for geotechnical or hydrogeologic purposes for common samplers, the split-spoon, thin-wall, and direct-push discrete soil sampler. For soil samples collected for geotechnical purposes, the samples must not be allowed to freeze.

5.9.6.1 Split-Spoon Samples

1. Following completion of PID screening of the split spoon, remove and dispose of soil at the top of the sample that is obviously sloughed material not representative of the soil at the sampled depth.
2. Measure the length of the sample and record as the recovered length.
3. If cohesive, perform a pocket penetrometer reading and describe the soil.
4. Carefully transfer the sample onto a sheet of aluminum or tin foil, taking care to maintain structure and bedding of the soil sample as much as possible. This may not be possible with non-cohesive soils with low silt or clay contents. The sample may need to be packaged in three 6- to 8-inch (15 to 20 cm) segments.
5. Roll the sample in the tin foil and fold over the ends to seal. Wrap in a second layer of tin foil.
6. Identify the top, middle, and bottom segments with a T, M, and B using an indelible marker.
7. For each segment record the "up" direction with an arrow.
8. Place the foil wrapped sample in a plastic bag and write the sample identification on the bag using an indelible marker. Storing the sample in foil, as opposed to a jar, has the advantage of retaining the soil's in-place structure and preventing loss of moisture.
9. If the soils are sandy and it is not possible to retain the soils structure by rolling it in tin foil, packaging the sample in a jar or zip-loc bag is also acceptable, provided the jar or zip-loc bag is filled to eliminate air space which could result in the soil sample drying out.

A split-barrel sample is approximately 4 inches (10 cm) in diameter and requires different handling than a split-spoon or Shelby tube sample. For a cohesive core sample, the section of drill core is wrapped in several layers of cheesecloth, coated with paraffin wax, and the process repeated until the entire sample is sealed adequately. These samples are usually utilized for specific bench-scale tests.

5.9.6.2 Shelby Tube Samples

1. Remove any sloughed material from the top of the sample using a knife or similar long bladed instrument. If it is not possible to distinguish sloughed soil from intact soil, do not remove.
2. Following removal of sloughed material, measure the tube length and the air space in the tube above the sample and record the difference as the sample recovery. In the unusual circumstance that there is also air space at the bottom of the sample, subtract this as well and record this latter measurement as a separate entry.



3. Seal the top and bottom of the sample with wax (wax is normally provided and prepared by the driller) and first pour the liquefied wax into the top of the sample to a thickness of about 1 inch (2.5 cm). Once this is cooled, remove approximately 1/2 inch (1.3 cm) of soil from bottom of sample (unless there is already a cavity at bottom of sample) and seal similarly.
4. Fill the remaining air space above the sample with loose soil to prevent the sample from shifting in the tube, and then cap both ends of the sample with plastic caps. Tape the caps on using duct tape.
5. Write the sample identification number on the cap using an indelible marker.

Shelby tubes containing soft clays and wet silts need to be handled with care to avoid damage to the sample. Keep samples in an upright position at all times and transport either in a specifically designed cushioned box or position in your vehicle with cushioning under and around the individual tubes. Do not allow geotechnical soil samples to freeze.

5.9.6.3 Direct-Push Soil Samples

1. Once removed to the ground surface, open the discrete soil sampler by removing the cutting shoe, and extract the soil liner (with recovered soil) from the sampler body.
2. Place the soil liner into a holder and cut lengthwise (using a liner knife) to expose the collected soil core.
3. Perform PID screening for organic vapors and record readings.
4. Measure length of sample and record as the recovered length.
5. If cohesive, perform pocket penetrometer reading and describe soil.
6. Carefully transfer the sample onto a sheet of aluminum or tin foil taking care to maintain structure and bedding of the soil sample as much as possible. This may not be possible with non-cohesive soils with low silt or clay contents. The sample may need to be packaged in multiple 6- to 8-inch (15 to 20 cm) segments.
7. Roll the sample in the tin foil and fold over the ends to seal. Wrap in a second layer of tin foil.
8. Identify the depth interval of each segment using an indelible marker.
9. For each segment record the "up" direction with an arrow.
10. Place the foil-wrapped sample in a plastic bag and write the sample identification on the bag using an indelible marker. Storing the sample in foil, as opposed to a jar, has the advantage of retaining the soil's in-place structure and preventing loss of moisture. If the soils are sandy and it is not possible to retain the soils structure by rolling it in tin foil, packaging the sample in one or more jars or zip-loc bags is also acceptable, provided each jar or bag is filled to eliminate air space which could result in the soil sample drying out.

The soil core is split lengthwise to allow inspection. Chemical samples can be removed from the soil core (if required), or soil record samples can be retained (if a component of the project scope). Soil record samples are often retained to allow sample collection for analysis later (depending upon analyte sensitivity/holding times), or for later inspection/geotechnical testing if required.



5.9.7 Communication of Field Findings

Field findings should be communicated frequently with the office technical staff responsible for the program. This communication allows the office staff to: confirm that the investigation meets the intent of the Work Plan; alter procedures and sampling protocol if soil conditions are markedly different from those assumed; and assist in determining screening intervals for piezometers or monitoring wells.

Call office staff no later than the completion of the first borehole, and sooner if possible. Be prepared to discuss the results by faxing the field logs beforehand (wherever possible) and by having a copy of the field log in hand when on the telephone. Call after each borehole and call before leaving the site.

5.9.8 Borehole Abandonment

Following completion of the borehole it must be properly abandoned in accordance with the project documents. Some jurisdictions have requirements or standards of practice that require filling the borehole with bentonite or cement grout.

Note: The integrity of any underlying confining layer must be restored to prevent chemical cross-contamination or hydraulic cross-connection. This is true for all sites, regardless of the known presence or absence of contaminants. This normally requires grouting of the borehole within the zone of the confining layer.

Whenever possible, the cuttings are returned to the borehole to within 1 foot (0.3 m) of the ground surface. The remainder of the borehole is topped off with material consistent with the surrounding ground surface. Excess cuttings are usually collected in drums or a lugger box or spread on the surrounding ground surface consistent with the protocols specified in the Work Plan and as required by federal, state, provincial, and local regulations.

Check with the Project Coordinator to determine the method for handling drill cuttings.

Note: Always include the method of abandonment in the field log book or on a Stratigraphic Log (Overburden) (Form SP-14)

5.9.9 Borehole Tie-In/Surveying

Recording the locations of boreholes on the site plan is extremely important, and may be accomplished by manual measurement (i.e., swing ties) and surveying. Manual measurements for each borehole must be tied into three permanent features (e.g., buildings, utility poles, hydrants). Include diagrams with measurements in the field book.

In addition to manual measurements, surveying with respect to a geodetic benchmark and a site coordinate system is often completed at larger sites for horizontal and vertical control.



Note: Manual field measurements are always necessary regardless of whether a survey is completed.

Manual measurements in field notes allow future identification of the sample/drill site without the need for a survey crew to locate positions using a grid system. This becomes important when trying to locate flushmount wells buried by snow or soils.

5.9.10 Field Notes

Field notes must document all the events, equipment used, calibration activities, and measurements collected during the sampling activities. The field notes must be legible and concise such that the entire borehole installation and soil sampling event can be reconstructed for future reference.

Field notes documenting events, equipment used, and related items are typically recorded in a standard GHD field book, while soil descriptions and PID readings are recorded on a Stratigraphic Log (Overburden) (Form SP-14). Standard GHD field books are available from all GHD equipment administrators. Form SP-14 is available as a printable linked document in this file or as a bound pad from each office.

Note: Use a Stratigraphic Log (Overburden) for recording all soil descriptions and related notes unless otherwise approved by the Project Coordinator/Manager.

Field book/form entries are made in black ink and any changes/corrections are stroked out with a single line, initialed, and dated to indicate when and by whom the correction was made.

The field notes should document the following for each borehole completed:

1. Identification of borehole
2. Depth
3. Static water level depth and measurement technique
4. Time started and completed
5. Measured field parameters
6. Sample appearance
7. Sample odors (if respiratory protection is not required)
8. Types of sample containers and sample identification numbers
9. Parameters requested for analysis
10. Field analysis data and method(s)
11. Sample distribution and transporter
12. Laboratory shipped to
13. Chain-of-custody number for shipment to laboratory
14. Field observations on sampling event
15. Name of collector(s)



16. Climatic conditions including air temperature
17. Problems encountered and any deviations made from the established sampling protocol

5.10 Procedures for Test Pit Excavation and Sampling

Once the prior planning and preparation activities are completed, the test pit excavation and subsurface soil sampling program can proceed. The typical series of events which takes place is:

1. Location and marking of test pit locations
2. Final visual examination of proposed excavation area for utility conflicts
3. Excavation of test pits and collection of the soil samples
4. Field screening of soil sample with specific air monitoring equipment (e.g., PID, LEL meter)
5. Description of soil sample and test pit
6. Completion of Test Pit Stratigraphy Log (Form SP-03)
7. Documentation, including photographs and/or videotape, as required
8. Chemical sample preparation and packaging
9. Backfilling of test pit excavation
10. Surveying of test pit locations
11. Field note completion and review.

5.10.1 Location and Marking of Test Pits/Final Visual Check

Proposed test pit locations marked on the site plan are located in the field and staked. The proposed test pit locations are usually strategically placed to assess site conditions, former facilities, waste areas, etc.

Once the final location for the proposed test pit has been selected and utility clearances are complete, one last check of the immediate area is performed before excavation proceeds to confirm the locations of any adjacent utilities (subsurface or overhead) and verify adequate clearance. If gravity sewers or conduits exist in the area, any access manholes or chambers are opened and the conduit/sewer alignments confirmed.

Caution: Do not assume site plan details regarding pipe alignments/position are correct. Visually check pipe position when excavating near sewers. Personnel should also be alert to the presence of additional piping, especially if the plans are outdated.

If it is necessary to relocate a proposed test pit due to terrain, utilities, access etc., the Project Coordinator must be notified and an alternate location will be selected.



5.10.2 Test Pit Location Setup

The test pit location is set up as follows:

1. The excavator is positioned such that the excavation spoils are deposited by the excavator downwind of all staff.
2. A sheet of polyethylene is placed downwind of the test pit location to accept spoils, if required by the Work Plan.
3. To the extent practicable, the investigation area is set up such that water or liquids that may be excavated, freely drain back into the excavation.
4. The excavation begins at one location with the excavator backing up (as required) to extend the pit.

5.10.3 Sample Collection

Soil samples can be collected from the backhoe/excavator bucket or from the test pit excavation face. Samples which require a discrete depth interval are collected from the excavator bucket following excavation of all or a portion of the test pit. Samples are collected using a cleaned steel trowel, shovel, or stainless steel spoon. Samples are placed in a stainless steel bowl and mixed (except VOCs). **Do not enter the test pit.** (Confined Space Entry requirements apply and proper shoring of the excavation walls may be necessary.)

Caution: Personnel observing or sampling test pit operations must never stand within the "turning radius" or "reach-zone" of the excavation equipment. Operator error or equipment failure could result in severe injury or death if struck by the backhoe bucket or the backhoe itself. Stand opposite the backhoe well beyond the far end of the trench for communication. Personnel should also be alert to test pit side wall conditions which typically undermine the ground surface and create unstable soils surrounding the test pit area.

Discrete Grab Sampling From Test Pits

When taking discrete grab samples from a test pit using an excavator bucket, the sampling location is considered a volume of soil in the bucket that has both a consistent soil type and a consistent level of contaminant impact. When sampling using an excavator bucket, the operator will dig to the desired depth and then provide a small volume of soil from a discrete position and depth in the test pit.

When collecting a discrete grab sample from the excavator bucket, use the following procedure:

1. Scrape off the top 2 inches (5 cm) of soil at the sampling location in the excavator bucket.
2. Using the sampling device (e.g., trowel, spoon) scoop the freshly exposed soil into the sample container. Ensure that the samples taken were not in contact with the excavator bucket to avoid the potential for cross-contamination.



3. Pushing the sample container into the soil in order to fill the container is not recommended. This could result in breaking the sample container and potential injury to field personnel (e.g., cutting hands on broken glass).
4. If the sample is being collected for VOC analyses, perform this step as quickly as possible in order to minimize the loss of volatile compounds from the soil.
5. Collect a field screening sample from the same sampling location as the discrete grab sample and at the same time. Scoop soil into a zip-loc bag until it is no more than one quarter full.
6. Do not mix the soil for samples collected for VOC analyses (for sample homogenization purposes) as this will promote the loss of volatile compounds from the soil. The laboratory will obtain a representative sample from the container by using coring techniques before the laboratory analysis is performed.

Composite Sampling

A composite sample can be obtained by combining a number of discrete grab samples from a test pit sampling location (i.e., excavator bucket). For preparation of a meaningful composite sample, the soils from the sub-samples taken from the different sampling locations should be from a single stratigraphic unit and have (by visual observation) similar contaminant concentrations.

When taking composite samples from multiple excavator buckets, consider each excavator bucket of soil to be a sampling location. When taking a composite sample using the excavator, use the following procedure:

1. Pick a number of discrete sampling locations that will give a representative sample of the horizon of interest in the test pit.
2. From each of these sampling locations, obtain a soil sample from the excavator bucket using the same methodology described in the previous subsection for a discrete grab sample.
3. The sample container should be partially filled with soil from each discrete grab sampling location. As much as practical, try to put approximately the same volume of soil from each sampling location into the container.
4. Move to the next sampling location and obtain another discrete grab soil sample.
5. Collect a maximum of five surface samples (to avoid the complete dilution of any hot spots).
6. When the last location has been sampled, ensure the sample container is filled with soil, leaving no headspace.
7. Since composite samples are used for SVOCs and inorganic parameters, minimizing the sample collection time is not as important as when discrete samples for VOC analyses are being collected. However, the preferred practice is that the sampler take no longer than necessary to obtain the sample.
8. Collect a field screening sample from the same sampling location as the composite sample and at the same time. As much as practical, try to put approximately the same volume of soil from each discrete grab sampling location into a zip-loc bag. The zip-loc bag should be no more than one quarter full after all the sub-samples have been added.



5.10.4 Field Sample Screening

Upon collection of a soil sample, the soil is screened with a PID (HNu, Microtip, or equivalent) for the presence of undifferentiated organic vapors. This is accomplished by running the PID across the soil sample. Record the highest reading and sustained readings.

Note: The PID measurement must be taken upwind of the excavating equipment or running motors so that exhaust fumes will not affect the measurements.

Another method of field screening is head space measurement. This consists of placing a portion of the soil sample in a sealable glass jar, placing aluminum foil over the jar top, and tightening the lid. The jar should only be partially filled. Shake the jar and set aside for at least 30 minutes. After the sample has equilibrated, open the lid of the jar, puncture the foil with the PID probe, and monitor the air (headspace) above the soil sample. Record this headspace reading on a Test Pit Stratigraphy Log (Form SP-03) or in the field book.

Note: Perform all headspace readings in an area that is not subject to wind.
Also, in winter it is necessary to allow the samples to equilibrate in a warm area (e.g., site trailer or van). This requirement is usually dictated by the Work Plan.

5.10.5 Sample Description and Logging of Test Pits

During the excavation of a test pit, samples may be collected to provide a geologic record, to assist the geologist/engineer in completing or characterizing the stratigraphic units, and to allow for physical or chemical testing.

Soil samples collected are described in the field using the USCS. The soil descriptions are recorded on the field form or field book in the following order:

1. USCS Soil Symbol of major component
2. Native or fill
3. Secondary and minor soil components
4. Relative densities/consistency
5. Grain size/plasticity
6. Gradation/structure
7. Color
8. Moisture content
9. Observations of odor or visual chemical presence (i.e., NAPL)

In addition to describing the soil properties, enter the following information into a Test Pit Stratigraphy Log (Form SP-03):

1. Presence of groundwater and the rate of seepage (if groundwater is encountered).
2. Thickness of each stratigraphic unit.



3. Description of bedding plane features (e.g., continuous, discontinuous, graded, wavy bedding).
4. Description of joints, fractures and faults, if bedrock is encountered (number and orientation).
5. Any appearance of weathering.
6. Description of fill and waste materials.

Note: When describing observed odors, be specific in terms of general odor category and strength of odor noted. Odors may typically be chemical, petroleum, or septic related, varying from slight, to moderate, to strong. Identification of specific chemical compounds (i.e., TCE or C-56 odor) is usually unnecessary and often inaccurate as a detailed analysis commonly shows an array of chemistry present.

When describing the presence of vegetative matter in the soil sample, do not use the term "organic" as this often leads to confusion with regards to the presence of organic chemicals (i.e., NAPL).

When describing the soil samples and the stratigraphy observed in the test pit, it is imperative that the sampler use consistent terms from one test pit to the next. As test pits are installed, compare the stratigraphy of completed test pits to the stratigraphy of the test pit you are currently excavating. Be aware of patterns and confirm all inconsistencies at the time the test pit is being excavated. Since soil stratigraphy is so important to understanding site conditions, soil samples are collected from each stratigraphic unit, and described in full.

5.10.6 Chemical Description

Representative portions of the soil sample should be retained as a geologic record along with a description. Place the soil portions into labeled, sealable, sample containers (usually mason jars) without destroying any apparent stratification.

All geologic record samples are to be retained by the client. Geologic record samples must not return to or be placed in storage at a GHD office.

An example of a properly completed Test Pit Stratigraphy Log is presented on Figure 3.12 and described in Section 3.4.1.5.

During soil examination and logging, carefully check for the presence of light or dense NAPL. NAPL may be present in gross amounts or present in small/minute quantities. The adjectives and corresponding quantities used when describing NAPL within a soil matrix are as follows:

Visual Description	Fraction of Soil Pore Volume Containing NAPL
Saturated	>0.5
Some	0.5 - 0.25
Trace	<0.25

A complete description of NAPL includes the following:

- Color
- Quantity



- Density (compared to water) (i.e., light/floats or heavy/sinks)
- Odor (if observed)
- Viscosity (i.e., mobile/flowable, non-mobile/highly viscous-tar like)

The presence of an iridescent sheen by itself does not constitute NAPL presence, but may be an indicator that NAPL is close to the area.

NAPL presence within a soil matrix may be confirmed by placing a small soil sample within water, shaking, and observing for NAPL separation (i.e., light or dense) from the soil matrix.

Trace amounts of NAPL are identified/confirmed by a close visual examination of the soil matrix, (i.e., separate soil by hand [wearing disposable gloves]) and perform a careful inspection of the soil separation planes/soil grains for NAPL presence.

Often during the sample examination with a knife, an iridescent sheen will be noted on the soil surface (i.e., clay/silts) if the knife has passed through an area of NAPL.

There are a number of more complicated tests available to confirm/identify NAPL presence, these are:

- UV fluorescent analysis
- Hydrophobic dyes
- Centrifugation
- Chemical analysis

GHD typically utilizes organic vapor detection results, visual examination, soil/water shake testing, and chemical analysis, to confirm NAPL presence. The more complex techniques described may be incorporated on sites where clear colorless NAPL is present and its field identification is critical to the program.

5.10.7 Chemical Sample Preparation and Packaging

Subsurface soil samples are usually grab samples, used to characterize the soil at a specific depth or depth interval (e.g., 2 to 4 feet [0.6 to 1.2 m]). On occasion, composite samples are collected from a test pit over a greater depth interval (e.g., 5 to 15 feet [1.5 to 4.6 m]).

The following describes the collection of grab samples for chemical analysis.

Clayey Soils

Scrape away the surface soils and collect the sample. Remove large stones and natural vegetative debris and homogenize the soil and place it directly into the sample jars.

Note: Samples for VOC analysis must not be homogenized. Remove the outer layer of soil from the excavation face then collect the sample and place it in the sample container. Completely fill the container. No air space (headspace) should remain.



Sandy Soils

As sandy soils have less cohesion than clayey soils, with a stainless steel spoon or other device scrape away surface soils which have likely contacted the backhoe/excavator bucket, then collect the sample.

Note: All soil samples collected for chemical analysis must be placed immediately into a cooler with ice.

Record all soil samples recorded in the sample log book as described in Section 3.4.1. Labeling of samples shall be consistent with Section 3.9.1.2.

5.10.8 Documentation

In addition to completing all field logs and books, it will generally be necessary for test pits to be documented with photographs and/or video tape. This requirement should be fully ascertained and coordinated in advance of field activities.

5.10.9 Test Pit Abandonment

Following completion of the test pit, backfill the excavation using the soil excavated from the pit. To the extent practicable, replace materials in the test pit in the same intervals from which they were extracted.

It should be noted that the material will tend to "bulk" after excavation. As a result, the excavator operator must be informed to compact the materials as they are replaced within the excavation.

5.10.10 Restoration

The test pit location must be fully restored. Ensure that restoration activities are properly designed and incorporated within the scope of services for the test pit contractor.

Restoration could include:

- Landscaping
- Paving
- Concrete

5.11 Follow-up Activities

Complete the following activities at the conclusion of the field work:

1. Double check the Work Plan to ensure all samples have been collected and confirm this with the Project Coordinator.
2. Ensure that all sample locations are surveyed such that the sample location could be readily re-established.



3. Clean equipment and return to the equipment administrator with the appropriate form dated and signed. Complete water disposal (if required), and cleaning fluid disposal requirements as specified in the Work Plan.
4. Notify the contract laboratory as to when to expect the samples. Enclose the chain-of-custody and covering letter, indicating the parameters and number of samples, in the sample cooler. Ensure that the GHD chemist has all relevant information required to track the progress of the sample analysis.
5. Submit a memo to the Project Coordinator indicating sampling procedures and observations (such as surface staining), grid layout, and all QA/QC documentation.
6. Prepare and distribute a Project Planning, Completion, and Follow-Up Checklist (Form SP-02).

5.12 References

For additional information pertaining to this topic, the user of this manual may reference the following:

Surficial Soil Sampling

ASTM D4547	Practice for Sampling Waste and Soils for Volatile Organics
ASTM D6044	Guide for Representative Sampling for Management of Waste and Contaminated Media
ASTM D6051	Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities

Subsurface Soil Sampling

ASTM D420	Guide for Site Characterization for Engineering, Design, and Construction Purposes
ASTM PS 89	Guide for Expedited Site Characterization of Hazardous Waste Contaminated Sites
ASTM D5434	Guide for Field Logging of Subsurface Explorations of Soil and Rock
ASTM D2487	Classification of Soils for Engineering Purposes (Unified Soil Classification System)
ASTM D2488	Practice for Description and Identification of Soils (Visual-Manual Procedure)
ASTM D5781	Guide for Use of Dual-Wall Reverse-Circulation Drilling for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices
ASTM D5782	Guide for Use of Direct Air-Rotary Drilling for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices
ASTM D5783	Guide for Use of Direct Rotary Drilling with Water-Based Drilling Fluid for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices



ASTM D5784	Guide for Use of Hollow-Stem Augers for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices
ASTM D5872	Guide for Use of Casing Advancement Drilling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
ASTM D5875	Guide for Use of Cable-Tool Drilling and Sampling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
ASTM D5876	Guide for Use of Direct Rotary Wireline Casing Advancement Drilling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
ASTM D4700	Guide for Soil Sampling from the Vadose Zone
ASTM D1586	Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils
ASTM D1587	Practice for Thin-Walled Tube Geotechnical Sampling of Soils
ASTM D4220	Practices for Preserving and Transporting Soil Samples
ASTM D6001	Guide for Direct-Push Water Sampling for Geoenvironmental Investigations

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 °C and at 130 °C before use?	
		Is anhydrous sodium sulfate used, which is dried at 400 °C for 4 hours and stored at 130 °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. 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 to 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 <u>very</u> 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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