

Mr. Peter Ramanauskas
U.S. Environmental Protection Agency Region 5
77 West Jackson Boulevard LU-9J
Chicago, Illinois 60604-3590

Arcadis of Michigan, LLC
28550 Cabot Drive
Suite 500
Novi
Michigan 48377
Phone: 248 994 2240
www.arcadis.com

Date: Original Submittal: September 26, 2023
Revised Submittal: November 28, 2023
Our Ref: 30167840
Subject: Pontiac North Campus – Supplemental RCRA Facility Investigation
Scope of Work
RACER Pontiac North Campus, Pontiac, Michigan

Dear Mr. Ramanauskas,

This scope of work (Scope) describes the methods and approach for an investigation to address current data gaps at several areas of interest (AOIs) located at the Revitalizing Auto Communities Environmental Response Trust (RACER) Pontiac North Campus properties (Site) located in Pontiac, Michigan (**Figure 1**). This Scope was prepared in response to soil impacts in excess of Michigan Department of Environment, Great Lakes, and Energy (EGLE) Site-Specific Volatilization to Indoor Air Criteria (SSVIAC), Volatilization to Indoor Air Pathway screening levels (VIAP), Direct Contact (DC) Criteria, and United States Environmental Protection Agency (USEPA) Toxic Substances Control Act (TSCA) screening levels. A re-screening of available Site data against applicable current EGLE criteria and USEPA TSCA screening levels has identified several locations across the Site that warrant additional investigation. Details regarding current conditions at the Site and re-screening results were provided on July 25, 2023, as the *Draft RCRA Corrective Action Summary Report*.

The objective of the additional work is as follows:

- Verify historical soil exceedances based on re-screening activities to assist in evaluating if further characterization or development and evaluation of potential remedies and/or corrective measures are warranted.

The proposed Scope includes utility locating, soil boring advancement, and soil sampling. Further details are provided in the following sections. It should be noted, per USEPA approval via email transmittal on November 3rd, 2023, the field work was completed on November 6th, 2023 through November 9th, 2023, and this revised Scope has been submitted to address comments received on the September 26, 2023 Draft Scope.

Data Quality Objectives

The data quality objective (DQO) process was developed by USEPA to “serve as the basis for designing a plan for collecting data of sufficient quality and quantity to support the goals of a study” (USEPA 2006). This section is organized around the key steps in the DQO process which include:

1. State the problem
2. Identify the goals of the study
3. Identify information inputs

4. Define the boundaries of the study
5. Develop analytical approach
6. Specify performance or acceptance criteria
7. Develop the detailed plan for obtaining data

State the Problem

The problem is to evaluate the historic soil detections above relevant criteria as defined in the *Draft RCRA Corrective Action Summary Report*, dated July 2023.

Identify the Goals of the Study

The overall objective of this effort is to collect information necessary to verify historical soil exceedances based on re-screening activities to assist in evaluating if further characterization or development and evaluation of potential remedies and/or corrective measures are warranted.

Identify Information Inputs

This Scope has been specifically designed to collect the information inputs necessary to evaluate the current conditions of historical soil impacts at the Site including:

- Obtaining coordinates of the existing boring so that the re-sample boring is located as close as possible to the existing location. If a location does not have corresponding coordinates, then a best approximate location will be selected based on figures and Site features.
- Targeted sample collection at specific intervals to duplicate the historical detections and vertical delineation samples collected, where appropriate.
- Laboratory analysis of specific compounds that exceeded relevant criteria to verify if the exceedance is still present.

Define the Boundaries of the Study

The re-sample investigation (based on re-screening conducted as described in the *Draft RCRA Corrective Action Summary Report*, dated July 2023) was conducted across the Site at areas where historic soil detections above applicable relevant criteria as defined in the *Draft RCRA Corrective Action Summary Report*, dated July 2023 were identified (**Figure 2A** through **Figure 5**). Soil borings will be advanced at the location of the historic borings. The borings will be located by using global positioning satellite (GPS) technology. Borings located at existing monitoring well locations will be placed approximately 5 feet away from the well to prevent damage to the well.

Develop the Analytical Approach

Information derived from the investigation will be used in evaluating if further characterization or development and evaluation of potential remedies and/or corrective measures are warranted. Samples will be collected from previously impacted intervals at several previous sampling locations across the Site. The re-sample data will be

screened against relevant criteria, as listed in the *Draft RCRA Corrective Action Summary Report*, dated July 2023, to assess if future work is warranted.

Specify Performance or Acceptance Criteria

Field activities described in this Scope will be executed in accordance with Technical Guidance Instruction (TGI) documents referenced and included in **Attachment 1**. Acceptance criteria for data will be governed by satisfactory adherence to TGIs and data validation procedures. Acceptance criteria will also include percent completion of planned data collection of 95% or greater.

Develop the Detailed Plan for Obtaining Data

This Scope provides the detailed plan for obtaining the required data and is presented in the sections below.

SCOPE OF WORK

Specifics of the Scope are provided below. Proposed boring locations are shown on **Figure 2A** through **Figure 5**.

Permitting/Notifications

Work on the Site will be coordinated with current owners, as necessary.

Utility Locating

Prior to commencing drilling activities, utility clearance will be performed using a minimum of three lines of evidence, which consist of contacting MISS DIG to clear public utilities, clearing using a hand auger to a depth of 5 feet below ground surface (bgs), and using Ground Penetrating Radar (GPR) and/or electromagnetic (EM) techniques to identify private lines by a private locator.

Soil Characterization

Based on the previous soil sample results and re-screening against current applicable criteria, several locations have been identified as warranting further investigation. Locations warranting further investigation are shown on **Figure 2A** through **Figure 5**. The proposed investigation will be completed in two phases. Phase 1 will consist of resampling the soil at the previous locations by advancing soil borings at each location. If a permanent feature, such as a monitoring well, is not present at the previous location where the resample is to occur, a high accuracy GPS unit will be used to determine the original location using coordinates logged during initial sampling. If a location does not have corresponding coordinates, then a best case location will be selected based on figures and Site features. Phase 2 will consist of step out borings to delineate impacts if criteria exceedances still remain at the resample locations. If no impacts are detected or if impacts are below criteria at a resample location no additional step out borings will be completed. All soil borings will be completed by the following procedure:

- All locations will have coordinates collected using a high accuracy GPS unit.

- All locations will be cleared for subsurface utilities using ground penetrating radar (GPR) and hand auger to 5 feet below ground surface (bgs).
- All locations will be advanced by direct-push drilling technology. Soil sampling will be continuous to allow for identifying geology and advanced in 5-foot runs. Each location will be backfilled with bentonite pellets upon completion.
- An Arcadis geologist will log each boring and each boring will be field screened with a photoionization detector (PID).
- Soil samples will be collected utilizing protocols provided in Arcadis' Technical Guidance Instruction (TGI) Documents for Soil Drilling and Sample Collection, which details protocols for hand drilling (Section 8.1.3), direct-push drilling (Section 8.1.2), field screening (Section 8.2.1), and sample collection (Section 8.3). Arcadis TGIs can be found in **Attachment 1** and are further explained in the Analytical Methods and Quality Control section on the following pages. Shallow soil samples collected between 0.0 and 5.0 feet bgs will be collected from hand auger cuttings during the utility clearance process. Soil samples for chemical analysis will be collected from 1-foot intervals based on pre-determined depths through the soil boring (including the previously identified impacted interval) as described in the following sections. Soil sample intervals may be adjusted based on field observations including photoionization detector (PID) readings, visual impacts, odors, etc. For example, if the proposed resample interval is 1-2 feet below ground surface (bgs), but visual impacts are observed from 1.5-2.5 feet bgs, the sample interval will be shifted to sample the impacted material and no additional samples will be added. If the proposed resample intervals are 1-2 feet bgs and 4-5 feet bgs, but visual impacts are observed at 3-4 feet bgs, then an additional sample will be collected.
- Soil samples will be collected from the vadose zone. If saturated soils are encountered soil sample collection depths will be adjusted to be collected above the water table.
- Laboratory quality assurance/quality control (QA/QC) samples will be collected at a frequency of 1 for every 20 for duplicate and matrix spike/matrix spike duplicate samples. Equipment blanks will be collected daily.
- Following the completion of Phase 1, the sample results will be evaluated, Phase 2 scope of work will be developed, and this information will be reviewed with USEPA. If USEPA agrees with the proposed scope of work, the Phase 2 activities will be scheduled. If USEPA determines it is necessary, a written Phase 2 scope of work will be developed and submitted to USEPA.

The following sections describe the proposed investigation for the various areas of the Site. Soil sampling depths are provided in the following sections; however, as described above soil sampling depths maybe adjusted based on field observations.

Northern Metal Fabrication Division

The following work is proposed for locations in the Northern Metal Fabrication Division (NMFD). All locations proposed for additional investigation in the NMFD are shown on **Figure 2A** and **Figure 2B**:

- Resample soils at location MWM32-08 for benzo(a)pyrene (BaP). In 2007, BaP was detected at 20,000 micrograms per kilogram ($\mu\text{g/kg}$) in the 5.0 – 6.0-foot sample, which is above the nonresidential DC criteria (8,000 $\mu\text{g/kg}$). A soil boring will be advanced approximately 10 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 5.0 – 6.0 feet bgs, and 9.0 – 10.0 feet bgs. All soil samples will be submitted for laboratory analysis of BaP via USEPA Method 8270D on a standard turnaround time (TAT).
- Resample soils at locations MWM30-01, BM30-01, and BM30-03 for polychlorinated biphenyls (PCBs). In 2004, PCBs were detected at 1.4 milligrams per kilogram (mg/kg), 2.02 mg/kg , and 45 mg/kg ; respectively. It

should be noted that a review of the table provided in Appendix C of the *July 2023 Draft Corrective Action Summary Report* confirmed that there is a typo in Section 7.5 of the report and location BM30-03 is the appropriate location to resample instead of BM30-02. The typo will be corrected in the Final Corrective Action Summary Report. These concentrations exceed the TSCA screening level for PCBs in soil (1 mg/kg). All exceedances were from the shallowest sample at each location ranging from 0.0 – 2.5 feet bgs. At each location, soil borings will be advanced to approximately 5 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 2.0 – 3.0 feet bgs, and 4.0 – 5.0 feet bgs. All soil samples will be submitted for laboratory analysis of PCBs via USEPA Method 8082A on a standard TAT.

Southern Metal Fabrication Division

The following work is proposed for locations in the Southern Metal Fabrication Division (SMFD). All locations proposed for additional investigation in the SMFD are shown on **Figure 3A** through **Figure 3C**:

- Resample soil at locations SM19-01, SM19-02, and SM19-03 for arsenic. In 2001, arsenic was detected at 54,500 µg/kg, 55,600 µg/kg, and 52,100 µg/kg; respectively. These samples exceed the nonresidential DC criteria (37,000 µg/kg). All samples were collected from the 0.0 – 2.0-foot sample. At each location, soil borings will be advanced to approximately 5 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 2.0 – 3.0 feet bgs, and 4.0 – 5.0 feet bgs. All soil samples will be submitted for laboratory analysis of arsenic via USEPA Method 6020/6020A on a standard TAT.
- Resample soils at location SM19-06 for PCBs. In 2001, PCBs were detected at 1.5 mg/kg in the 0.0 – 2.0-foot sample, which is above the TSCA screening levels for PCBs (1 mg/kg). A soil boring will be advanced approximately 5 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 2.0 – 3.0 feet bgs, and 4.0 – 5.0 feet bgs. All soil samples will be submitted for laboratory analysis of PCBs via USEPA Method 8082A on a standard TAT.
- Resample soils at location BW5-06 for PCBs. In 2006, PCBs were detected at 11 mg/kg in the 11.0 – 12.0-foot sample, which is above the TSCA screening levels for PCBs (1 mg/kg). A visual evaluation of the area will be conducted to ensure the location, based on coordinates, is not already located under the soil cap in the area. If so, the location will not be advanced. If not, a soil boring will be advanced approximately 15 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 5.0 – 6.0 feet bgs, 11.0 – 12.0 feet bgs, and 14.0 – 15.0 feet bgs. All soil samples will be submitted for laboratory analysis of PCBs via USEPA Method 8082A on a standard TAT.
- Resample soils at location MWW1-04 for PCBs. In 2001, PCBs were detected at 5.56 mg/kg in the 2.0 – 4.0-foot sample and 5.11 mg/kg in the 4.0 – 6.0-foot sample, which is above the TSCA screening levels for PCBs (1 mg/kg). A soil boring will be advanced approximately 10 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 2.5 – 3.5 feet bgs, 4.5 – 5.5 feet bgs, and 9.0 – 10.0 feet bgs. All soil samples will be submitted for laboratory analysis of PCBs via USEPA Method 8082A on a standard TAT.

Former Fiero Properties

The following work is proposed for locations in the Former Fiero Properties. All locations proposed for additional investigation in the Former Fiero Properties are shown on **Figure 4A** and **Figure 4B**:

- Resample soils at location BF17-21 for tetrachloroethylene (PCE). In 2006, PCE was detected at 88 µg/kg in the 0.0 – 2.0-foot sample, which is above the residential SSIVAC (6.2 µg/kg). Residential criteria were used to evaluate this location since it is within 100 feet of the Site property boundary that borders off-site residential

properties to the south. A soil boring will be advanced approximately 5 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 2.0 – 3.0 feet bgs, and 4.0 – 5.0 feet bgs. All soil samples will be submitted for laboratory analysis of PCE via USEPA Method 8260C on a standard TAT.

- Resample soils at location MWF7-01 for PCBs and arsenic. In 2001, PCBs were detected at 1.6 mg/kg in the 0.0 – 2.0-foot sample and 1.4 mg/kg in the 8.0 – 10.0-foot sample, which are above the TSCA screening levels (1 mg/kg). In addition, arsenic was detected at 39,400 µg/kg in the 8.0 – 10.0-foot sample, which is above the nonresidential DC criteria (37,000 µg/kg). A soil boring will be advanced approximately 15 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 4.0 – 5.0 feet bgs, 8.0 – 9.0 feet bgs, and 14.0 – 15.0 feet bgs. The proposed 14-15 feet bgs sample is being collected for vertical delineation. All soil samples will be submitted for laboratory analysis of PCBs via USEPA Method 8082A and arsenic via USEPA Method 6020/6020A on a standard TAT.
- Resample soils at location MWF12-01 for naphthalene. In 2001, naphthalene was detected at 390 µg/kg in the 0.0 – 2.0-foot sample, which is above the residential SSIVAC (67 µg/kg). Residential criteria were used to evaluate this location since it is within 100 feet of the Site property boundary that borders off-site residential properties to the south. A soil boring will be advanced approximately 5 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 2.0 – 3.0 feet bgs, and 4.0 – 5.0 feet bgs. All soil samples will be submitted for laboratory analysis of naphthalene via USEPA Method 8260C on a standard TAT.

Stormwater Detention Facility

The following work is proposed for one location at the former stormwater detention facility (SWDF). All locations proposed for additional investigation in the former SWDF are shown on **Figure 5**:

- Resample soils at location MWDP-01 for trichloroethylene (TCE). In 2001, TCE was detected at 1.7 µg/kg in the 1.0 – 3.0-foot sample, which is above the residential VIAP screening levels (0.33 µg/kg). Residential criteria were used to evaluate this location since it is within 100 feet of the SWDF property boundary that borders off-site properties. A soil boring will be advanced approximately 5 feet bgs and soil samples will be collected from 0.0 – 1.0 feet bgs, 2.0 – 3.0 feet bgs, and 4.0 – 5.0 feet bgs. All soil samples will be submitted for laboratory analysis of TCE via USEPA Method 8260C on a standard TAT.

Analytical Methods and Quality Control

Merit Laboratories Inc. of East Lansing, Michigan will be the laboratory company supporting the environmental sample analyses for this project.

Laboratory Analytical Methods

Soil samples will be analyzed for the compounds identified in previous sections, including VOCs (PCE, TCE and naphthalene), benzo(a)pyrene, arsenic, and PCBs by the project laboratory by Method 8260C, Method 8270D, Method 6020/6020A, and Method 8082A, respectively. Relevant laboratory Standard Operating Procedures (SOPS) are summarized below and provided in **Attachment 1**.

Index of SOPs and TGIs

Laboratory SOP	Polychlorinated Biphenyls (PCBs) by GC Method 8082A
	Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry Method SW-846 8260C/ EPA 624.1
	Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry Method SW-846 8270D/ EPA 625.1
	Metals by Inductively Coupled Plasma – Mass Spectrometry Methods 6020, 6020A, 200.8
Arcadis TGI	Groundwater and Soil Sampling Equipment Decontamination
	Sample Chain of Custody
	Soil Drilling and Sample Collection

Samples will be preserved, handled appropriately and hand delivered or delivered by a courier to the laboratory for analysis packed within laboratory provided coolers at temperatures required.

Quality Assurance/Quality Control Procedures

Field Quality Assurance / Quality Control

Field Quality Assurance/Quality Control Procedures (QA/QC) samples will be collected during field sampling include:

- Equipment blank samples to determine the existence and magnitude of sample contamination resulting from ambient conditions or sampling procedures.
- Equipment blank samples will be collected at a frequency of one per day, following sampling equipment decontamination procedures. These samples will be collected by routing laboratory-provided deionized water through decontaminated sampling equipment. Equipment blank samples will be analyzed to check procedural contamination and/or ambient conditions and/or sample container contamination at the Site that may cause sample contamination.
- Field duplicate samples will be collected at a minimum frequency of 1 per 10 or fewer investigative samples. Field duplicate samples will be analyzed to assess the precision of the field sample collection procedures.
- Sufficient sample volume will be provided to the laboratory (as necessary) for matrix spike and spike duplicate (MS/MSD) analyses. The data from MS/MSD analyses provide an indication of the precision and accuracy of the analytical method relative to the sample matrix. Samples for MS/MSD analysis will be designated at a minimum frequency of 1 per 20 or fewer samples.

Samples will be collected and packed in laboratory supplied containers and transported in accordance with the laboratory container, preservation, shipping, and packaging requirements.

Laboratory Quality Assurance / Quality Control

Laboratory QA/QC requirements for the analysis of soil samples includes analyzing method blanks, initial calibration verification standards, continuing calibration verification standards, MS/MSD samples, and laboratory Control Samples (LCS). The analysis frequency for these QA/QC samples is identified in the applicable laboratory

SOP provided in **Attachment 1**. The acceptance criteria for these QC checks will be consistent with the analytical methods and laboratory SOP.

Laboratory Report Deliverables

Laboratory reports for samples collected will consist of the following data deliverables:

1. Case Narrative:
 - a. Date of issuance
 - b. Project name and number
 - c. Any deviations from intended analytical strategy
 - d. Condition of samples "as received"
 - e. Discussion of whether or not sample holding times were met
 - f. Discussion of technical problems or other observations that may have created analytical difficulties
 - g. Discussion of any laboratory quality control checks that failed to meet project criteria
2. Chemistry Data Package
 - a. Dates of sample collection, receipt, preparation, and analysis
 - b. Cross-reference of laboratory to project sample identification numbers
 - c. Description of data qualifiers used
 - d. Methods of sample preparation and analysis
 - e. Sample results in tabular format
 - f. Method blank data, surrogate data, LCS data, duplicate sample data, MS/MSD data,
 - g. Fully executed chain-of-custody document

Data Review and Validation

Upon receipt of the final data packages from the project laboratory the data will be reviewed and validated by Arcadis staff not associated with the sample collection. The data review will evaluate the final analytical results, holding time period compliance, equipment blank sample data, field duplicate sample data, method blank data, LCS data, laboratory duplicate data, surrogate compound spike data, and MS/MSD sample data. Validation of the data will consist of a level 2 review evaluating the QA/QC data (duplicates, blanks, etc.) based on the applicable review criteria specified in "National Functional Guidelines for Inorganic Superfund Methods Data Review", EPA 540-R-2017-001, January 2017 and "National Functional Guidelines for Organic Superfund Methods Data Review", EPA 540-R-2017-002, January 2017. During the data validation process the following items are checked: blanks, holding times, surrogate recoveries (when applicable), LCS/LCSD recoveries and RPDs, MS/MSD recoveries and RPDs, total and dissolved metals (when applicable) and field duplicate RPDs (when applicable). The results of the data review and validation process will be documented in memoranda that identify all limitations on the usability of the analytical data.

Mr. Peter Ramanauskas
United States Environmental Protection Agency
November 28, 2023

Phase 1 Data Review and EPA Discussion

The data obtained from Phase 1 will be summarized, a Phase 2 scope of work will be developed, and this information will be reviewed with USEPA. The data summary will include figures and tables showing the results of Phase 1. Following the review of the data summary package and scope of work with USEPA, either the Phase 2 activities will be scheduled or USEPA will request a written Phase 2 scope of work be prepared and submitted to USEPA for approval.

Upon completion of all necessary phases of work, the activities associated with this Scope and subsequent related phases will be summarized in an addendum to the *RCRA Corrective Action Summary Report* previously submitted to USEPA in July 2023 and will include the following information:

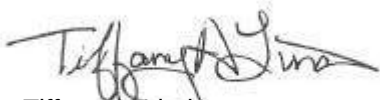
- Brief description of the field activities performed
- Boring and Well Construction logs
- Analytical results
- Conclusions

Schedule

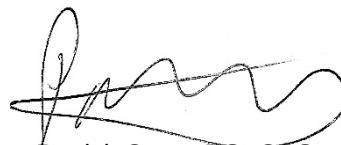
Per USEPA approval, the field work was completed on November 6th, 2023 through November 9th, 2023, and this revised Scope has been submitted to address comments received on the September 26, 2023 Draft Scope. A review of the Phase 1 data and proposed Phase 2 scope of work will be prepared and a virtual meeting scheduled to review the information with USEPA within approximately 45 days of receipt of all laboratory results.

Please let us know if you have additional questions or would like to discuss further.

Sincerely,
Arcadis of Michigan, LLC



Tiffany A. Linder
Certified Project Manager
Email: tiffany.linder@arcadis.com
Direct Line: 810 225 1928



Patrick Curry, PG, CPG
Technical Expert
Email: patrick.curry@arcadis.com
Direct Line: 810 225 1926

CC. Mr. Dave Favero, RACER Trust
Mr. Brendan Mullen, RACER Trust

Mr. Peter Ramanauskas
United States Environmental Protection Agency
November 28, 2023

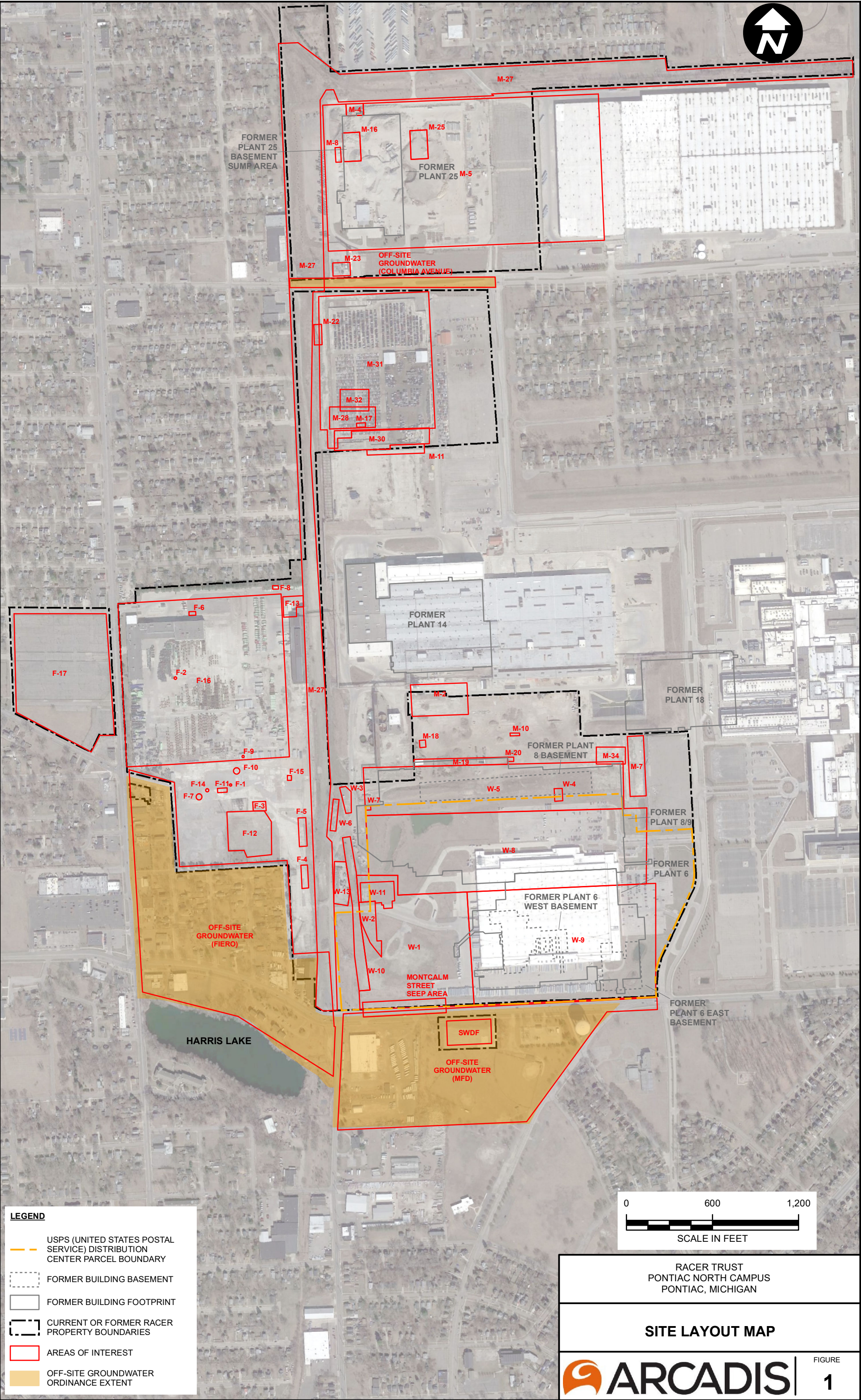
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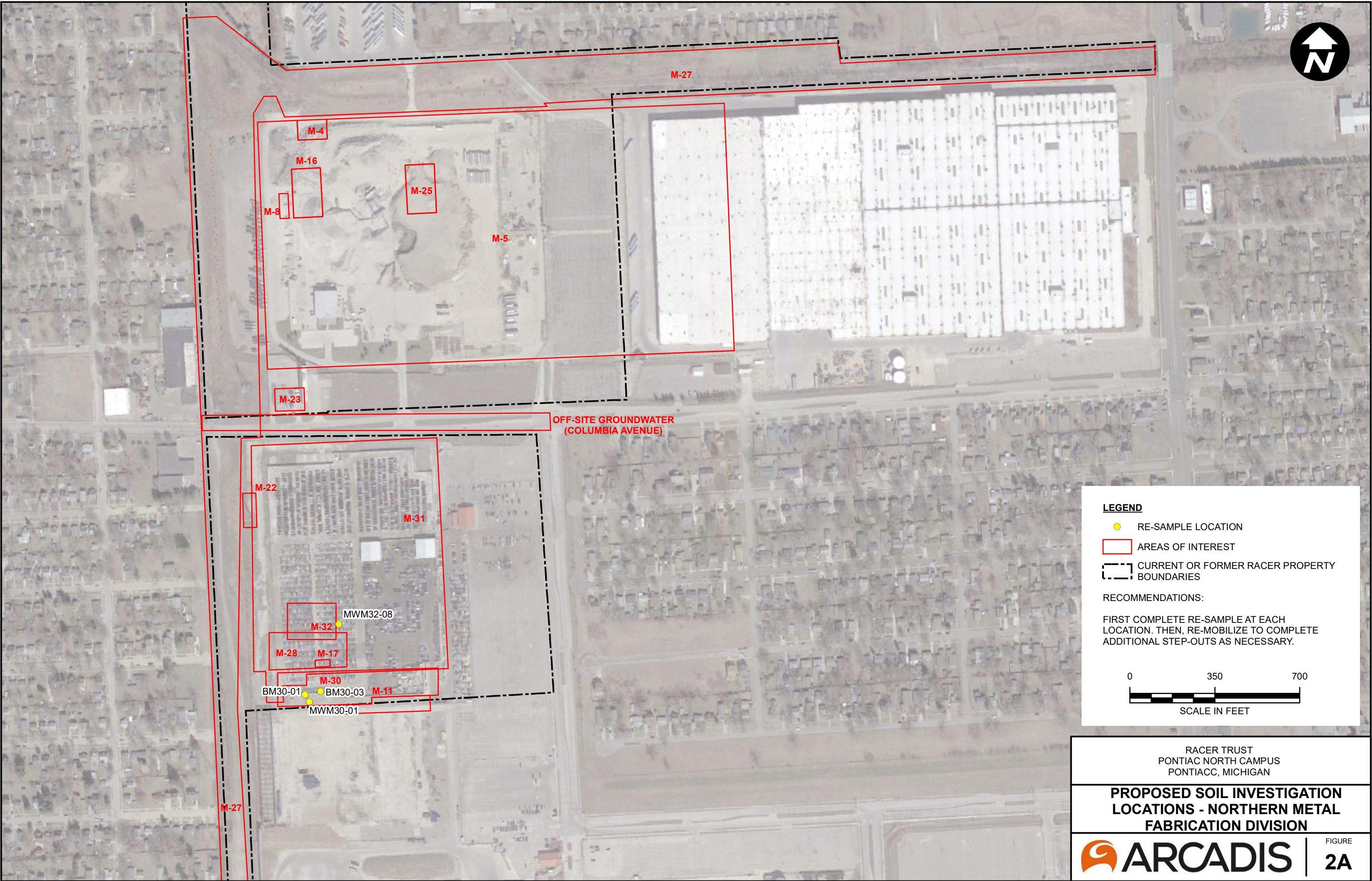
Figures

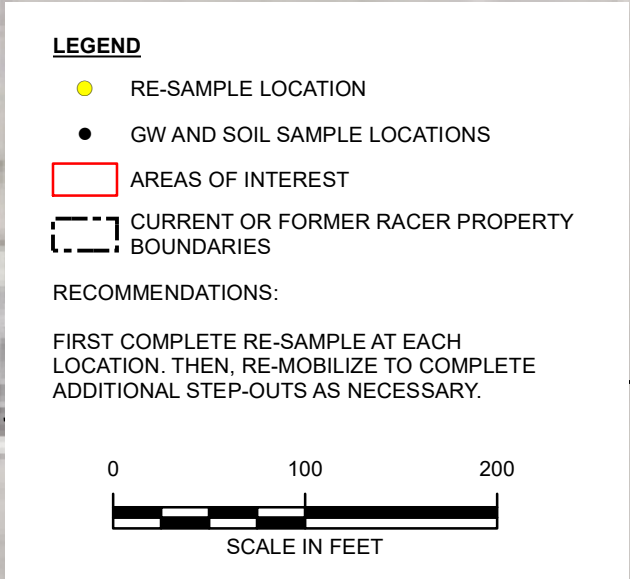
- Figure 1. Site Layout Map
- Figure 2A. Proposed Soil Investigation Locations – Northern Metal Fabrication Division
- Figure 2B. Proposed Soil Investigation Locations – Northern Metal Fabrication Division (Detail)
- Figure 3A. Proposed Soil Investigation Locations – Southern Metal Fabrication Division and Demo Area
- Figure 3B. Proposed Soil Investigation Locations – Southern Metal Fabrication Division and Demo Area (Detail)
- Figure 3C. Proposed Soil Investigation Locations – Southern Metal Fabrication Division and Demo Area (Detail)
- Figure 4A. Proposed Soil Investigation Locations – Fiero Properties
- Figure 4B. Proposed Soil Investigation Locations – Fiero Properties (Detail)
- Figure 5. Proposed Soil Investigation Locations – SWDF (Detail)
- Attachment 1. Laboratory SOPs and Arcadis TGIs

FIGURES

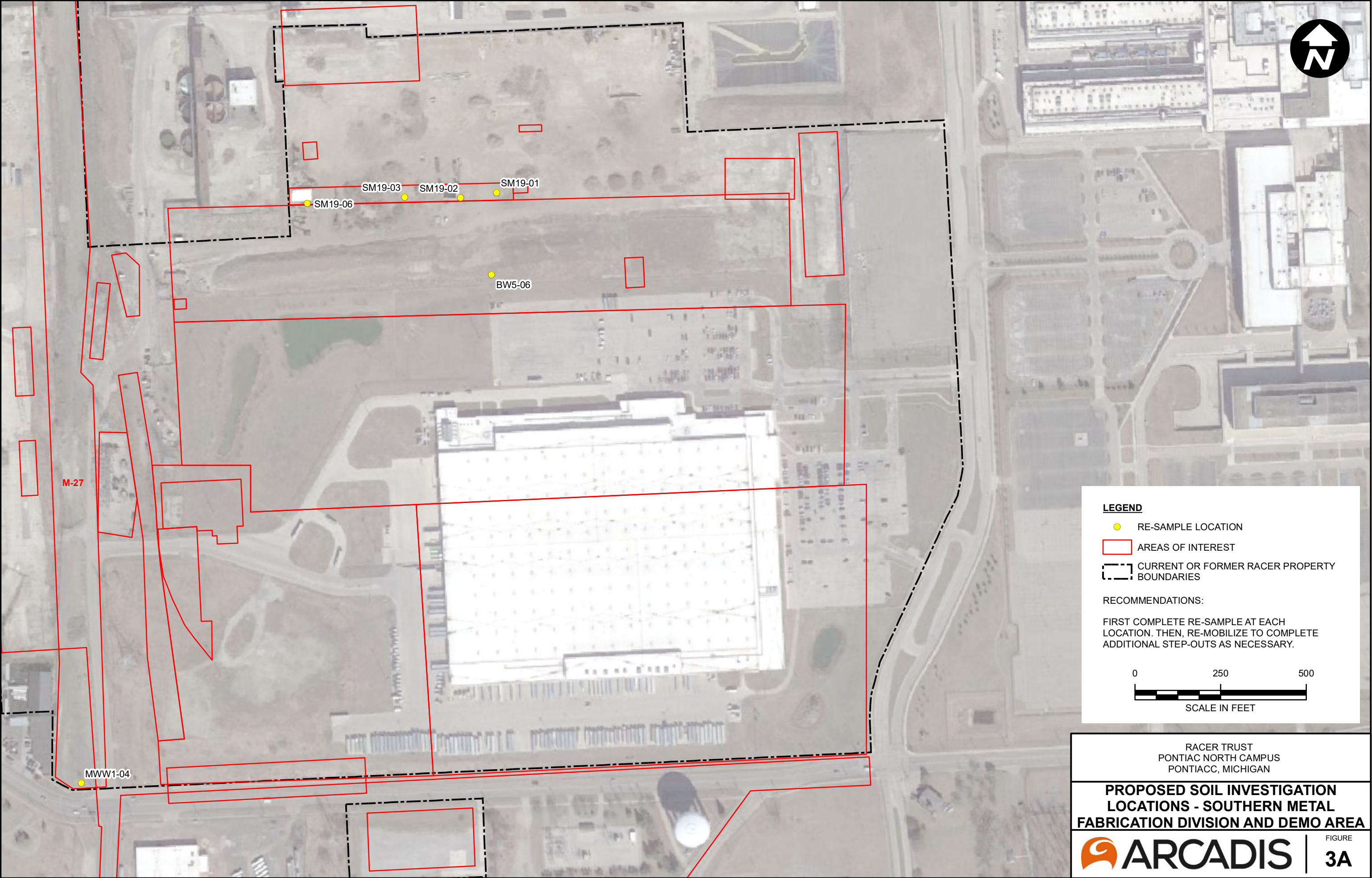
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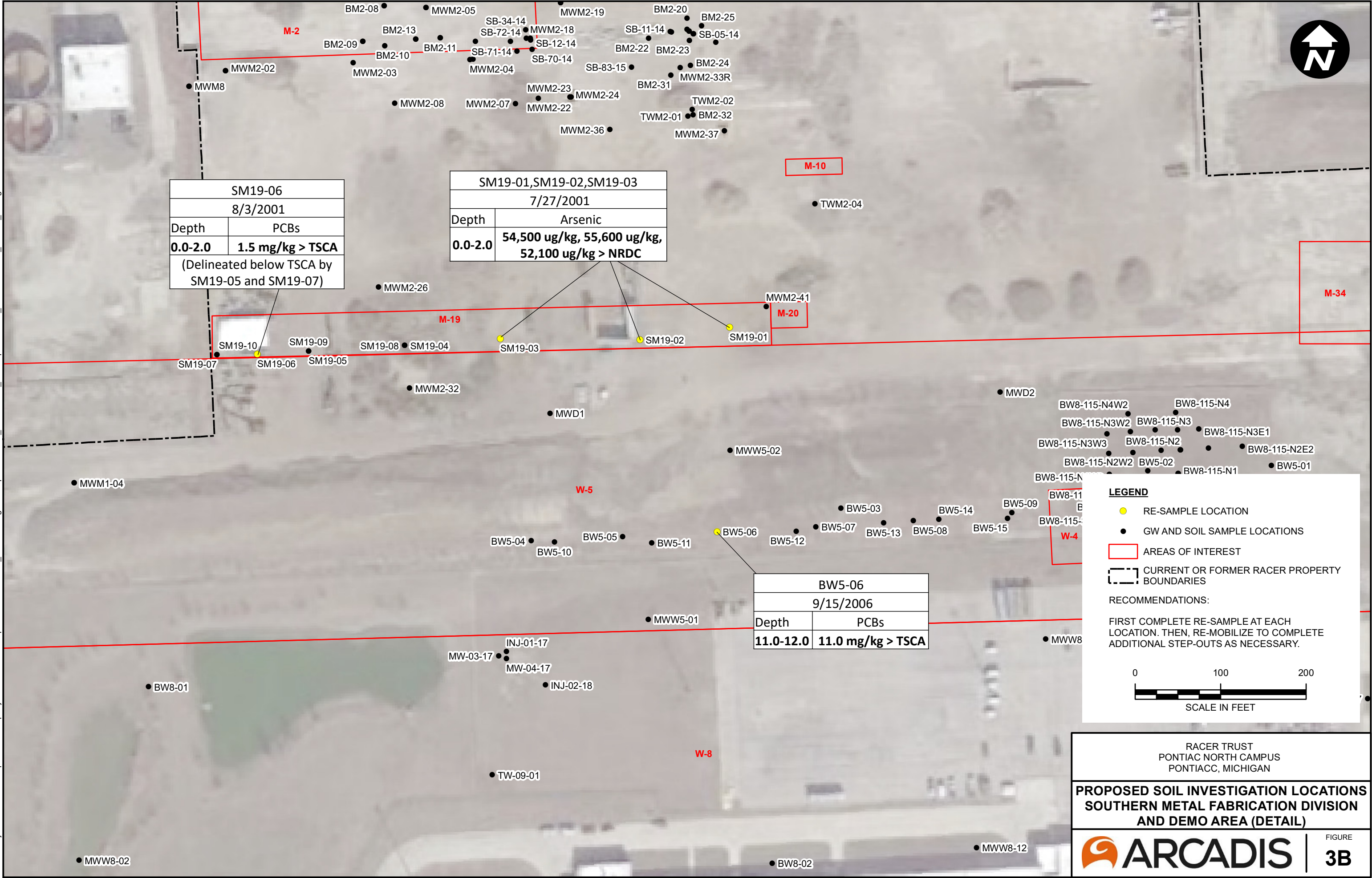


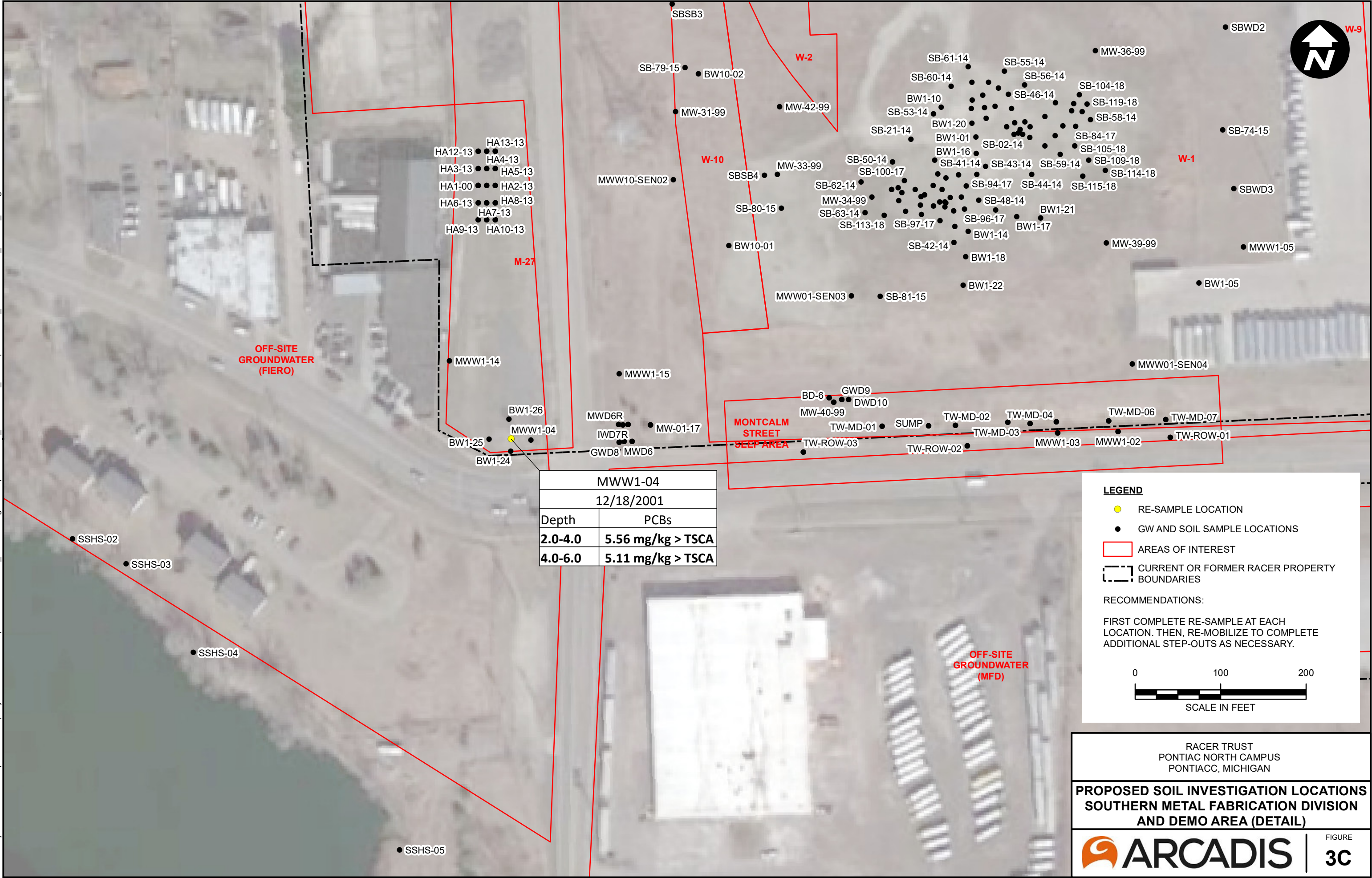


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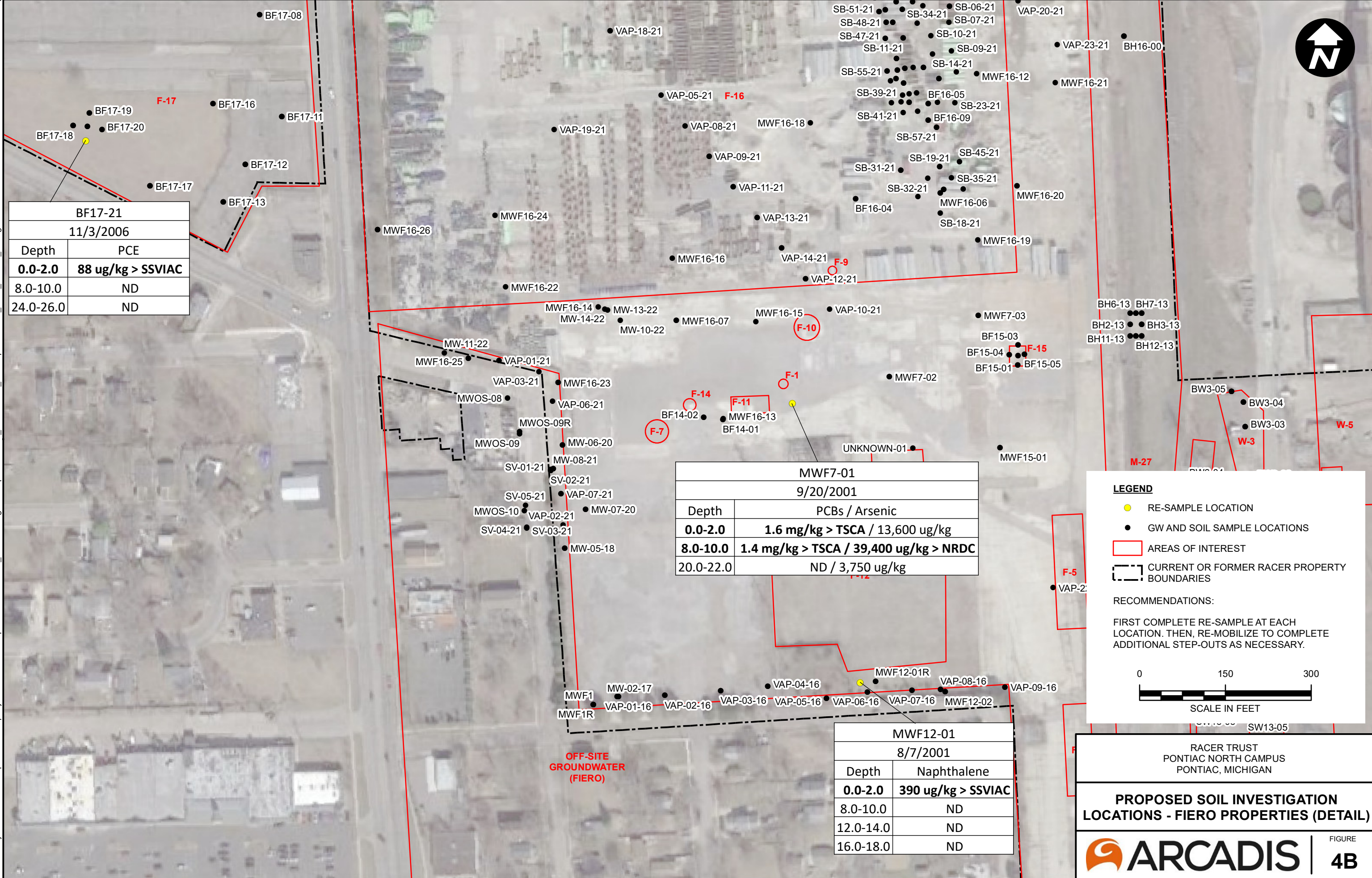
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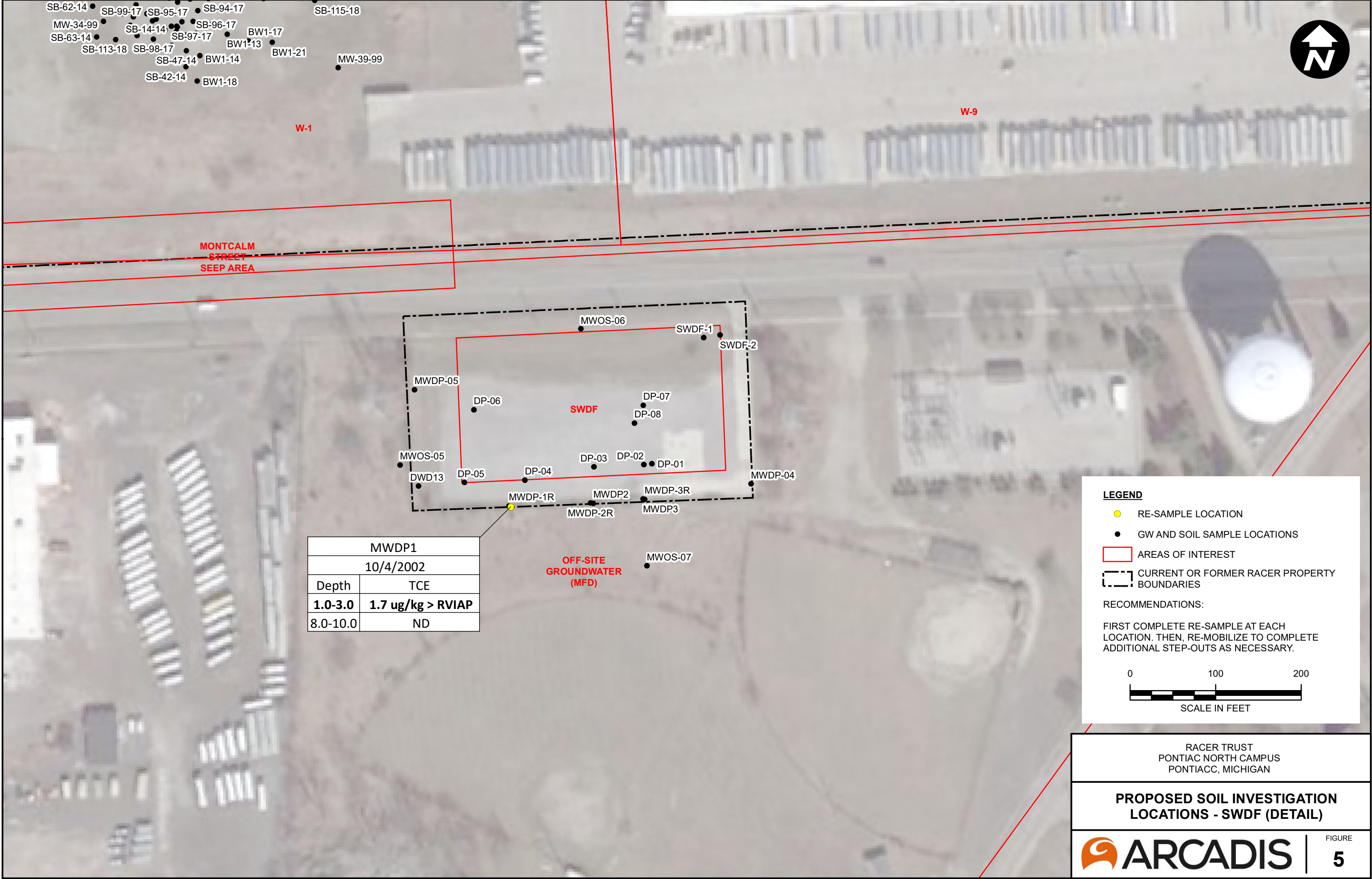






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Attachment 1

Laboratory SOPs and Arcadis TGIs



STANDARD OPERATING PROCEDURE

*METALS BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY METHODS 6020, 6020A,
200.8*

APPROVALS:

A handwritten signature in black ink, reading "Barbara Ball".

02/08/2021

QA Officer

Date

A handwritten signature in black ink, reading "Mike Muehlebach".

02/08/2021

Technical Director

Date

Number	Description of Change	Date
001	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
002	Emergency SOP Amendment Form updates	02/09/16
003	Updated to comply with DoD QSM 5.0 standards.	03/10/16
004	Updated to comply with DoD QSM 5.1 standards.	01/15/18
005	Emergency SOP Amendment Form updates	02/13/19
006	DOD Audit Corrective Action	10/01/2020
007	2020 Internal Audit revisions	02/08/2021
008		
009		
010		
011		
012		

1.0 SCOPE AND APPLICATION

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable for the determination of sub- $\mu\text{g/L}$ concentrations of a large number of elements in water samples and in waste extracts or digestions. When dissolved constituents are required, samples are filtered through 0.45 μm membrane filters and acid-preserved prior to analysis. No digestion is needed prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is performed for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are needed. Acid digestion is also needed prior to analysis to dissolve elements in water samples with turbidity >1 NTU. This SOP follows the guidelines of the EPA Methods 200.8, 6020, and 6020A. The metals that are determined by using this SOP are listed in Table 1 with associated reporting limits (RL) and quantitation limits (QL) and which methods can be used for each element.

If this SOP is followed to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method as well as method detection limit (MDL) and multi-point calibration. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality. Use of this SOP is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical and physical interferences in ICP-MS.

2.0 SUMMARY OF METHOD

Prior to analysis, samples which require total ("acid-leachable") values are digested using appropriate sample digestion procedures (Document #'s MET-003 and MET-001). This SOP describes the measurement of ions produced by radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios, and quantified with a channel electron multiplier. Potential interference from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundance. Interference corrections include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

3.0 INTERFERENCES

There are three fundamentally different sources of interference in ICP-MS: spectroscopic interferences, physical interferences, and memory interferences.

- ◆ **Spectroscopic Interferences** are interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass-to-charge (m/z ratio of the analyte elements). They can be isobaric elemental and isobaric molecular interferences (polyatomic, refractory oxide, and doubly charged ions).
- Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the analyte element. These are managed by the selection of an alternate isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobaric interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca . In this case, the use of ^{43}Ca or ^{44}Ca is recommended. The appropriate elemental interference equations are incorporated in the methods (or parameter) used for calibration and data acquisition.
 - Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that affect ICP-MS determinations have been identified. Examples include ArCl^+ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundance, the most precise coefficients for an instrument is determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable ($<1\%$) counting statistics.
 - Example for As is as follows: Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic is calculated (approximately) as follows (where the $^{38}\text{Ar}^{37}\text{Cl}^+$ contribution at m/z 75 is a negligible 0.06% of the $^{40}\text{Ar}^{35}\text{Cl}^+$ signal): Corrected arsenic signal (using natural isotopes abundance for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}\text{Se}^+$ (e.g., $^{81}\text{BrH}^+$ from bromine wastes⁶).

- Example for Cd is as follows: corrected cadmium signal (using natural isotopes abundance for coefficient approximations) = (m/z 114 signal) - (0.027) (m/z 118 signal) - (1.63) (m/z 108 signal), (where last 2 terms adjust for any tin or MoO⁺ contributions at m/z 114).

NOTE: Cadmium values are biased low by this type of equation when ⁹²ZrO⁺ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct (⁹⁴ZrOH⁺) and indirect (⁹⁰ZrO⁺) additive interferences when Zr is present.

NOTE: Since there is a certain degree of uncertainty as to which equation is better to use, and in what cases, it is up to the analyst to determine how the interference is corrected, upon the evaluation of data. It is suggested that the elemental isobaric interference equations be included in all methods (parameters) from the beginning, but potential polyatomic species (masses) that could interfere be only monitored (except for ⁴⁰Ar³⁵Cl⁺ on As). When species monitored indicate that an isobaric molecular interference is present, the equations can be adjusted to correct for such interference and data be reprocessed to produce an interference free summary report. Generally, an interference is easy to spot when multiple isotopes of an element show different results. Since the interference is additive, the use of the isotope with the lowest result is suggested for data reporting, providing that all other QC criteria are met (See Table 6a & 6b for summary of QC requirements).

- Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Wing overlap interference can occur when a small ion peak is being measured adjacent to a large one. The potential for these interferences must be recognized, and the spectrometer resolution adjusted to minimize them. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require matrix separation, or analysis using another verified and documented isotope.
- ◆ **Physical Interferences** are associated with the physical processes, which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences can result in differences between instrument responses for the samples and calibration standards. Physical interferences can

occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects). To minimize some of these effects, acid composition and concentration must be matched for all standards, blanks, and samples. Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. Internal standardization is effectively used to compensate for many physical interference effects. Internal standards must ideally display similar analytical behavior to the elements being determined. Generally, an internal standard must be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li , ^{45}Sc , ^{89}Y , ^{103}Rh , ^{115}In , ^{159}Tb , ^{169}Ho , ^{185}Re , and ^{209}Bi .

- ◆ **Memory Interferences** result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition can occur is dependent on the sample and needs to be minimized through the use of a rinse blank between samples. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run must be recognized and suitable rinse times must be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition. High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If memory interference is suspected, the sample must be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.

4.0 APPARATUS AND MATERIALS

Inductively coupled plasma-mass spectrometers:

- ◆ **Perkin Elmer (PE) NexION 350X**
- ◆ **Perkin Elmer (PE) NexION 1000**

Argon gas supply: liquid argon cylinders

Analytical balance, 510 g capacity, minimum accuracy ± 0.001 g.

Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 μl to 5,000 μl .

Note: dispensers are calibrated quarterly according to SOP #010010.

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Disposable Pasteur pipettes.

Polypropylene vessels, 50 mL.

Plastic cups to support minimum of 200 ml.

Plastic bottles.

5.0 REAGENTS & STANDARDS

Nitric Acid (HNO_3), concentrated, Trace Metal Grade. Acids used in the preparation of standards and for sample processing must be of high purity. Trace metal grade (also known as re-distilled) acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at 2% (v/v) or less in the solution to be analyzed is required for ICP-MS, in order to minimize damage to the interface.

Hydrochloric Acid (HCl), concentrated, Trace Metal Grade. Several polyatomic ion interferences result when HCl is used. However, its use is recommended to maintain stability in solutions containing high concentrations of antimony and silver. When used, corrections for the chloride polyatomic ion interference must be applied to all data.

Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

Internal Standard stock solutions:

- ◆ Lithium 6, 1000 $\mu\text{g}/\text{ml}$ stock solution.
- ◆ Scandium, 1000 $\mu\text{g}/\text{ml}$ stock solution.
- ◆ Yttrium, 1000 $\mu\text{g}/\text{ml}$ stock solution.
- ◆ Rhodium, 1000 $\mu\text{g}/\text{ml}$ stock solution.
- ◆ Rhenium, 1000 $\mu\text{g}/\text{ml}$ stock solution.
- ◆ Internal Standard Working Solution (IS-WS): From the above stock solution, 2.5 ml of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight), which corresponds to 2.5 $\mu\text{g}/\text{ml}$. This represents the internal standard working solution from which 1 ml (for a 50 ml final volume) must be added to all calibration standards and blanks. This provides a 0.05 ppm of internal standard concentration in all calibration standards, similar to analytical samples. Internal standard mixture can also be purchased.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for blank page of standard preparation log book page.

Multi-element standard stock solution from three of four different vendors:

- ◆ Inorganic Venture (IV), 100 mg/L each of Ag, Al, B, Ba, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of standards.
- ◆ High Purity Standards (HM), 100 µg/ml each of Ca, Mg, K, and Na. This solution is used for the preparation of the calibration standards and for the minerals standard.
- ◆ SPEX Industries (S), 100 µg/ml each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of the initial calibration verification (ICV) standards.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for Standard Prep Log and Appendix 2 for ICV prep log.

Multi-element calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 2% (v/v) HNO₃ in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. The calibration standards are kept in plastic bottles and prepared every two weeks or more frequent if needed. They must be verified using a quality control standard (ICV). Table 2 (metals) and Table 3 (minerals) are used as guidance, when preparing standards.

Blanks: Three types of blanks are required for the analysis. The calibration blank (std-0.00) is used in establishing the calibration curve. The Laboratory Reagent Blank (LRB) also known as method blank is used to monitor possible contamination resulting from the sample preparation procedure. The rinse blank (also called optional rinse or autosampler wash) is used to flush the system between all samples and standards.

- ◆ The calibration blank (std-0.00), the initial calibration blank (ICB), and the continuing calibration blank (CCB) consists of the same concentration(s) of the same acid(s) used to prepare the calibration standards, along with the appropriate concentration of internal standard. The preparation of these blanks can be found in the standards prep-log. The calibration blank is used in the calibration process, the ICB is used to check the instrument before analyzing samples, and the CCB is used to verify the instrument in the middle and end of analytical runs.
- ◆ The Laboratory Reagent Blank (LRB) also known as method blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

- ◆ The rinse blank consists of 2% HNO₃ (v/v) in reagent water. Prepare a sufficient quantity to flush the system between all standards, quality control samples, and analytical samples. Rinse blank is prepared by adding 20 ml of concentrated HNO₃ to 1000 ml of DI water in a large plastic container.

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interference such as ³⁵Cl¹⁶O⁺ on ⁵¹V⁺ and ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

- ◆ Interference check stock solution A, containing 1000 µg/ml each of Al, Ca, Fe, Mg, Na, P, K, and S, 2000 µg/ml of C, 10000 µg/ml of Cl, and 20.0 µg/ml each of Mo and Ti. The ICS-A solution is prepared by weighing 10.0 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO₃, and dilution to 100 g on the scale with reagent water.
- ◆ Interference check stock solution AB, containing 2.0 µg/ml each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn. The ICS-AB solution is prepared by weighing 1.00 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO₃, and dilution to 100 g on the scale with reagent water.
- ◆ The final concentration of the elements in ICS-A and ICS-AB is listed in Table 4. These solutions are prepared fresh every 2 weeks or as needed.

The initial calibration verification solution (ICV) is used to verify the calibration before samples are analyzed. The ICV must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard (known as a second source) is defined as a standard from a source different from those used in the standards for instrument calibration.

Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Number 5, Section 7.0). This solution is also used to verify that the instrument has reached thermal stability (See See Number 4, Section 7.0).

- ◆ Tuning solution for PE ICP-MS: 10µg/ml each of Li 7, Be 9, Mg 25, Co 59, In 115, Tl 205, and Pb 208.

Working standards and solutions are prepared every two weeks according to recipes in the standards prep log. The logbook is available in the metals lab. Concentrations of the LCS can be found on the laboratory bench sheet.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are collected in appropriate plastic or glass containers.

- ◆ Water samples are collected in HNO₃ pre-preserved plastic containers (approximately 125 ml volume), and are acidified to pH of <2.
- ◆ Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ±2 C° upon receipt.

Holding times for metals are 6 months from the date of sampling to analysis. For TCLP samples the holding time is 6 months from sampling to TCLP extraction then 6 months from TCLP extraction to analysis.

7.0 PROCEDURE

1. Solubilization and digestion procedures are presented in the Sample Preparation Document #'s (MET-003 and/or MET-001). A sample digestion log sheet is found in Figure 3.
2. Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.
3. Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.
4. Operating conditions: The analyst must follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. The thermal stability must be verified by analyzing a tuning solution described in Section 5.0.
5. For all analysis tune instrument according to following parameters.
 - ◆ The tuning must include beryllium, magnesium, cobalt, indium, and lead. Conduct mass calibration and resolution checks in the mass regions of interest.

- ◆ The mass calibration and resolution parameters are required criteria that must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value.
- ◆ The resolution must be verified to be within 0.6-0.9 amu full width at 5 percent peak height.

Note: A peak height of 5 percent is used instead of 10 percent because 5 percent is the tighter restriction and this SOP is written to meet the requirements of methods 200.8, 6020, and 6020A.

- ◆ Perform tune after machine is warmed up and every 12 hours following.

Note: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

6. The instrument is calibrated daily and re-calibrated as needed. Calibrate the instrument for the analytes of interest (recommended isotopes for the elements in Table 1 are provided in Table 5a and Table 5b), using the calibration blank and at least three non-zero calibration standards according to the instrument manufacturer's procedure. A multi-point calibration curve is analyzed and evaluated. For the calibration curve to be acceptable, a correlation coefficient of greater than or equal to 0.998 must be achieved. If the required correlation coefficient is not achieved then the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. If narrowing the linear range does not improve the correlation coefficient to 0.998, then replace the calibration standards and re-calibrate the instrument. The reporting limit (RL) must be greater than or equal to the lowest calibration point or the concentration of low level initial calibration verification (LLICV), whichever is lower.

The principle of calculation for the linear curve fit and the coefficient of determination (COD) is found in SW 846 method 8000C Sections 11.5.2.1 through 11.5.2.3. ICP-MS manufacturer software is preprogrammed for this calculation.

The multi point calibration is verified with a mid level ICV standard with control limits of 90%-110% and a low-level ICV with limits of 70%-130% (80%-120% for DoD projects). Table 2 and Table 3 (Section 5.0) provide information to what calibration standards are used. (More information on limits and corrective actions can be found in Section 8 and Table 6a & 6b). Flush the system with the rinse blank (Section 5.0) between

each standard solution. The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

7. All masses that affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. Preferred isotopes are referenced in Tables 5a and 5b.
8. Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the initial calibration verification solution (ICV, Section 5.0) using a second source standard. When measurements exceed $\pm 10\%$ of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. During the course of an analytical run, the instrument may require re-calibration to correct for instrument drift. A re-calibration must then be followed immediately by a new analysis of an ICV, LLICV, and initial calibration blank (ICB) before any further samples are analyzed. Corrective actions for specific situations are found in Section 8 and summarized in Table 6a & 6b.
9. A low-level initial calibration verification (LLICV) must be analyzed after every calibration to verify the linearity near the lower end of the calibration curve. The LLICV is made from the same source as the calibration standards at a concentration comparable to the reporting limits of elements being reported. When the LLICV measurements exceed $\pm 30\%$ ($\pm 20\%$ for DoD projects) of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).
10. Flush the system with the rinse blank solution (Section 5.0) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (CCV), and the continuing calibration blank (CCB) at a frequency of at least once every 10 analytical samples (limits and corrective action information can be found in Section 8.0 and is summarized in Table 6a & 6b).
11. Dilute and reanalyze samples that are more concentrated than the linear range (LR) (Section 8.0) for an analyte or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (Numbers 6 through 8, Section 7.0).
12. Interference Check Solutions (ICS) are run to verify the magnitude of elemental and molecular-ion isobaric interferences. This is performed every 12 hours. This is done by analyzing interference

check solutions A and AB. (Concentration of elements in solution found in Table 4, other reagent information is in Section 5.0)

Corrective Action: The ICS needs to be within 70-135% ($\pm 20\%$, of true value, for DoD projects). If the ICS fails, re-evaluate the equations used for the corrections, make the necessary adjustments, recalibrate the instrument and re-analyze the samples associated with the failed ICS. See Table 6a & 6b for ICS summary and Section 8.0 for more information.

Note: Precipitation from solution AB can occur with some elements, specifically silver. Rinse the instrument 5 –10 minutes before analyzing any other samples to help improve performance.

13. Calculations: the quantitative values are reported in appropriate units, such as milligrams per liter (mg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples.
- ◆ The appropriate dilution factor (DF) on water samples resulted from sample preparation (see Document # MET-003) is entered in the data system for each sample at the time of programming the sequence to be analyzed. If additional dilutions are performed, the appropriate corrections must be applied to the dilution factor, using the following equation

$$C \times DF = SC$$

Where, C = digest concentration

DF = Dilution Factor

SC = Sample Concentration

The ICP/MS software carries out this calculation for the analyst.

- ◆ Generally, for solid samples, DF includes the correction necessary for the determination of a dry weight result. If this is not the case or if a dry weight result is requested at a later time, calculate results for solids on a dry-weight basis as follows:

- (1) A separate determination of percent solids must be performed.
- (2) A new DF is calculated, based on the original wet weight of the sample (from the preparation log) and the percent total solids. The sequence is updated with the new DF, data reprocessed, and a new quantitation report is generated by the data system.
- (3) Manual calculation of the dry weight concentration (DWC) by the formula:

$$DWC (mg / kg) = \frac{C \times V}{W \times S}$$
 Where, C = Digest Concentration (mg/L).
 V = Final volume in liters after sample preparation.
 W = Weight in kg of wet sample.
 S = (% Total Solids)/100.

- ◆ Calculations performed by the data system include appropriate interference corrections, internal standard normalization, and the summation of signals (for example 206, 207 and 208 m/z for lead) to compensate for any differences in the abundances of these isotopes between samples and standards.

Note: The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

- ◆ Hardness by Calculation

The preferred method for calculating Hardness Standard Method 2340B. Hardness is calculated from the Calcium and Magnesium results from this procedure using the following equation:

$$CaCo3/L = 2.497 [Ca] + 4.118[Mg]$$

Where:

CaCO3 is the total hardness by calculation

Ca is the total Calcium by 6020A in mg/L

Mg is the total Magnesium by 6020A in mg/L

Relative Percent Difference:

$$RPD = \frac{(S - D)}{\left[\frac{S + D}{2} \right]} \times 100$$

Where: S = Initial sample result

D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result

SR = Sample (unspiked) result

SA = Spike added

% Difference (%D)

Used for serial dilution test in metals.

$$\%D = \left| \frac{X_1 - X_2}{X_1} \right| \times 100\%$$

where: %D = percent difference

X₁ = Initial concentration

X₂ = Duplicate concentration

8.0 QUALITY CONTROL

All quality control data must be maintained and be available for easy reference or inspection.

Demonstration of Performance.

- ◆ The demonstration of performance is used to demonstrate instrument performance and has two parts. The first is initial demonstration of performance this is done by performing method detection limit (MDL) studies, linear range studies, and precision and accuracy studies prior to the analysis of samples. The second is continual demonstration of performance is done by annual MDLs and linear range studies. MDL studies are performed by following SOP #060004 (Determination of Method Detection Limit). Analyst performance is demonstrated by analysis of proficiency test and blind samples multiple times per year.
- ◆ Linear calibration ranges: Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range must be established by determining the signal responses from a minimum of five different concentration standards. Care must be taken to avoid potential damage to the detector during this process. The linear calibration range, which is used for the analysis of samples, must be judged by the analyst from the resulting data. The upper LR is defined as the maximum concentration for which the measured concentration is within $\pm 10\%$ of the true value. Determined sample analyte concentrations that are greater than the upper LR limit must be diluted and reanalyzed. The LR must be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined. See Section 7.6 for curve specific criteria.

To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If an interference source is present, and cannot be corrected, the sample elements impacted must be flagged. The ICS is used to verify the correction equations used by the instrument. Requirements are found in Section 8.0 and Table 4 and preparation information is in Section 5.0.

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard falls outside the control limits as compared with the first calibration standard (Calibration Blank or std-0.00), the following procedure is followed. Check for instrument drift, instrument drift is characterized by internal standards outside control limits for QC samples (Section 8.0), recalibrate instrument

and reanalyze samples. If matrix interference is suspected, the sample must be diluted at least fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. (Summary of control limits and corrective actions can be found in Table 6a & 6b)

- ◆ The intensity levels of the internal standards for the ICV/ICB/LLICV, CCV/CCB, LCS/LRB must also be within the specified acceptance limits (refer to Section 8.0 for limits and Section 7.0, Numbers 6-12 for procedure information). If they are not within limits, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

Check the instrument calibration by analyzing appropriate quality control solutions as follows (Summarized in Table 6a & 6b):

- ◆ Initial Calibration must include a blank and minimum of three non-zero points. A correlation coefficient of 0.998 must be achieved. Section 7.0 for calibration procedure.
- ◆ Immediately after instrument calibration check instrument calibration by analyzing the ICV described in Section 5.0. ICV limits are 90%-110%. The ICB has to be less than the lower limit of quantitation for every target element. The lower limit of the calibration must be checked by analyzing the low-level initial calibration verification (LLICV) with acceptance limits of 70%-130% ($\pm 20\%$ for DoD projects). Summary of limits and corrective actions are found in Table 6a & 6b, the procedure for this is found in Section 7.0, Numbers 6 through 9.
- ◆ When running samples verify calibration at a frequency of every 10 analytical samples with the CCV standard with limits of 90-110% and the continuing calibration blank (CCB) with acceptance criteria of less than the lower limit of quantitation for every target element. These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. See Table 6a & 6b for summary of acceptance criteria and corrective actions, the procedure for this information for this is found in Section 7.0, Number 10.
- ◆ Corrective action for out of compliance ICV, LLICV, and CCV, is to terminate the analysis, correct the problem, and recalibrate the instrument. Control limits and corrective actions are found in Section 8.0 and summarized in Table 6a & 6b.

Laboratory Reagent blank (LRB) also known as Method blank. Method blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB is prepared by using a volume or

weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate analytical process. The LRB has to be below the RL divided by the dilution factor for each target analyte. If the LRB does not contain target analytes at a level that interferes with the project specific requirements, then the LRB is acceptable. Control limits and corrective actions are summarized in Table 6a & 6b.

A Laboratory Control Sample (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS must be prepared and analyzed for each sample batch at a frequency of one LCS for a least every 20 samples or every 10 samples for drinking waters. The recovery limits for the LCS are 85-115% of the true value (stated in the preparation log). If the LCS is outside of the control limits the entire sample batch must be re-digested and re-analyzed. Control limits and corrective actions are summarized in Table 6a & 6b. (In method 200.8, the LCS is referred to as the Laboratory Fortified Blank, LFB).

Analyze one matrix spike (MS) sample for every 10 analytical water samples or every 20 analytical soil samples. For majority of the elements, the aqueous samples are spiked at levels similar to the LCS (0.05 ppm in the analysis solution). For solid samples, a concentration of 0.10 mg/kg is added pre-digestion. The acceptable limits for performance are summarized in Section 8.10 and Table 6a & 6b.

- ◆ Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery must be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

where: R = percent recovery.

C_s = spiked sample concentration.

C = sample background concentration.

S = concentration equivalent of analyte added to fortify the sample.

Analyze one matrix duplicate (Dp) sample for every 10 water samples or every 20 soil samples. In some cases, a matrix spike duplicate (MSD) is used instead of the matrix duplicate, especially if the analytes in the sample are of low concentration. A control limit of 20% RPD must not be exceeded for analyte values greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user must be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and

corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed. Control limits and corrective actions are summarized in Table 6a & 6b.

The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

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

where: RPD = relative percent difference.

D₁ = first sample value.

D₂ = second sample value (duplicate).

The Quality Control requirements and limits vary slightly, based upon the method referenced in the analytical report (i.e. 6020A vs. 200.8). For both methods, the calibration is verified by the analysis of ICV/ICB and CCV/CCB. Recalibration is required when either one falls outside the limits. The performance of the method is evaluated by the analysis of the LCS/LRB pair for every batch of 20 samples, and MS/MSD/Dp for every 10 water samples and 20 soil samples. The acceptable limits for performance are summarized in Table 6a & 6b and the procedures can be found in Section 7.0, Numbers 6-12.

◆ Requirements for all methods:

- When the recovery for ICV/CCV falls outside ±10% terminate the analysis and recalibrate the instrument. The samples from the last CCV that was within limits are to be re-analyzed, after recalibration of the instrument.
- The MS is represented by a spiked sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular spike fails to meet QC criteria. An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 75 to 125 percent of the known value. The spike addition must be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample is spiked and re-analyzed according to Figure 1. The same recovery limits apply to the spiked dilution.
- The MSD is represented by a spiked duplicate sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular duplicate spike fails to meet QC criteria. The evaluation of the MSD is similar to the evaluation of the duplicate analysis described in Section 8.0.
- When the intensity of any internal standard in the sample to falls outside 70-125% of the intensity of that internal standard in the initial calibration standard (Calibration Blank or std-0.00), follow the procedure described in Section 8.0. The intensity levels of the internal

standards for the ICV/LLICV/ICB and CCV/CCB must agree within ± 20 percent of the intensity level of the initial calibration standard (Calibration Blank or std-0.00). If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

◆ Method 6020/6020A specific requirements:

- Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 x MDL), an analysis of a fivefold (1+4) dilution must agree within $\pm 10\%$ of the original determination. If not, an interference effect must be suspected, and the results flagged. One dilution test must be included with every batch of twenty samples.
- Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. This is done by analyzing the interference check solutions ICS-A and ICS-AB. The recovery of the elements of interest in ICS-AB (listed in Table 4 at a concentration of 0.02 ppm) must be between 70-135% ($\pm 20\%$ for DoD projects) (see Section 7.0, Number 12 for procedure information and Table 6a & 6b for a summary).
- The LLICV is used to verify the linearity of the low end of the calibration curve. The LLICV must be analyzed after every new calibration with the measurements not exceeding $\pm 30\%$ ($\pm 20\%$ for DoD projects) of the true value. If the LLICV is outside of these limits the run must be stopped and the instrument recalibrated and the new calibration verified (see Section 7.0, Number 9 for procedure information and Table 6a & 6b for a summary).

The analyst will follow SOP #QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method. In an EPA multi-laboratory study, laboratories applied the ICP-MS technique to both aqueous and solid samples. The results are listed at the end of methods 200.8, 6020 and 6020A.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

Computer software and firmware can be found on Merit's network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- ◆ Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.
- ◆ Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
- ◆ Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.
- ◆ The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

12.0 WASTE DISPOSAL

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

Samples.

- ◆ All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory wastewater.
- ◆ As a “small generator” of metals, Merit Laboratories has been approved for this type of disposal from the local government.

Acid bottles.

- ◆ Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: also referred to as a Laboratory Reagent Blank. an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Sample (however named, such as laboratory fortified blank, spiked blank, or QC check sample): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.

Matrix Spike (spiked sample or fortified sample): a sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.

Matrix Spike Duplicate (spiked sample or fortified sample duplicate): a second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

Laboratory Duplicate: aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

Internal Standard: a known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. An acceptable MDL standard check must produce a signal at least three times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Calibration Standards: a series of known standard solutions used for calibration of the instrument within the measurable linear range. Calibration standards shall contain, in correct proportion, all reagents required by the method. A minimum of 4 calibration points are used for calibration. Acceptance of the calibration requires a correlation coefficient of 0.997 or better. No samples shall be analyzed without acceptable calibration.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

Initial calibration blank (ICB): a reagent blank solution, which is analyzed immediately following the ICV. The ICB is analyzed to check for drifts in calibration or possible analyte carry-over.

Continuing Calibration Blank (CCB): a reagent blank solution, which is analyzed immediately following the CCV. The CCB is analyzed to check for drifts in calibration or possible analyte carry-over.

14.0 REFERENCES

Method 200.8, Revision 5.4, 1998.

SW-846, Method 6020A Revision 1, 2007.

SW-846, Method 8000C Revision 3, 2003.

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, ISO/IEC 17025:2005,

ISO/IEC 17025:2017 and The NELAC Institute (TNI) Standards, Volume 1, September 2009, Version 5.3,
May 7, 2019

Table 1. List of elements analyzed.

Element	Symbol	CAS#	Reporting Limits		Method Reference			DoD Reportable	Quantitation limit * ug/L	Laboratory performance based
			mg/L	mg/kg	6020	200.8	6020A			
Aluminum	Al	7429-90-5	0.05	0.5	X	X	X	X	0.5	
Antimony	Sb	7440-36-0	0.002	0.3	X	X	X	X	2.0	
Arsenic	As	7440-38-2	0.001	0.1	X	X	X	X	0.5	
Barium	Ba	7440-39-3	0.01	1.0	X	X	X	X	0.5	
Beryllium	Be	7440-39-3	0.001	0.50	X	X	X	X	0.5	
Boron	B	7440-42-8	0.01	1.0						X
Cadmium	Cd	7440-43-9	0.0005	0.2	X	X	X	X	0.5	
Calcium	Ca	7440-70-2	0.05	10.0	X		X	X	200	
Chromium	Cr	7440-47-3	0.005	2.0	X	X	X	X	0.5	
Cobalt	Co	7440-48-4	0.01	0.5	X	X	X	X	0.5	
Copper	Cu	7440-50-8	0.004	1.0	X	X	X	X	0.5	
Iron	Fe	7439-89-6	0.1	1.0	X		X	X	2.0	
Lead	Pb	7439-92-1	0.003	1.0	X	X	X	X	0.5	
Lithium	Li	7439-93-2	0.01	1.0						X
Magnesium	Mg	7439-95-4	1.0	4.0	X		X	X	200	
Manganese	Mn	7439-96-5	0.02	1.0	X	X	X	X	2.0	
Molybdenum	Mo	7439-98-7	0.005	0.50		X		X	2.0	
Nickel	Ni	7440-02-0	0.005	1.0	X	X	X	X	0.5	
Potassium	K	7440-09-7	1.0	5.0	X		X	X	200	
Selenium	Se	7782-49-2	0.005	0.2	X	X	X	X	0.5	
Silver	Ag	7440-22-4	0.0002	0.1	X	X	X	X	0.5	
Sodium	Na	7440-23-5	0.05	10.0	X		X	X	200	
Strontium	Sr	7440-24-6	0.005	0.50					1.0	X
Tin	Sn	7440-31-5	0.02	1.0						X
Titanium	Ti	7440-32-6	0.005	1.0					0.5	X
Thallium	Tl	7440-28-0	0.001	0.50	X	X	X	X	0.5	
Vanadium	V	7440-62-2	0.004	1.0	X	X	X	X	0.5	
Zinc	Zn	7440-66-6	0.01	1.0	X	X	X	X	2.0	
* Quantitation limit for individual samples is affected by sample dilutions										

Table 2.
Standard Preparation PE

Inorganic Stock Solution IV-28 (100 ppm) + CGSN1-1 (1000 ppm)

I. Working Stock Solution 1 (WS1)

10 mls IV-28 + 1 ml CGSN1-1 + 2 mls HNO₃;
Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Spiking Solution

50 mls of WS1 to a final volume of 100 mls = 5.0ppm

IV. STANDARDS

Standards	Volume Working Stock Solution	Internal Standard 5.0 ppm	HNO₃	Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.001 ppm	1.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls
0.0002 ppm	0.20 mls WS2	2 mls	2 mls	100 mls
0.0001 ppm	0.10 mls WS2	2 mls	2 mls	100 mls
0.00 ppm	0.00 mls	2 mls	2 mls	100 mls

Table 3. Standard preparation for Ca, Mg, K, Na (minerals).

Standards ppm	Volume of Working Stock	Source and Lot # of Working Stock (100ppm)	Internal Standard 5.0 ppm	HNO₃	Final Volume
0.0	0.0	High Purity (HM) –	2 mls	2 mls	100 mls
0.20	0.2	High Purity (HM) –	2 ml	2 ml	100 ml
0.50	0.5	High Purity (HM) -	2 ml	2 ml	100 ml
1.0	1.0	High Purity (HM) -	2 ml	2 ml	100 ml
2.0	2.0	High Purity (HM) -	2 ml	2 ml	100 ml
5.0	5.0	High Purity (HM) -	2 ml	2 ml	100 ml
10.0	10.0	High Purity (HM) -	2 ml	2 ml	100 ml
ICV- 5.0	5.0	Spex –	2 ml	2 ml	100 ml

Table 4. ICS Components and Concentration.

Solution Component	ICS-A (ppm)	ICS-AB (ppm)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.020
Cd	0.0	0.020
Cr	0.0	0.020
Co	0.0	0.020
Cu	0.0	0.020
Mn	0.0	0.020
Ni	0.0	0.020
Ag	0.0	0.020
Zn	0.0	0.020

Table 5a. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
<u>19</u>	K	Sc, Rh		
<u>23</u>	Na	Sc, Rh		
<u>24</u>	Mg	Sc, Rh		
43	Ca	Sc, Rh		
<u>44</u>	Ca	Sc, Rh	$(-0.0271)^{(^{88}\text{C})}$	Sr^{++}

- Notes:**
- † Recommended for PE instrument.
 - ‡ Recommended for HP instrument.
 - C = Counts at specified mass.
 - When the concentration of Na in the samples is high, the ionization of Sc is suppressed leading to positive bias of the results, therefore Rh must be used as the internal standard, even if more than 50 amu removed from the element of interest.

Table 5b. Recommended analytical isotopes (underlined> and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
6	Li	I.S.	-(0.0813)(⁷ C)	
<u>7</u>	Li	⁶ Li, Sc		
<u>9</u>	Be	⁶ Li, Sc		
10	B	⁶ Li, Sc		
<u>11</u>	B	⁶ Li, Sc		
<u>27</u>	Al	⁶ Li, Sc		
45	Sc	I.S.		CO ₂ H ⁺
47	Ti	⁶ Li, Sc		
<u>49</u>	Ti	⁶ Li, Sc		
<u>51</u>	V	⁶ Li, Sc	-(3.127)(⁵³ C)+(0.352)(⁵² C)	³⁵ ClO ⁺ , ³⁴ SOH ⁺
<u>52</u> [†]	Cr	Sc, Y, Rh		ArC ⁺ , ArO ⁺ , ³⁵ ClHO ⁺
<u>53</u> [‡]	Cr	Sc, Y, Rh		³⁷ ClHO ⁺
<u>54</u> [†]	Fe	Sc, Y, Rh	-(0.0284)(⁵² C)	
<u>55</u>	Mn	Sc, Y, Rh		ArNH ⁺
56	Fe	Sc, Y, Rh		
<u>57</u> [†]	Fe	Sc, Y, Rh		
<u>58</u> [†]	Ni	Sc, Y, Rh		
<u>59</u>	Co	Sc, Y, Rh		
<u>60</u>	Ni	Sc, Y, Rh		
62	Ni	Sc, Y, Rh		TiO
<u>63</u> [†]	Cu	Sc, Y, Rh		³¹ PO ₂ ⁺ , ⁴⁰ ArNa ⁺ , TiO
<u>65</u> [†]	Cu	Sc, Y, Rh		TiO
<u>66</u>	Zn	Sc, Y, Rh		TiO
68	Zn	Sc, Y, Rh		
<u>75</u>	As	Y, Rh	-(3.132)(⁷⁷ C)+(2.736)(⁸³ C)	⁴⁰ Ar ³⁵ Cl ⁺
76	⁴⁰ Ar ³⁶ Ar ⁺	Y, Rh		⁴⁰ Ar ³⁷ Cl ⁺
77	Se	Y, Rh		
<u>78</u> [†]	Se	Y, Rh	-(0.1869)(⁷⁶ C) [‡]	⁴⁰ Ar ³⁸ Ar ⁺
<u>82</u> [†]	Se	Y, Rh		⁸¹ BrH ⁺
83	Kr	Y, Rh		
<u>88</u>	Sr	Y, Rh		
89	Y	I.S.		
90	Zr	Y, Rh		
<u>95</u>	Mo	Y, Rh		⁷⁹ BrO ⁺
98	Mo	Y, Rh	-(0.146)(⁹⁹ C)	⁷⁹ BrHO ⁺
99	Ru	Y, Rh		
103	Rh	I.S.		
105	Pd	Rh		
106	Pd, Cd	Rh		ZrO,
<u>107</u>	Ag	Rh		ZrO
108	MoO	Rh		ZrO, MoO
109	Ag	Rh		ZrO, MoO
<u>111</u>	Cd	Rh		ZrO, MoO
112	Cd	Rh	-(0.040)(¹¹⁸ C)	ZrO, MoO
<u>114</u>	Cd	Rh	-(0.0269)(¹¹⁸ C)	MoO
<u>118</u>	Sn	Rh		
119	Sn	Rh		
120	Sn	Rh	-(0.0127)(¹²⁵ C)	
<u>121</u>	Sb	Rh	-(0.124)(¹²⁵ C)	⁴⁰ Ar ⁸¹ Br ⁺
123	Sb	Rh		
125	Te	Rh		
<u>137</u>	Ba	Rh		
138	Ba	Rh	-(8.91E-04)(¹³⁹ C)-(2.82E-04)(¹⁴⁰ C)	
139	La	Rh		
140	Ce	Rh		
185	Re	I.S.		
203	Tl	Re		
<u>205</u>	Tl	Re		
206	Pb	Re		
207	Pb	Re		
<u>208</u>	Pb	Re	+(1.0)(²⁰⁶ C)+(1.0)(²⁰⁷ C)	

Notes: • † Recommended for the PE instrument.

• ‡ Recommended for the HP instrument.

Table 6a. Summary of Quality Control Items, Frequency, and Corrective Action.*

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tuning	After warm-up Every 12 hours	Manufacturer specifications	Check operating parameters, clean cones, replace malfunctioning components if necessary. Reevaluate the tuning.
Calibration Curve	Once a day and as necessary	$R \geq 0.998$ The lowest non-zero calibration point must be at or below reporting limit	Remove allowed points keeping minimum of 3 non-zero points, replace calibration standards if needed and recalibrate instrument.
ICV	After every calibration	90-110%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, and recalibrate the instrument.
ICB	After every ICV	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank and/or increase the rinse time between analyses; reanalyze ICB; if within limits, continue the run; if still outside limits, determine the source of the problem, make the necessary corrections, and start from the beginning with a new calibration.
LLICV	After initial calibration	70-130% Not required for 200.8	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, prepare a fresh calibration blank, and recalibrate the instrument.
CCV	After Every 10 sample or less	90-110%	Recalibrate the instrument. Follow method specific requirements (6020, 6020A or 200.8) as to what data prior to the CCV can be used.
CCB	After Every 10 sample or less	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank; reanalyze CCB; if within limits, continue the run; if still outside limits, eliminate the source of the contamination, clean the sample introduction system if necessary, and recalibrate the instrument. Reanalyze all samples from the last good CCB.
LCS	Every batch of 20 samples or less	85-115%	Re-digest the entire sample batch and reanalyze.
LRB (MB)	Every batch of 20 samples or less	<RL/Dilution factor	Re-digest the entire sample batch and reanalyze.
Dp	Every 10 water samples or every 20 soil samples	0-20%	If all other QC acceptable continue the run; sample result must be flagged; otherwise recalibrate instrument and reanalyze samples.
MS	Every 10 water samples or every 20 soil samples, prior to digestion	75-125%	The sample is spiked and re-analyzed according to Figure 1.
MSD [†]	Every 10 water samples or every 20 soil samples, prior to digestion	0-20%	Same as for duplicate.
Dil [‡]	Once with every batch of 20 samples or less	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.
ICS-A [‡]	Every 12 hours	<RL for water samples Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
ICS-AB [‡]	Every 12 hours	70-135% Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
IS Samples	With every sample	70-125%	Verify matrix interference by ruling out instrument drift by unacceptable IS recoveries in standards. Dilute 4+1 and reanalyze. Repeat until inside control limits.
IS QC Samples	With every QC Sample	80-120% for ICV/ICB and CCV/CCB	For CCV/CCB's recalibrate the instrument and reanalyze the affected samples.

- NOTE:**
- *This is a summary table for more information see Sections 8.4 to 8.10
 - RL = Reporting Limit.
 - Dil = Dilution Test.
 - † MSD optional instead of duplicate sample.
 - ‡ When Method 6020 & 6020A referenced in the analytical report.
 - IS = Internal Standard

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Linear Dynamic Range (LDR) or High-level Check Standard	At initial set-up and checked every 6 months with a high standard at the upper limit of the range.	Within $\pm 10\%$ of true value.	Dilute samples within the calibration range, or re-establish/verify the LDR.	Flagging is not appropriate.	Data cannot be reported above the calibration range without an established/passing high-level check standard.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial Calibration (ICAL) for All Analytes	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, $r^2 \geq 0.99$.	Correct problem, then repeat ICAL.	Flagging is not appropriate.	Minimum one high standard and a calibration blank. No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes, within $\pm 10\%$ of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All reported analytes within $\pm 10\%$ of the true value.	Recalibrate, and reanalyze all affected samples since the last acceptable CCV; or Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects					
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Low-level Calibration Check Standard (Low Level ICV)	Daily.	All reported analytes within $\pm 20\%$ of the true value.	Correct problem and repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the LOQ.
Internal Standards (IS)	Every field sample, standard and QC sample.	IS intensity in the samples within 30-120% of intensity of the IS in the ICAL blank.	If recoveries are acceptable for QC samples, but not field samples, the field samples may be considered to suffer from a matrix effect. Reanalyze sample at 5- fold dilutions until criteria is met. For failed QC samples, correct problem, and rerun all associated failed field samples.	Flagging is not appropriate.	Samples suffering from matrix effect should be diluted until criteria are met, or an alternate IS should be selected.
Method Blank (MB)	One per preparatory batch.	No analytes detected $> \frac{1}{2}$ LOQ or $> 1/10$ the amount measured in any sample or $1/10$ the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank (ICB/CCB)	Before beginning a sample run, after every 10 field samples, and at end of the analysis sequence.	No analytes detected $> \text{LOD}$.	Correct problem and repeat ICAL. All samples following the last acceptable calibration blank must be reanalyzed.	Flagging is not appropriate.	Results may not be reported without a valid calibration blank. For CCB, failures due to carryover may not require an ICAL.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects					
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Interference Check Solutions (ICS) (also called Spectral Interference Checks)	After ICAL and prior to sample analysis.	ICS-A: Absolute value of concentration for all nonspiked project analytes < LOD (unless they are a verified trace impurity from one of the spiked analytes); ICS-AB: Within $\pm 20\%$ of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the failed ICS.	All analytes must be within the LDR. ICS-AB is not needed if instrument can read negative responses.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then re-prepare and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all reported analytes. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes $\leq 20\%$ (between MS and MSD or	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference.

Table 6b. Quality Control Items, Frequency, and Corrective Actions for DoD Projects					
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		sample and MD).			
Dilution Test	One per preparatory batch if MS or MSD fails.	Five-fold dilution must agree within $\pm 10\%$ of the original measurement.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Only applicable for samples with concentrations > 50 X LOQ (prior to dilution). Use along with MS/MSD or PDS data to confirm matrix effects.
Post Digestion Spike (PDS) Addition	One per preparatory batch if MS or MSD fails (using the same sample as used for the MS/MSD if possible).	Recovery within 80-120%.	No specific CA, unless required by the project.	For the specific analyte(s) in the parent sample, apply J flag if acceptance criteria are not met and explain in the case narrative.	Criteria apply for samples with concentrations < 50 X LOQ prior to dilution.
Method of Standard Additions (MSA)	When dilution or post digestion spike fails and if the required by project.	NA.	NA.	NA.	Document use of MSA in the case narrative.

DoD Appendix C LCS Limits
Method 6020 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	78	124
7440-36-0	Antimony	72	124
7440-38-2	Arsenic	82	118
7440-39-3	Barium	86	116
7440-41-7	Beryllium	80	120
7440-42-8	Boron	74	128
7440-43-9	Cadmium	84	116
7440-70-2	Calcium	86	118
7440-47-3	Chromium	83	119
7440-48-4	Cobalt	84	115
7440-50-8	Copper	84	119
7439-89-6	Iron	81	124
7439-92-1	Lead	84	118
7439-93-2	Lithium	75	120
7439-95-4	Magnesium	80	123
7439-96-5	Manganese	85	116
7439-97-6	Mercury	74	126
7439-98-7	Molybdenum	83	114
7440-02-0	Nickel	84	119
7440-09-7	Potassium	85	119
7782-49-2	Selenium	80	119
7440-22-4	Silver	83	118
7440-23-5	Sodium	79	125
7440-24-6	Strontium	75	129
7440-28-0	Thallium	83	118
7440-29-1	Thorium	81	116
7440-29-1	Tin	82	121
7440-32-6	Titanium	83	117
7440-61-1	Uranium	83	120

7440-62-2	Vanadium	82	116
7440-66-6	Zinc	82	119

Method 6020 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
7429-90-5	Aluminum	84	117
7440-36-0	Antimony	85	117
7440-38-2	Arsenic	84	116
7440-39-3	Barium	86	114
7440-41-7	Beryllium	83	121
7440-42-8	Boron	73	130
7440-43-9	Cadmium	87	115
7440-70-2	Calcium	87	118
7440-47-3	Chromium	85	116
7440-48-4	Cobalt	86	115
7440-50-8	Copper	85	118
7439-89-6	Iron	87	118
7439-92-1	Lead	88	115
7439-93-2	Lithium	78	126
7439-95-4	Magnesium	83	118
7439-96-5	Manganese	87	115
7439-97-6	Mercury	70	124
7439-98-7	Molybdenum	83	115
7440-02-0	Nickel	85	117
7440-09-7	Potassium	87	115
7782-49-2	Selenium	80	120
7440-22-4	Silver	85	116
7440-23-5	Sodium	85	117
7440-24-6	Strontium	82	118
7440-28-0	Thallium	82	116
7440-29-1	Thorium	87	121

7440-29-1	Tin	86	115
7440-32-6	Titanium	83	115
7440-33-7	Tungsten	85	122
7440-61-1	Uranium	87	120
7440-62-2	Vanadium	86	115
7440-66-6	Zinc	83	119

[illegible]

Exp. Date: _____

[illegible]

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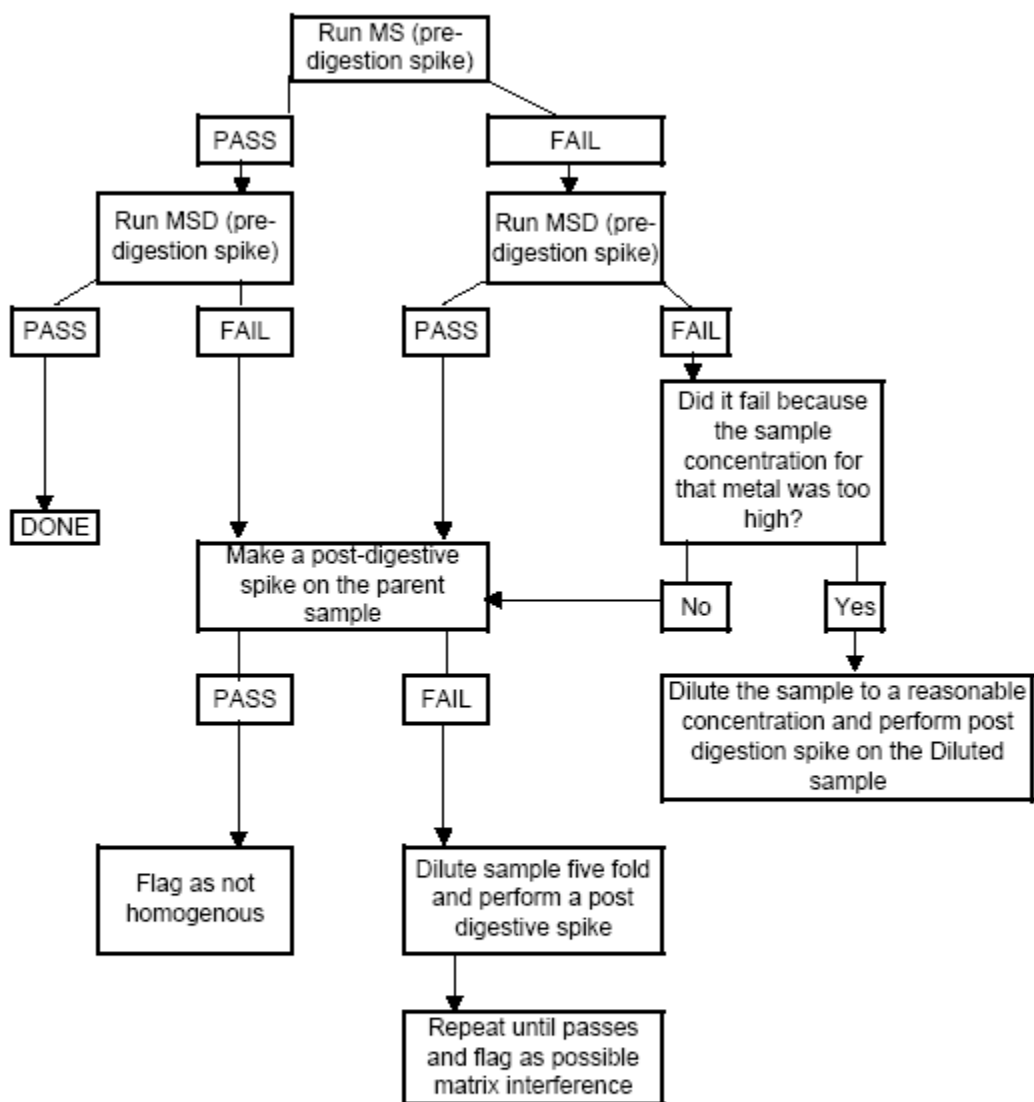
ANALYST

Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria	Pipet #	Test #	Pipet Volume Setting mL	Wt. of water from pipet, g	Criteria
2	1			Bias: Mean $\pm$ 2% of nominal value Precision: RSD $\leq$ 1% of nominal value	3	1			Bias: Mean $\pm$ 2% of nominal value Precision: RSD $\leq$ 1% of nominal value
	2					2			
	3					3			

[illegible]

Reviewed by _____ On _____

FIGURE 4 MS/MSD CORRECTIVE ACTION FLOW CHART





STANDARD OPERATING PROCEDURE

POLYCHLORINATED BIPHENYLS (PCBS) BY GC METHOD 8082A

APPROVALS:

A handwritten signature in cursive script, reading "Barbara Ball".

03/09/2023

QA Officer

Date

A handwritten signature in cursive script, reading "Maya Muehlebach".

03/09/2023

Technical Director

Date

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Number	Description of Change	Date
001-010	Previous changes were not documented	
011	Updated to comply with DoD QSM and ISO 17025 standards.	6/3/11
012	Updated to include 8082A Method references	7/19/11
013	Updated to comply with DoD QSM 5.0 standards.	03/03/16
014	Updated to comply with DoD QSM 5.1 standards.	01/16/18
015	DOD Audit Corrective Action	09/28/2020
016	2020 Internal Audit revisions	02/09/2021
017	Emergency SOP Amendment Form	03/09/2023
018		
019		
020		
021		

1.0 SCOPE AND APPLICATION

This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD). The target compounds listed below may be determined by a dual-column analysis system.

<i>Parameter</i>	<i>CAS #:</i>
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards. Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment.

This method also includes different clean-up procedures used to assist in removing some of the more common found interferences.

This method describes a dual-column GC set up for the determination of total PCB Aroclor concentrations. A hardware configuration of two analytical columns joined to a single injection port is utilized.

The Method Detection Limits (MDLs) for Aroclors are determined annually on all instruments analyzing PCBs. Estimated method detection limits are available on Merit's network and VLIMs.

This method is restricted to use by, or under the supervision of trained analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method as well as a working knowledge of Chrom Perfect and the PCB calculator software.

2.0 SUMMARY OF METHOD

A measured volume or weight of sample (approximately 1 L for liquids, 20 g for soil, and 0.3 g for oil samples) is extracted using the appropriate matrix-specific sample extraction technique^[1].

Note: Unusually contaminated samples may be extracted with lower sample amounts. The reporting limits are corrected accordingly. Sample specific notes are added and samples flagged.

Aqueous samples are extracted at neutral pH with methylene chloride using Merit's SOP #: EXL-003 (PCB Extraction Liquid).

Solid samples are extracted with hexane using Merit's SOP#: EXL-004 (PCB Ultrasonic Extraction Solid) or SOP EXL-017 (PCB Microwave Extraction Solid).

Extracts for PCB analysis are subjected to a sulfuric acid cleanup (Method 3665) designed specifically for PCBs. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, the analysis of pesticides is not covered by this SOP.

After the acid clean-up, a sulfur clean-up is performed. The activated copper reacts with the sulfur interference to form a precipitate (ex. $2RSH + Cu^{++} \rightarrow Cu(SR)^2 + 2H^+$, where R is the organic radical and SH is the mercaptan radical).

After the clean-up procedures, the extract is analyzed by injecting a 1-2 uL aliquot into a gas chromatograph with narrow-bore fused silica capillary column and electron capture detector (GC/ECD).

The chromatographic data is used to determine the seven Aroclors in Section 1.0.

3.0 INTERFERENCES

Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are provided, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.

- ◆ Contaminated solvents, reagents, or sample processing hardware.
- ◆ Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
- ◆ Compounds extracted from the sample matrix to which the detector will respond.

Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.

^[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Liquid Liquid Separatory Funnel Extraction, and, Method 3550C, Ultrasonic Extraction.

- ◆ Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters are minimized by avoiding contact with any plastic materials and checking all solvents and reagents for interferences.
- ◆ Exhaustive cleanup of solvents, reagents, and glassware may be required to eliminate background phthalate ester contamination. These materials can be removed through the use of procedure described in Number 2, Section 7.0 (sulfuric acid/permanganate cleanup), which is required for all PCB analysis.
- ◆ Cross-contamination of clean glassware is avoided by scrupulously cleaning and then baking glassware in a 550°C oven for 4 – 12 hours.
 - Clean all glassware as soon as possible after use by rinsing with the last solvent used. This is followed by detergent washing with hot water, and rinses with tap water and DI water. Drain the glassware, and let dry for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.
 - Elemental sulfur (S₈) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur is removed using procedure described in Section 7.0).

4.0 APPARATUS AND MATERIALS

Gas chromatograph - An analytical system complete with a gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and a data system.

GC columns - The dual-column arrangement used by this method involves a single injection that is split between two columns mounted in a single gas chromatograph. Each column is connected to a separate ECD detector.

- ◆ Narrow-bore columns are installed in split/splitless (Grob-type) injectors.
- ◆ 30m x 0.25mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, 0.25um film thickness).
- ◆ 30m x 0.25mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, 0.25um film thickness)
- ◆ Column pair is mounted in a press-fit Y-shaped glass 3-way fused-silica connector (Supelco)

Column rinsing kit - Bonded-phase column rinse kit.

Glass vials for sample storage, cleaning, and standard preparation.

Hamilton Syringes (1ul to 1000 ul).

Sample Vials: 1.8 ml screw cap with PTFE liner and 4.0 ml calibrated screw cap.

Maintenance Logbook.

Disposable Pipettes.

Beakers.

5.0 REAGENTS

Reagent grade or pesticide grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents must conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

Note: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at $4 \pm 2^{\circ}\text{C}$ in polytetrafluoroethylene (PTFE)-sealed amber containers, or in a dark area. When a lot of standards is prepared, the aliquots of that lot are stored in individual small vials. All stock standard solutions are replaced every 12 months or sooner depending if the QC indicates a problem. All working standard solutions are replaced after six months or sooner if routine QC indicates a problem.

Sample extracts are prepared by liquid - liquid extraction (SOP#: EXL-003 for waster samples or ultrasonic extraction (SOP#: EXL-004) for solid and oil samples. Both procedures undergo a solvent exchange step prior to analysis. The following solvents are necessary for dilution of sample extracts. All solvent lots must be pesticide quality or equivalent.

- ◆ n-Hexane, C_6H_{14} .
- ◆ Methanol, CH_3OH .
- ◆ Acetone, CH_3COCH_3 .
- ◆ Ethyl Ether (6%)

Deionized (DI) Water.

Stock standard solutions (1000 mg/L). Commercially prepared stock standard solutions are used. All standards that are purchased must be certified by the manufacturer or by an independent source.

Calibration standards for Aroclors.

- ◆ A standard containing a mixture of Aroclor 1016 and Aroclor 1260 includes many of the peaks represented in the other five Aroclor mixtures. A multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations demonstrates the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors.
- ◆ The 1016/1260 mixture is used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, if they are present in a sample. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with hexane. The curve concentrations bracket the linear range of the detector. (0.1 to 1.0 ppm, see Table 6).
- ◆ Method 8082A states that: “Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor...The concentrations should correspond to the mid-point of the linear range of the detector.” During a sample batch, if an Aroclor is identified in a sample, a standard of that Aroclor is analyzed. If the standard concentration falls within the control limits for that Aroclor, the sample is quantitated using the 5-point curve for that Aroclor.

Copper balls, pre-cleaned. A method blank must be analyzed demonstrating that there is no interference.

Copper powder.

Sodium Sulfate Na_2SO_4 , pre-cleaned with Methylene Chloride, a method blank must be analyzed demonstrating that there are no interferences.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

All samples are sampled using 1L Amber glass jars or 4 –8 oz. glass jars for solids. Oil and wipe samples must only be collected in glass jars.

Aqueous samples are extracted within 7 days from sample collection. Solid samples must be extracted within 14 days of sample collection.

Extracts are stored under refrigeration at $4 \pm 2^\circ\text{C}$ and are analyzed within 40 days of extraction.

7.0 PROCEDURE

1. Samples are extracted using the SOP#'s EXL-003, EXL-004, or EXL-017.

- ◆ Water samples are extracted at a neutral pH with methylene chloride using a separatory funnel.
- ◆ Solid samples are extracted with ultrasonic extraction.
- ◆ Spiked samples are used to verify the applicability of the selected extraction technique for each new sample type (*i.e.* water, soil, oil, *etc.*). These samples are spiked with Aroclor 1016/1260 mixture at 0.500 mg/l concentration.

2. Extract clean-ups.

- ◆ **Sulfuric Acid Clean-up^[2]:** this method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method is used to reduce elevated baselines in overly complex chromatograms that prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate. (MANDATORY FOR ANALYSIS AND QC SAMPLES)
 - Place up to 2 ml of concentrated sulfuric acid into the final hexane extract 4 ml vial. Make sure this is done only in the hood area. Safety glasses must be worn at all times.
 - Place the cap on the vial and shake the extract with the acid causing a visible vortex. The acid will dissolve and carbonize the interferences commonly found in PCB samples.
 - Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.
 - Allow the phase to separate for at least one minute. Examine the hexane (hexane) layer, it must not be highly colored, nor have a visible emulsion or cloudiness. If a clean phase separation is achieved, proceed to Number 2.
 - If the acid is “carbonized” or turns a dark brown color remove the sulfuric acid layer from the vial and dispose of it properly. Add another portion of the sulfuric acid and repeat bullets three and four under Number 2.
 - Transfer the hexane to a clean 4 ml vial. Take care not to include any of the acid layer in this clean vial, as it can cause damage to the instrumentation. Once the hexane layer is removed, perform a second extraction of the acid layer.

^[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665: Sulfuric Acid
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- Add an additional 1 ml of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitated transfer of the PCBs, when needed. If still dirty, go to the alumina cleanup.

- ◆ **Sulfur Clean-up^[3]:** This clean-up is performed at the GC laboratory station. Elemental sulfur is encountered in many liquid and sediment samples (commonly found in industrial wastes). The solubility of sulfur in various solvents is very similar to the organochlorine compounds of interest. Therefore, the sulfur interference follows along with the target compounds through the normal extraction and Florisil cleanup techniques. Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors. (MANDATORY FOR ANALYSIS AND QC SAMPLES)
 - Add approximately 1g of high grade, activated copper shots or copper powder to the final hexane sample extract. The activated copper is prepared by rinsing the copper with diluted nitric acid, rinsed with acetone and dried before use.
 - Vortex for 1 minute. Allow the copper to settle to the bottom. If a high precipitate occurs, the sample can be centrifuged. If the copper seems to be saturated, more can be added.
 - If copper powder is used, follow Sulfur Clean-up and Alumina Clean-up and then carefully transfer the “cleaned” extract using a disposable pipette into another vial to prevent the “powder” from plugging up the auto syringe.

- ◆ **Alumina Clean-up** is an adsorption technique used when the chromatogram base line is still elevated after the two clean-up procedures listed above were performed. Alumina clean-up^[4] is used to separate the high molecular weight petroleum wastes from PCBs using liquid chromatography.

Alumina Column Clean-up: the column is packed with the required amount of adsorbent, topped with a water adsorbent (Na₂SO₄), and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The elute is then concentrated (if necessary).

^[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.

^[4] Reference for Alumina clean-up is SW-846, Revision 3, December 1996 Method 3611B: Alumina Column Clean-up & Separation of Petroleum Products.

- Place a clean glass wool plug in the bottom of a 50 ml disposable chromatographic column.
- On top of this plug, add 2 cm of anhydrous Na_2SO_4 and tap it down.
- Pour about 10 g of activated (130°C for 12 hours) Alumina (150 mesh) into the column.
- Tap it down and place 2 cm of anhydrous (130°C for 12 hours) Na_2SO_4 on top of the Alumina.
- Rinse the column with 25 ml hexane.

Note The column must not be allowed to become dry throughout the rest of the analysis. The disposable column will stop flowing naturally when the solvent level is at the top of the Na_2SO_4 .

- Using a long pasture pipette, place the sample extract on the column followed by rinse of the sample vial and the column with 2 ml hexane.
- Wash the column with 20 ml hexane and place the eluted hexane in a beaker labeled “Dirty Used Hexane”. This washes the aliphatic interferences out of the sample.
- Elute 20 ml 6% ethyl ether in hexane through the column and collect it for the analysis of PCBs.
- Elute 20 ml 6% ethyl ether in hexane again for a total of 40 ml of sample
- Concentrate the eluted hexane to 0.5 ml inside the Zymark Evaporation Station.
- Transfer it quantitatively to a graduated 4 ml vial rinsing the evaporating tube with 0.5 ml hexane, bringing the volume of cleaned sample in the vial to 1 ml.
- Add 2 ml Sulfuric Acid (H_2SO_4) (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds.*
- Record alumina cleanup on bench sheet.

- ◆ **Dioxin cleanup:** This cleanup is similar to alumina but with a finer mesh column. The columns are pre-made and located in second drawer under the glassware ovens in the organic prep lab.

- Set up is the same as alumina, except the columns are pre-made and placed in the slots in back.
- Place clean beakers under the columns. All solvent extracted in this process will be kept. Label beakers with sample ID #.
- Flush column with 150 ml hexane, and collect the flushed hexane.
- Add sample to column, place columns over evaporation tubes, and flush column with collected hexane (120 ml)
- Evaporate samples in the evaporation tubes to make room for additional hexane.
- Once sufficiently evaporated, place tube back under the respective column and add 120 ml more of Hexane for a total of 240 mL hexane.
- Evaporate to 0.5 ml, transfer and adjust to final of 1 ml of sample and analyze.
- Add 2 ml Sulfuric Acid (H₂SO₄) (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds.*
- Record dioxin cleanup on bench sheet and write “dx” on sample label.

3. GC conditions.

- ◆ **Dual-column analysis:** The dual-column/dual-detector has two 30m x 0.25mm ID fused-silica open-tubular columns of different polarities, and thus has different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors. For types of columns see Table 1.
- ◆ GC temperature programs and flow rates are listed in Table 1.

4. Calibration.

- ◆ Prepare calibration standards as described in the standard preparation logbook for PCBs/Pesticides (See Table 6). Both initial calibration and calibration verification standards are prepared using two different vendors to insure the quality and correctness of the standards.

Note: Prior to calibration, GC operating conditions must be established which optimize both peak resolution and sensitivity. The total run time must be long enough permit the elution of the second surrogate standard (DCBP). Once established, the same operating conditions must be used for both calibrations and sample analyses.

Note: Because of the sensitivity of the electron capture detector, the injection port and column must always be cleaned prior to performing the initial calibration.

- ◆ PCBs are quantitatively determined as Aroclors. The initial calibration consists of the following protocols:
 - o A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Therefore, this mixture of 1016/1260 is used to demonstrate the linearity of the detector (RPD value of the curve) and that a sample does *not* contain peaks that represent any one of the Aroclors. This standard is also used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, if they are present in a sample. Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260.
 - o Standards of the other five Aroclors are necessary for pattern recognition. SW 846 states: “These standards are also used to determine a single-point calibration factor for each Aroclor... The Aroclor 1016/1260 mixture is used to determine correct detector response.” Positive identification of Aroclors other than 1016 or 1260, require the appropriate Aroclor standard to be run and samples re-analyzed.
 - o In situations where only a few Aroclors are of interest for a specific project, the analyst can use a five-point initial calibration of each of the Aroclors of interest (*e.g.*, five standards of Aroclor 1254 if this Aroclor is of concern) and not use the 1016/1260 mixture.
- ◆ An auto sampler is used to inject 1-2uL volumes of each calibration standard. Depending on the volume of sample injected (*i.e.* 1 or 2 uL), the initial calibration, the QC samples, and samples must be analyzed with the same injection volume.
- ◆ Record the peak area for each characteristic Aroclor peak to be used for quantitation using the Chrom Perfect Software.
- ◆ A minimum of three peaks is chosen for each Aroclor, and preferably 5 peaks (See Table 2 for Quantification Peaks). The peaks are characteristic of the Aroclor in question. If possible, choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of three to five peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.

- ◆ Tables 2a and 2b list recommended diagnostic peaks in each Aroclor, along with their retention times on two GC columns suitable for dual-column analysis.
- ◆ Calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

- ◆ Calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. The PCB calculator initial calibration report is generated which involves the calculation of the mean calibration factor, the standard deviation, and the relative standard deviation (RSD) for each Aroclor. The RSD for a given calibration range must be $\leq 20\%$ in order to employ the calibration method described in the seventh main bullet under Number 6.^[5]
- ◆ A better representation of the calibration data may be obtained by narrowing the calibration range (by lowering the upper level standard) or by using a least-squares regression in accordance with SW-846, Method 8000. A linear regression may be used with a 5-point calibration curve, and the coefficient of determination (C.O.D.) must be > 0.99 . Additional standards must be analyzed in order to utilize a non-linear calibration (*see* Method 8000). All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior.

5. Retention Time Windows.

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. The width of the retention time window is established by analyzing successive calibration standards of the same Aroclor mixture. The standard deviation (σ) of these repeated measurements is used to determine this window. The window is defined as the mean retention time $\pm 3\sigma$. The results of this analysis are contained in Table 3. Given that the maximum window for an individual PCB is approximately 0.08 min., a nominal identification window of 0.1 minutes is utilized for all PCBs.

6. Gas chromatographic analysis of sample extracts.

^[5] Reference for RSD values is SW-846, Revision 3, December 1996 Method 8000B Determinative Chromatographic Separations

- ◆ The same GC operating conditions used for the initial calibration are used for sample analyses and calibration verification.
- ◆ An analytical sequence of laboratory samples and QC samples is templated using the following:
 - Calibration verification mixture (1016/1260)
 - Laboratory control sample
 - Blank
 - Reagent Blank
 - Up to 20 samples
 - Duplicate sample
 - Matrix spike and/or matrix spike duplicate sample
 - Batch-terminating standard.
- ◆ Verify the calibration each 12-hour shift by injecting a calibration verification standard prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples. The calibration verification standard is a mixture of Aroclor 1016 and Aroclor 1260 from a different source than the initial calibration standards.
- ◆ The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than ± 20 % when compared to the mean calibration factor from the initial calibration curve:
$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$
- ◆ Corrective action: if this criterion is exceeded for any calibration factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements based on the last initial calibration, then a new initial calibration must be performed. Please refer to Table 8 Quality Control Items, Frequency and Corrective Action.
- ◆ Inject a 1-2 uL (third main bullet under Number 6) aliquot of the concentrated sample extract.

- ◆ Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in Number 9.
 - ◆ Quantitative results are determined for each identified Aroclor, using the procedures described in Number 10. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.
 - ◆ Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.
 - ◆ A batch of 20 sample injections (including QC samples, see above) may continue as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. A smaller batch than 20 samples can be analyzed in order to minimize the number of samples that must be re-injected if the standards fail the QC limits. The sequence ends when the set of samples has been injected or when quantitative QC criteria are exceeded.
 - ◆ If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample or additional clean-ups are warranted.
 - ◆ Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.
7. Qualitative Identification (The equations governing the quantification, recovery and precision are referenced in the glossary section of the QA/QC manual).
- ◆ The identification of PCBs as Aroclors using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention times and windows established through the analysis of standards of the target analytes (*see* Tables 2a, 2b, and 3).
 - ◆ Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification is confirmed using a second GC column of dissimilar stationary phase (as in

the dual-column analysis), based on a clearly identifiable Aroclor pattern. The second column is calibrated and utilized for purposes of qualitative identification only.

- ◆ Tentative identification of an Aroclor pattern is based upon an approximate match of the relative characteristic peak heights between the sample and reference standard. Use the individual Aroclor standards (not the 1016/1260 mix) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 are evident in the mixed calibration standards (See Figure 1).
- ◆ Positive identifications require a second column confirmation. Both QC samples and calibrations are verified with the second (confirmation) column.
- ◆ Project-specific requirements must be followed when reporting data. If project-specific requirements have not been specified, method requirements must be followed. If the method does not include reporting requirements, then report the results from the primary column or detector, unless there is a scientifically valid and documented reason for not doing so.

8. Quantitation of PCBs

- ◆ The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.
- ◆ The characteristic quantitative peaks for each Aroclor are listed in Tables 2a and 2b and illustrated in Figure 1. The amount of Aroclor is calculated using the 5-point calibration curve for each of the 3 to 5 characteristic peaks chosen. The concentration is determined using the average concentration for each of the characteristic peaks.
- ◆ In the event that the data system is unable to properly integrate the peaks of interest (typically due to peak co-elution or matrix interference), a manual integration procedure is performed. The applicability, procedure, and documentation of the manual integration are addressed in the SOP Manual Integration of Chromatographic Data # ORL-003.
- ◆ Compound identifications are supported by at least one additional qualitative technique (i.e., second column confirmation).
 - For Ohio VAP samples and DoD Projects, both columns must meet the calibration and QC criteria.

- ◆ The second column quantitation can be applied upon request to any project. In this case, all QC requirements listed above are applied to each set of chromatographic data. PCB concentrations from each column are reported.

Note: Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems.

9. Chromatographic System Maintenance as Corrective Action.

- ◆ When system performance does not meet the established QC requirements, corrective action is required, and can include one or more of the following.
 - Splitter connections for dual columns which are connected using a press-fit a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent back-flush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.
- ◆ Metal injector body.
 - Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.
 - Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.
 - Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.
- ◆ Column rinsing.
 - The column is rinsed with hexane.

10. Calculations

Relative Percent Difference:

$$RPD = \frac{(S - D)}{\left[\frac{S + D}{2} \right]} \times 100$$

Where: S = Initial sample result
D = Duplicate sample result

Spike Recovery Percent Recovery: $\frac{SSR - SR}{SA} \times 100$

Where: SSR = Spike sample result
SR = Sample (unspiked) result
SA = Spike added

8.0 QUALITY CONTROL

Quality control procedures necessary to evaluate the GC system operation include evaluation of retention time windows, calibration verification and chromatographic analysis of samples are listed in Table 8a and 8b. In addition the tables indicate the frequency of the QC item along with the course of corrective action.

The QC Reference Sample is a sample that is analyzed prior to any analysis to demonstrate the initial proficiency of the analyst or the instrument. In cases when a new instrument is introduced or a new analyst, this sample when analyzed within the control limits of $\pm 20\%$ demonstrates the initial proficiency of the method. The QC reference sample must be spiked with in the linear calibration range. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260.

Method Detection Limit (MDL). The MDL is performed annually based on the procedure in SOP # QA-009. MDL are available on Merit's network and in VLIMS.

Accuracy & Precision - Accuracy & Precision are determined for sample matrices of interest by computing the mean recovery and relative standard deviation of the LCS analysis. The upper and lower control limits for matrix spike recovery are determined as the mean $\pm 3\sigma$. The results for the water and solid matrices are given in Table 4.

The Continuing Calibration Verification (CCV) concentrate must contain PCBs as Aroclors at mid-point of the curve. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the CCV.

- ◆ The frequency of analysis of the CCV analysis is equivalent to a minimum of 1 per 12 hours not to exceed 20 samples between CCVs. A closing calibration verification is required at the end of the run.

- ◆ If the averaged recovery of compounds found in the CCV is less than 80% or greater than 120% of the true value, the laboratory performance is judged to be out of control, and the problem must be corrected. Please refer to Table 8 Quality Control Items, Frequency and Corrective Action.
- ◆ Include a calibration standard after each group of 20 samples. The response factors for the calibration must be within 20 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory must halt the analysis and take corrective action. Please refer to Table 8a and 8b Quality Control Items, Frequency and Corrective Action.

Sample Quality Control for Preparation and Analysis – A batch includes the analysis of QC samples including a method blank, a matrix spike, matrix spike duplicate and/or a duplicate (per client request), and a laboratory control sample (LCS). Surrogates are added to each field and QC sample.

- ◆ Documenting the effect of the matrix must include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories must use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors must be used for spiking. If samples are expected to contain target analytes, then laboratories can use one matrix spike and a duplicate analysis of an unspiked field sample.
- ◆ If a sample is qualitatively identified as having an Aroclor which was *not* analyzed as part of the QC samples, the sample is subsequently re-analyzed along with a calibration check standard of the appropriate type.
- ◆ A Laboratory Control Sample (LCS) is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

Surrogate recoveries - Surrogate recovery data is analyzed from individual samples in order to determine matrix-specific control limits. The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). TCX will be evaluated on a client/project specific basis. The surrogate standard is prepared by the GC analyst at a concentration of 0.03mg/l. and utilized by the extraction analyst. Table 5 contains surrogate recovery data and laboratory-established control limits, and is

inclusive of the effect of copper and sulfuric acid clean-up procedures. The surrogate standards are calibrated using a 5-point curve.

The MS/MSD and LCS spikes contain a mixture of Aroclor 1016/1260. This spike must be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.5mg/l.

The analyst will follow SOP# QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

Laboratory specific data are provided in this document.

The MDLs and PQLs can be found on Merit's network and in VLIMs.

Table 5 presents the lower and upper acceptance criteria for all surrogates.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings must be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual must be followed. Maintenance includes: clipping/replacing the column, replacing the heat detector, solvent backflushing, cleaning injector port, and replacing the calibration standard. Refer to Number 9 in Section 7.0 for specific procedures.

Computer software and firmware can be found on Merit's network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has an eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit. A reference file of material safety data sheets (MSDSs) is available to all personnel.

Specific attention be paid (but not limited) to:

- ◆ Sodium sulfate is mildly toxic by ingestion, not considered an explosion hazard, and oxides of sulfur and sodium may form when heated to decomposition. Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from incompatible substances.

Containers of this material may be hazardous when empty since they retain product residues (dust, solids); observe all warnings and precautions listed for the product.

- ◆ Hexane is extremely flammable liquid and vapor, causes irritation to skin, eyes, and respiratory tract, and overexposure may cause lightheadedness, nausea, headache, and blurred vision. Above flash point, vapor-air mixtures are explosive within flammable limits. Contact with oxidizing materials may cause extremely violent combustion. Sensitive to static discharge.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested) and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

Matrix Spike (MS): an aliquot of sample spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): intra-laboratory split samples spiked with 1016/1260 Aroclors (unless a specified Aroclor(s) is requested). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Method Reporting Limit (MRL): the method reporting limit is a threshold value below which the laboratory reports a result as non-detect. The highest value reported for the method reporting limit is dependent upon

project-specific action or decision levels. Method reporting limits are adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

Method Detection Limit (MDL): the method detection limit is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. Depending on project specifics, MDLs will be in the form of a MDL check standard or the MDL is subject to extraction procedures. An acceptable MDL standard check must produce a signal at least three times the instrument's noise level. Also, a MDL check injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Surrogate (SURR): an organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The surrogates are; 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl.

Initial Calibration (ICAL): an analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of Aroclors 1016/1260. This relationship is depicted graphically, and referred to as a "calibration curve". Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte. Alternative ICALs for Aroclors can be substituted for the 1016/1260 ICAL if specified by project or program.

Initial Calibration Verification (ICV): the initial calibration verification standard (different lot # or manufacture from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): a standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, ISO/IEC 17025:2005, ISO/IEC 17025:2017 and The NELAC Institute (TNI) Standards, Volume 1, September 2009, Version 5.3, May 7, 2019

USEPA, SW-846, Revision 3; Method 3510C.

USEPA, SW-846, Revision 2; Method 3550B.

USEPA, SW-846, Revision 1; Method 3665A.

USEPA, SW-846, Revision 2; Method 3611B.

USEPA, SW-846, Revision 2; Method 3660B.

USEPA, SW-846, Revision 2; Method 8000B.

USEPA, SW-846, Revision 1; Method 8082A.

Varian/Brueker User Manual 450 GC.

Table 1. GC Operating Conditions For PCBs As Aroclors (Dual Column)

<i>Property</i>	<i>Setting</i>
Column #1	DB-5, 30m x 0.25mm ID, 0.25µm film thickness
Column #2	DB-608, 20 m x 0.25 mm ID, 0.25 µm film thickness
Carrier gas flow (He)	6ml/min
Makeup gas flow (N ₂)	20ml/min
Temperature program	T _o = 180°C, hold 1.0min 180°C to 250°C, ramp at 6.0°C/min T _f = 250°C, hold 2.34min
Injector temperature	250°C
Detector temperature	320°C
Injection volume	1-2 µl, no air plug
Solvent	Hexane
Injector	On-column
Detector	Dual ECD
Range attenuation	10/8
Splitter	Supelco press-fit Y-shaped inlet splitter

Table 2a. Summary of Characteristic PCB Peak Retention Times (DB-5 Column) used for quantitation

<i>Peak</i>	<i>1016</i>	<i>1221</i>	<i>1232</i>	<i>1242</i>	<i>1248</i>	<i>1254</i>	<i>1260</i>
1	3.20	2.53	2.68	3.04	3.46	4.34	5.10
2	3.45	2.61	3.46	3.21	4.07	4.56	5.33
3	3.54	2.67	3.55	3.46	4.32	4.88	5.57
4	3.61		3.61	3.55	4.35	5.12	6.17
5	4.06		4.07	4.07	4.50	5.57	6.42

Table 2b. Summary of Characteristic PCB Peak Retention Times (DB-608 Column)

<i>Peak</i>	<i>1016</i>	<i>1221</i>	<i>1232</i>	<i>1242</i>	<i>1248</i>	<i>1254</i>	<i>1260</i>
1	3.11	2.89	3.11	3.53	3.88	4.90	5.62
2	3.52	3.04	3.52	3.89	4.51	4.96	5.70
3	3.88	3.10	3.88	4.04	4.77	5.45	6.14
4	4.04		4.04	4.77	4.82	5.56	6.60
5	4.17		4.82	4.82	5.45	6.10	7.02

Table 3. Retention Time Extraction Windows

<i>Aroclor</i>	<i>Main Peak Retention Time</i>			σ (min)	<i>Window (min)</i>
PCB-1016	3.459	3.455	3.45	0.004509	±0.013527
PCB-1260	5.567	5.572	5.564	0.004041	±0.012123

Table 4. Matrix Spike Accuracy and Precision Data

<i>Aroclor</i>	<i>Matrix</i>	<i>Spike</i>	<i>n</i>	<i>%Rec.</i>	<i>%RSD</i>	<i>LCL(%)</i>	<i>UCL(%)</i>	<i>LCL(%)</i>	<i>UCL(%)DOD</i>
							)	DOD	
PCB-1016/1260	Water	0.5 µg/l	457	91.4	10.8	59.1	123.7	46/45	129/134
PCB-1016/1260	Soil	25.0 µg/kg	567	88.2	11.8	52.9	123.4	47/53	134/140

Key:
n: number of runs
% Rec: % Recovery
% RSD: % Relative Standard Deviation
LCL: Lower Control Limits
UCL: Upper Control Limits

Table 5. Surrogate Standard Recovery Ranges

<i>Compound</i>	<i>Matrix</i>	<i>Spike</i>	<i>n</i>	<i>%Rec.</i>	<i>%RSD</i>	<i>LCL(%)</i>	<i>UCL(%)</i>	<i>LCL(%)</i>	<i>UCL (%)</i>
							)	DOD	DOD
TCX (Tetrachloro-m-xylene)	Water	0.01 µg/l	845	85.7	16.8	34.1	137.1	44	130
	Soil	0.50 µg/kg	445	82.6	16.8	33.0	135.3		
DCBP (Decachlorobiphenyl)	Water	0.01 µg/l	810	81.9	18.8	30.0	138.6		
	Soil	0.50 µg/kg	393	81.8	18.8	30.0	137.0		

Key:
n: number of runs
% Rec: % Recovery
% RSD: % Relative Standard Difference
LCL: Lower Control Limits
UCL: Upper Control Limits

Table 6. Calibration Concentration Mixtures

<i>Aroclor</i>	<i>C₁ (ppm)</i>	<i>C₂ (ppm)</i>	<i>C₃ (ppm)</i>	<i>C₄ (ppm)</i>	<i>C₅ (ppm)</i>
PCB-1016	0.1	0.3	0.5	0.8	1.0
PCB-1221	0.1	0.3	0.5	0.8	1.0
PCB-1232	0.1	0.3	0.5	0.8	1.0
PCB-1242	0.1	0.3	0.5	0.8	1.0
PCB-1248	0.1	0.3	0.5	0.8	1.0
PCB-1254	0.1	0.3	0.5	0.8	1.0
PCB-1260	0.1	0.3	0.5	0.8	1.0
PCB-1016/1260 [†]	0.1	0.3	0.5	0.8	1.0

[†]: The concentration for the 1016/1260 mixture is the concentration of each Aroclor.

Table 7. Standard Preparation for Calibration Mixtures

Mixture Volume: 1000 ul
Mixture Concentration: 100 mg/l
Mixture Name: **PCB 1016/1260**

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016	1000	100	100.00
PCB 1260	1000	100	100.00
Solvent - Hexane			800.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.5 mg/l**

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.5	5.00
TCX/DCBP	1.0	0.006	6.00
Solvent - Hexane			989.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.1 mg/l**

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.1	1.00
TCX/DCBP	1.0	0.002	2.00
Solvent - Hexane			997.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.8 mg/l**

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.8	8.00
TCX/DCBP	1.0	0.008	8.00
Solvent - Hexane			984.00

Mixture Volume: 1000 ul
Mixture Concentration: **0.3 mg/l**

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.3	3.00
TCX/DCBP	1.0	0.004	4.00
Solvent - Hexane			993.00

Mixture Volume: 1000 ul
Mixture Concentration: **1.0 mg/l**

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	1	10.00
TCX/DCBP	1.0	0.010	10.00
Solvent - Hexane			980.00

Table 8. Quality Control Items, Frequency and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (IC)	Prior to all analytical runs	Method-based	Examine the entire analytical system; perform some or all of the following: clip/replace column, replace heat detector, change injection septum, replace calibration standards, re-calibrate.
Continuing Calibration (CCV)	20 Samples / 12 hours	80 – 120%	Examine the entire analytical system; perform some or all of the following: clip/replace column, replace heat detector, change injection septum, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Table 4	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	≤20% RPD	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	< Reporting Limit	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated extraction glassware should result in a thorough re-cleaning of the affected glassware. If the method blank contamination for a batch is above the reporting limit, the blank should be re-extracted and re-analyzed. If additional sample exists, the samples associated with a failed, re-extracted blank should also be re-extracted and re-analyzed.
Surrogate Standard	All samples	Table 5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Breakdown check(Endrin/DDT Method 8081 only)	Before sample analysis and at the beginning of each 12-hour shift.	Degradation of DDT and Endrin must each be $\leq 15\%$.	Correct problem, then repeat breakdown checks.	Flagging is not appropriate.	No samples shall be run until degradation of DDT and Endrin is each $\leq 15\%$.
Initial Calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	ICAL must meet one of the three options below: Option 1: RSD for each analyte $\leq 20\%$; Option 2: linear least squares regression for each analyte: $r^2 \geq 0.99$; Option 3: non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. Quantitation for multicomponent analytes such as chlordane, toxaphene, and Aroclors must be performed using a 5-point calibration. Results may not be quantitated using a single point. No samples shall be analyzed until ICAL has passed.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and surrogate.
Retention Time (RT) window width	At method set-up and after major maintenance (e.g., column change).	RT width is ± 3 times standard deviation for each analyte RT from the 72-hour study or 0.03 minutes, whichever is greater.	NA.	NA.	Calculated for each analyte and surrogate. Only applicable if internal standard calibration is not used.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source standard prior to sample analysis.	All reported analytes within established RT windows. All reported analytes within $\pm 20\%$ of true value.	Correct problem, rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing Calibration Verification (CCV)	Before sample analysis, after every 10 field samples, and at the end of the analysis sequence with the exception of CCVs for Pesticides	All reported analytes and surrogates within established RT windows. All reported analytes and surrogates within $\pm 20\%$ of true value.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

	multi-component analytes (i.e. Toxaphene, Chlordane and Aroclors other than 1016 and 1260), which are only required before sample analysis.		fails, or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	results for the specific analyte(s) in all samples since the last acceptable calibration verification.	
Internal Standards (IS)	If employed, every field sample, standard, and QC sample.	Retention time within ± 0.06 RRT UNITS from retention time of the midpoint standard in the ICAL; Internal standard signal (area or height) within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the Case Narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging is not appropriate for failed standards.	NA.
Method Blank (MB)	One per preparatory batch.	No analytes detected $> 1/2$ LOQ or $> 1/10^{\text{th}}$ the amount measured in any sample or $1/10^{\text{th}}$ the regulatory limit, whichever is greater.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

				preparatory batch.	
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference (i.e., matrix effect or analytical error).
Matrix Spike Duplicate (MSD) or Matrix Duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. RPD $\leq$ 30% (between MS and MSD or sample and MD).	Examine the project specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate Spike	All field and QC samples.	QC acceptance criteria specified by the project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed.	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available.	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

Table 8b: Quality Control Items, Frequency and Corrective Action for DoD Projects

			If obvious chromatographic interference is present, reanalysis may not be necessary, but the client must be notified prior to reporting data, and the failures must be discussed in the Case Narrative.		
Confirmation of positive results (second column)	All results > the DL must be confirmed (except for single column methods such a TPH by Method 8015 where confirmation is not an option or a requirement).	Calibration and QC criteria for second column are the same as for initial or primary column analysis. Results between primary and secondary column RPD $\leq$ 40%.	NA.	Apply J-flag if RPD > 40%. Discuss in the case narrative.	Use project-specific reporting requirements if available; otherwise, use method requirements if available; otherwise report the result from the primary column.

DoD Appendix C LCS Limits

Method 8082 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
12674-11-2	Aroclor 1016	47	134
11097-69-1	Aroclor 1254	67	135
11096-82-5	Aroclor 1260	53	140
877-09-8	Tetrachloro-m-xylene	44	130

Method 8082 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
12674-11-2	Aroclor 1016	46	129
11097-69-1	Aroclor 1254	34	127
11096-82-5	Aroclor 1260	45	134

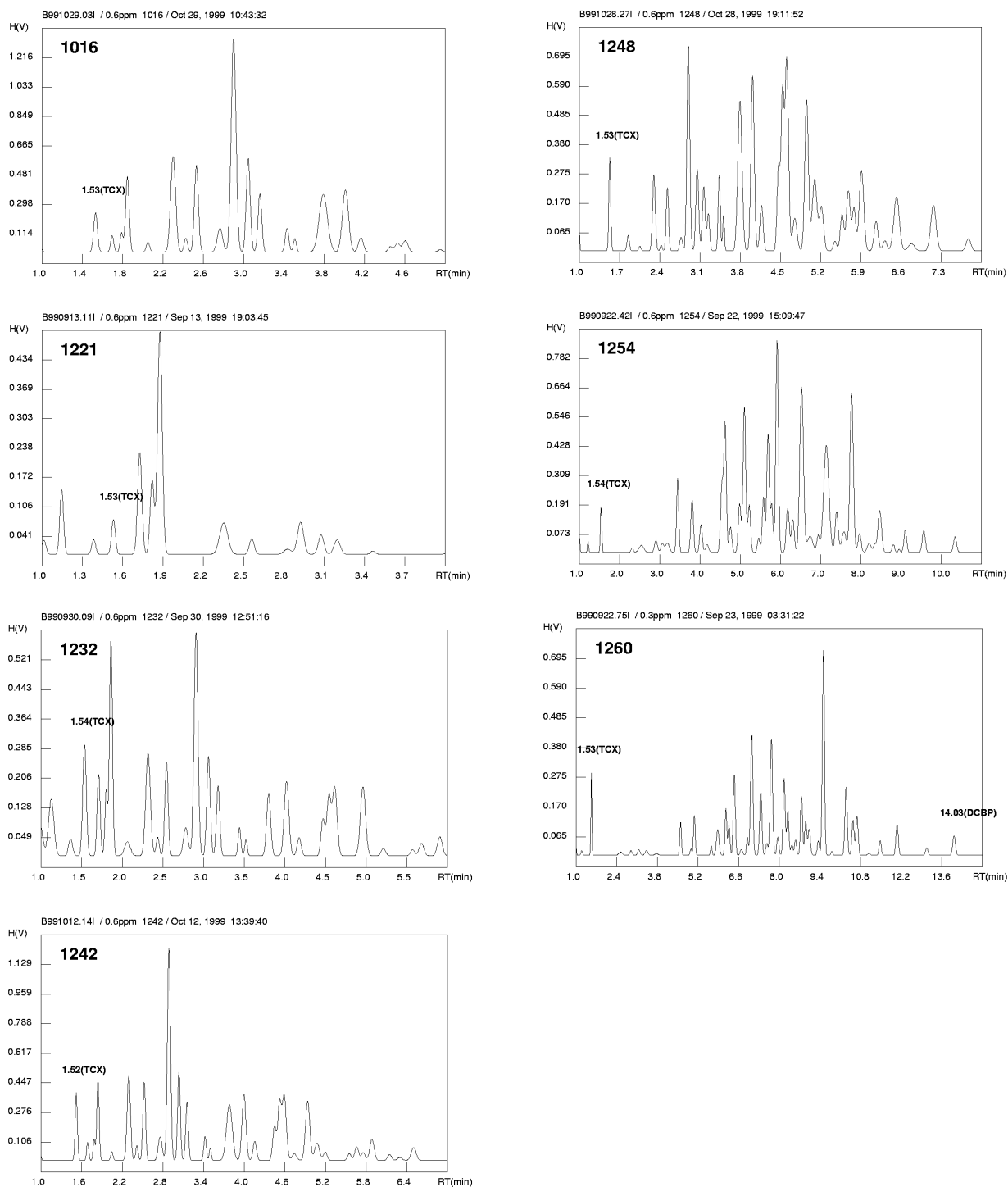


Figure 1. Example Aroclor chromatographic patterns from midpoint calibration standards for PCB 1016, 1221, 1232, 1242, 1248, 1254, and 1260 (column DB-5).

STANDARD OPERATING PROCEDURE

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
METHOD SW-846 8270D/ EPA METHOD 625.1

APPROVALS:

Barbara Ball

02/09/2021

QA Officer

Date

Maya Muehle

02/09/2021

Technical Director

Date

Number	Description of Change	Date
001-010	Previous revisions not documented	
011	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
012	Updated to method 8270D	9/4/13
013	Emergency SOP Amendment Form updates	2/9/16
014	Updated to comply with DoD QSM 5.0 standards.	04/01/16
015	Updated to comply with DoD QSM 5.1 standards.	01/16/18
016	NY NELAC Audit Finding	03/13/19
017	DOD Audit Corrective Action	09/29/2020
018	2020 Internal Audit revisions	02/09/2021
019		
020		

1.0 SCOPE AND APPLICATION

- 1.1 This SOP can be used to quantitate most basic, neutral and acidic organic compounds (BNAs) that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons (PNAs), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. This SOP is applicable to groundwater, surface water, aqueous sludges, water oily solvents, wastes, soil and sediment samples. See Tables 1a and 1b for a list of compounds (along with their characteristic ions) that have been evaluated.
- 1.2 In most cases, this method is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, *etc.*, because of limited sensitivity for those analytes. When these analytes have been identified by another technique, this method is appropriate for confirmation of the presence of these analytes when concentration in the extract permits.
- 1.3 The following compounds may require special treatment when being determined by this method:
- Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.
 - Under the alkaline conditions of the extraction step from aqueous matrices, α -BHC, β -BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.
 - Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
 - N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
 - N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
 - Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline,

4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the gas chromatograph (GC) system is contaminated with high boiling material.

- Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.
- In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.

1.4 The practical quantitation limits (PQL) for determining an individual compound is approximately 330 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples. PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

- *Method Detection Limits (MDL) and Practical Quantitation Limits (PQL) are available in Merit's LIMs system.*

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF THE METHOD

2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Methods 3500, 3510C, 3535A, 3546, & 3550C).

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a GC with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards.

Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point (or more) calibration curve.

- 2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

- 3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.
- 3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. This is virtually never a problem for direct injection GC/MS analysis, provided that the sample syringe is rinsed with solvent between sample injections. If carryover is suspected, questionable samples should be re-injected after the system has been demonstrated to be free of contamination.

4.0 APPARATUS AND MATERIALS

Gas chromatograph/mass spectrometer system

- 4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
- 4.1.2 Column - 30 m × 0.25 mm ID × 0.5 µm film thickness silicone-coated fused-silica capillary column (Hewlett Packard HP-5ms SV or equivalent).
Column - 30 m × 0.25 mm ID × 0.25 µm film thickness silicone-coated fused-silica capillary column.
- 4.1.3 Mass spectrometer capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 4 when 1 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP)
- 4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and

achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.

4.1.5 Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

4.2 Syringes - 5 to 1000 μ L Hamilton syringes are used in the preparation of standards, spiking solutions, and standards.

4.3 Balance - Analytical, capable of weighing 0.0001 g.

4.4 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

4.5 Maintenance logbooks

5.0 REAGENTS

5.1 Reagent grade organic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

5.3 Stock standard solutions

5.3.1 Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.

5.3.2 Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a stock solution of 1000 to 10000 mg/L).

5.3.3 Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.

5.3.4 Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicates a problem.

5.4 Internal standard solutions - The internal standards used are 1,4-Dichlorobenzene-d₄, Naphthalene-d₈, Acenaphthene-d₁₀, Phenanthrene-d₁₀, Chrysene-d₁₂, and Perylene-d₁₂

(see Table 2a). Internal standards are spiked into the sample extracts and calibration standards at a uniform concentration of 40 ng/μL ($\equiv$ 40 mg/L).

- 5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP), pentachlorophenol, and benzidine is used to evaluate GC/MS tuning criteria, injection port inertness, and GC column performance.
- 5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. If possible, the lowest calibration standard corresponds to a sample concentration at or below the standard reporting limit. The remaining standards should correspond to the working range of the GC/MS system (10-100 ng/μL for BNAs, and 2-100 ng/μL for PNAs). Each standard should contain each analyte for detection by this method. The preparation instructions for the creation of calibrations standards from stock solutions commonly used in BNA and PNA analysis can be found in the SVOC.QC-Reference Document.
- 5.7 Surrogate standards - The surrogates used are Phenol-d₆, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitrobenzene-d₅, 2-Fluorobiphenyl, and p-Terphenyl-d₁₄. See Method 3500 for instructions on preparing the surrogate solutions. For BNA analysis, all six surrogate standards are used. For PNA analysis, only Nitrobenzene-d₅, 2-Fluorobiphenyl, and p-Terphenyl-d₁₄ are used.
 - 5.7.1 Surrogate spiking mixes are created at 100 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract as 100ng/μL.
 - 5.7.2 Surrogate Standard Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.
- 5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard is used as the laboratory control standard (LCS).
 - 5.8.1 Matrix spiking mixes for single component analytes are generally created at 50 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract is 50ng/μL.
 - 5.8.2 Matrix Spike Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of matrix spike standards. It is

recommended that this check be done whenever a new matrix spiking solution is prepared.

- 5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.

6.0 SAMPLE HANDLING AND PRESERVATION

Unanalyzed samples are refrigerated at 4 ± 2 degrees Celsius and protected from light in amber sealed containers.

Aqueous samples are shall be extracted within 7 days from sample collection and analyzed within 40 days from extraction.

Soil samples shall be extracted within 14 days from sample collection and analyzed within 40 days thereafter.

7.0 PROCEDURE

Sample preparation

- 7.1.1 Soil and water are prepared via an extraction procedure (*cf.* SW-846 Methods 3500, 3510C, 3535A, 3546, & 3550C; SOPs# EXL-005, EXL- 006, EXL-018, & EXL-019) prior to GC/MS analysis.
- 7.1.2 In cases where the sample is an oil or solvent, the sample is simply diluted with methylene chloride and analyzed at a concentration appropriate for the level of analytes/interferences in the sample. In this situation, the sample is reported on a weight basis and analyzed in a batch of soil samples.
- 7.2 GC/MS operating conditions - see Table 3 for routine operating conditions for both BNA and PNA analysis.
- 7.3 Initial calibration
- 7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP prior to the analysis of calibration standards and samples.
- 7.3.1.1 In the absence of any other manipulations, evaluate the mass spectrum of the highest intensity level from the total ion chromatogram for the DFTPP peak. This is the default approach used.

- 7.3.1.2 If the above evaluation is adversely affected by ion peak asymmetry or background contamination, average the three highest intensity scans for the DFTPP peak. Perform a background subtraction with a spectrum within 20 scans of the DFTPP peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.
- 7.3.1.3 The DFTPP mass intensity criteria in Table 4 are used as tuning acceptance criteria.
- 7.3.1.4 All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.
- 7.3.1.5 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol should be present at their normal responses, and the peak tailing factor should be less than 2.
- 7.3.1.6 The injection port is replaced prior to any calibration sequence or 12-hour BNA analytical sequence. If chromatography is still poor, it may also be necessary to clip off the first 6-12 in. of the capillary column. Clipping the column may necessitate recalibration, as retention times and responses can shift considerably.
- 7.3.2 Analyze 1-2 μL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Tables 1a and 1b). A set of at least five calibration standards is necessary. The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Depending on the current state of the GC/MS system, a 2 μL injection may be required to achieve appropriate responses for the lower levels of the least sensitive compounds. When possible, however, a 1 μL can be used to yield a better dynamic range for the high sensitivity compounds.
- 7.3.3 Calculate response factors (*RFs*) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. Likewise,

C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.

7.3.4 Minimum Response Factor compounds

7.3.4.1 A system performance check must be performed to ensure that minimum *RF*s are met before the calibration curve is used. It is also recommended that a minimum response factor for the most common target analytes as noted in Table 2c, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration level is important in demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed, some compounds will fail to meet this criteria. In particular, late eluting compounds, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene and Benzo(g,h,i)perylene are likely to fail this criteria but have been demonstrated to perform adequately overall.

7.3.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. Replacing the calibration standards, and/or clipping/replacing the column will likely solve this problem.

7.3.5 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. The retention time extraction windows are set in the Chemstation software.

7.3.6 Linearity of target analytes - If the %RSD of any target analyte is 20% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation

7.3.6.1 Refer to SW-846 Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Note that quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at

very low responses. (All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior). In any event, the coefficient of determination (COD) for any regression fit should be ≥ 0.99 . In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters. If more than 10% of the compounds included with the initial calibration exceed the 20% RSD limit and do not meet the minimum correlation coefficient (0.99) for alternate curve fits, then the chromatographic system is considered too reactive for analysis to begin. Compounds that fail the 20% and (0.99) criteria should not be reported unless estimated values are acceptable to project goals.

7.3.6.2 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc.*

7.3.6.3 The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and the quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve. The recalculated concentration of the low calibration point should be within 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives. For analytes which do not meet the minimum quantitation calibration re-fitting criteria reporting those analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.

7.3.6.4 The initial calibration function should be verified immediately after performing the standard analyses using a second source standard at a concentration near the midpoint of the calibration range. The acceptance

limits are 70-130% or project specific. Analytes that fail this criteria are considered estimated values.

7.3.6.5 The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e.* average RF or regression coefficients), and the appropriate calibration quality metric (*i.e.* %RSD or COD).

7.3.6.6 Refer to Table 5b for DoD project requirements.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the DFTPP.

7.4.2 The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration (50 ng/ μ L) for the calibration range of the GC/MS. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the target compounds. In addition the internal standards should be within 30s of those in the midpoint calibration standard and the internal standard responses should be 50-200% of those in the midpoint calibration standard.

7.4.3 A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants.

7.4.4 Minimum Response Factor compounds

7.4.4.1 A calibration verification standard must be analyzed during every 12-hour analytical shift. Each of the most common target compounds in the calibration verification standard should meet the minimum response factor

noted in Table 2c. This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins (see previous).

7.4.5 Calibration check compounds

7.4.5.1 After the minimum response factor check is met all target compounds of interest must be evaluated using a 20% variability criterion. If the percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when a failed compound is present, the concentration is an estimated value. Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = |C - C_{spike}| / C_{spike}$

7.4.5.2 Problems similar to those listed under initial calibration could affect the calibration verification. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

7.4.5.3 Refer to Table 5b for DoD project requirements.

7.5 GC/MS analysis of samples

7.5.1 Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

- 7.5.2 Allow the sample extract to warm to room temperature. 3 μL of the internal standard solution is added to a 300 μL aliquot of sample in a crimp-top vial for subsequent autosampler analysis. If the sample extract is to be diluted prior to analysis, a smaller sample volume is used (even though the net volume of nominally 300 μL remains the same). SVOC Dilution Reference Document has a list of commonly used dilutions as well as the required amount of sample, solvent, and internal standard for each dilution.
- 7.5.3 Inject a 1-2 μL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration.
- 7.5.4 The extracted ion current potential (EICP) area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Tables 5a and 5b). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.

7.6 Qualitative analysis

- 7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Tables 1a and 1b. Compounds are identified when the following criteria are met.

7.6.1.1 Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time.

- 7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.
- 7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)
- 7.6.1.4 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
- 7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
- 7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.
- 7.6.1.7 In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of continued uncertainty, the analyst should preferentially make a conservative judgement and accept an identified hit, allowing the potential for a false positive.

- 7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose

of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within $\pm 20\%$.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

- 7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.
- 7.7.2 The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1[C_s/C_i] + k_2[C_s/C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th} -order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv \langle \text{RF} \rangle$, while $k_0, k_2 \equiv 0$.
- 7.7.3 The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the TIC areas for the nearest internal standard and target compound. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

- 7.7.4 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-cresol).

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 5a and 5b. In addition, the tables indicate the frequency of each QC item along with appropriate courses of corrective action. Control limits for surrogates and matrix spikes are listed in Table 6. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Laboratory specific performance data is provided on in Merit's LIMs system. Each sample batch contains a method blank, laboratory control sample and matrix spike samples. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

Computer software and firmware can be found on Merit's network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange

system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention shall be paid (but not limited) to:

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.

Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Laboratory Control Spike (LCS): Milli-Q water (for water) or Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias, to verify the analytical system performance, and to document method accuracy for each matrix.

Laboratory Control Spike Duplicate (LCSD): A duplicate Milli-Q water (for water) or Organic-Free Soil (for soil) is spiked with the target analytes and carried through the complete sample preparation and analytical procedure. The control spike duplicate is used to document the precision and bias of a method. This QC type is only performed when sufficient amount of sample is unavailable for performing a matrix spike and matrix spike duplicate.

Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analytes. The spiking occurs prior to sample preparation and analysis. It is used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with identical concentration of target analytes. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Method Reporting Limit (MRL): The method reporting limit is a threshold value below which the laboratory reports a result as a non-detect. The highest value reported for the method reporting limit is dependent upon project-specific action or decision levels. Method reporting limits are adjusted based on the sample matrix and any sample dilution/concentrations when necessary.

Method Detection Limit (MDL): The method detection limit is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. It is determined from analysis of a sample in a given matrix containing the analyte. Depending on project, specific MDL checks are either in the form of an MDL check standard or the MDL is subject to extraction procedures. An acceptable MDL standard check must produce signals for the qualifier ions. An MDL standard injection must be made after each major instrument repair or changing of instruments (prior to sample analysis) to determine the performance sensitivity of the analysis.

Surrogate (SURR): Organic compound which is similar to the target analytes in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples. Its use is to monitor the performance of the extraction, cleanup (as needed), the analytical system, and the effectiveness of the method. The acid surrogates are at twice the concentration of the Base/Neutral surrogates. The acid surrogate compounds are: 2-Fluorophenol, Phenol d₅, and 2,4,6-Tribromophenol. The base/neutral surrogates are: Nitrobenzene d₅, 2-Fluorobiphenyl, and p-Terphenyl d₁₄. o-Terphenyl d₁₄ is also added when the samples are analyzed for PAHs in selected ion monitoring (SIM) mode.

Initial Calibration (ICAL): An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of an analyte. This relationship is depicted graphically and referred to as a “calibration curve”. Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte.

Initial Calibration Verification (ICV): The initial calibration verification standard (different lot # or manufacturer from the initial calibration standard) shall verify the initial calibration curve. The initial calibration verification standard involves the analysis of all target analytes each time the initial calibration is performed.

Continuing Calibration Verification Standard (CCV): A standard solution that is used to check the validity of a calibration curve on a daily basis. It also provides information on satisfactory maintenance and adjustment of the instrument during sample analysis. A CCV must be made during each 12 hour shift.

DFTPP: Decafluorotriphenylphosphine. This compound is used in tuning the GC/MS. To acquire the mass spectrum of DFTPP, three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction to eliminate column bleed or instrument background noise is accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The DFTPP standard must also contain Pentachlorophenol, Benzidine, and DDT to assess GC column performance and injection port inertness. Benzidine and Pentachlorophenol must have tailing factors less than 2. Breakdown of DDT to DDD and DDE must be less than 20%

Internal standard (ISTD): Internal Standard involves the comparison of instrument responses from the target compounds in the sample to the responses of specific standards added to the sample extract prior to injection. The ratio of the peak area of the target compound in the sample extract to the peak area of the internal standard in the sample extract is compared to a similar ratio derived for each calibration standard. The internal standards are; 1,4-Dichlorobenzene d_4 , Naphthalene d_8 , Acenaphthene d_{10} , Phenanthrene d_{10} , Chrysene d_{12} and Perylene d_{12} . In addition, Benzo[a]anthracene d_{12} is added when the samples are analyzed for PAHs in selected ion monitoring (SIM) mode.

System Performance Check Compounds (SPCC): SPCCs are system performance compounds that are a part of the Continuing Calibration Verification standard (CCV). The SPCCs must meet a minimum response factor of 0.050. The SPCC criteria also apply to the average response factor of the initial calibration curve.

Calibration Check Compounds (CCC): CCCs are calibration check compounds that are a part of the Continuing Calibration Verification standard (CCV). The CCC percent difference must be less than or equal to 20%.

Instrument Blanks: Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it can be followed by the analysis of an instrument blank (methylene chloride + Internal Standards) to check for cross-contamination.

14.0 REFERENCES

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, ISO/IEC 17025:2005, ISO/IEC 17025:2017 and The NELAC Institute (TNI) Standards, Volume 1, September 2009, Version 5.3, May 7, 2019

U.S. EPA 40 CFR Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule*, October 26, 1984.

EPA SW-846, *Test Methods for Evaluation Solid Waste*, 3rd Edition, Update I dated 7/92, Update II dated 9/94, Update IIA dated 8/93, Update IIB dated 1/95, Update III dated 12/96, Update IV dated 1/08.

International Standards Organization (ISO), 2005. *General Requirements for the Competence of Testing and Calibration Laboratories*. ISO 17025.

National Environmental Laboratory Accreditation Conference (NELAC), 2003. *Standards, Chapters 1–6*, EPA/600/R-04/003.

EPA Method 625.1, December 2016

Table 1a. Summary of Retention Times[†] and Characteristic Ions for Base/Neutral/Acid Semi-Volatile Organics

#	Compound	t _R (min)	t _R /t _{R,I} (-)	t _R -t _{R,I} (min)	1 ⁰ m/z	2 ⁰ m/z	3 ⁰ m/z	4 ⁰ m/z
1)	1,4-DICHLOROBENZENE-D4	6.92	1.000	0.00	152	150	115	
2)	N-Nitrosodimethylamine	3.79	0.548	-3.13	74	42	43	
3)	2-Picoline	4.61	0.666	-2.31	93	92	66	
4)	Methyl methanesulfonate	5.16	0.746	-1.76	80	79	95	
5)	2-Fluorophenol	5.31	0.767	-1.61	112	92	64	
6)	Ethyl methanesulfonate	5.99	0.866	-0.93	79	109	97	
7)	Phenol-d5	6.45	0.932	-0.47	99	71	42	
8)	Phenol **	6.47	0.935	-0.45	94	66	65	
9)	Aniline	6.53	0.944	-0.39	93	65	66	
10)	2-Chlorophenol **	6.68	0.965	-0.24	128	130	92	
11)	Bis(2-chloroethyl)ether	6.59	0.952	-0.33	93	63	95	
12)	1,3-Dichlorobenzene	6.94	1.003	0.02	146	148	111	
13)	1,4-Dichlorobenzene **	6.94	1.003	0.02	146	148	111	
14)	1,2-Dichlorobenzene	7.18	1.038	0.26	146	148	111	
15)	Bis(2-chloroisopropyl)ether	7.3	1.055	0.38	45	121	77	
16)	Benzyl Alcohol	7.09	1.025	0.17	108	107	79	77
17)	Acetophenone	7.46	1.078	0.54	105	77	120	
18)	o-Cresol	7.24	1.046	0.32	108	107	79	
19)	p,m-Cresol	7.42	1.072	0.50	107	108	79	
20)	Hexachloroethane	7.59	1.097	0.67	117	119	201	
21)	N-Nitrosodi-n-propylamine*	7.48	1.081	0.56	70	43	42	41
22)	NAPHTHALENE-D8	8.59	1.000	0.00	136	68	108	
23)	Nitrobenzene-d5	7.66	0.892	-0.93	82	128	98	
24)	Nitrobenzene	7.69	0.895	-0.90	123	123	65	
25)	N-Nitrosopiperidine	7.89	0.919	-0.70	114	55	56	
26)	Isophorone	7.98	0.929	-0.61	82	95	138	
27)	2-Nitrophenol	8.11	0.944	-0.48	139	109	65	
28)	2,4-Dimethylphenol	8.12	0.945	-0.47	107	122	121	
29)	Bis(2-chloroethoxy)methane	8.25	0.960	-0.34	93	63	95	
30)	2,4-Dichlorophenol	8.4	0.978	-0.19	162	164	98	

#	Compound	t _R (min)	t _R /t _{R,I} (-)	t _R -t _{R,I} (min)	1 ⁰ m/z	2 ⁰ m/z	3 ⁰ m/z	4 ⁰ m/z
31)	1,2,4-Trichlorobenzene **	8.52	0.992	-0.07	180	182	145	
32)	Naphthalene	8.61	1.002	0.02	128	127	129	
33)	4-Chloroaniline	8.69	1.012	0.10	127	129	65	
34)	2,6-Dichlorophenol	8.71	1.014	0.12	162	164	127	
35)	Hexachlorobutadiene	8.83	1.028	0.24	225	223	227	
36)	N-Nitroso-di-n-butylamine	9.13	1.063	0.54	84	116	158	
37)	4-Chloro-3-methylphenol **	9.28	1.080	0.69	107	142	77	
38)	2-Methylnaphthalene	9.5	1.106	0.91	141	142	115	
40)	1,2,4,5-Tetrachlorobenzene	9.77	1.137	1.18	216	214	218	
41)	Hexachlorocyclopentadiene	9.79	1.140	1.20	237	235	239	
42)	2,4,6-Trichlorophenol	9.94	1.157	1.35	196	198	200	
43)	2,4,5-Trichlorophenol	9.94	1.157	1.35	196	198	132	
44)	2-Fluorobiphenyl	9.98	1.162	1.39	172	171	173	
45)	2-Chloronaphthalene	10.13	1.179	1.54	162	127	164	
46)	1-Chloronaphthalene	10.18	1.185	1.59	162	164	127	
47)	2-Nitroaniline	10.29	1.198	1.70	138	65	92	
48)	Acenaphthylene	10.67	1.242	2.08	152	151	150	
49)	Dimethyl Phthalate	10.54	1.227	1.95	163	164	77	
50)	2,6-Dinitrotoluene	10.64	1.239	2.05	165	121	148	
51)	3-Nitroaniline	10.82	1.260	2.23	138	92	65	
52)	Acenaphthene **	10.91	1.270	2.32	154	153	152	
53)	2,4-Dinitrophenol	10.95	1.275	2.36	184	63	107	
54)	Dibenzofuran	11.12	1.295	2.53	168	169	139	
55)	4-Nitrophenol **	10.99	1.279	2.40	65	139	81	109
56)	2,4-Dinitrotoluene **	11.15	1.298	2.56	165	89	63	
57)	2,3,4,6-Tetrachlorophenol	11.32	1.318	2.73	232	230	234	131
58)	Fluorene	11.56	1.346	2.97	166	165	167	
59)	Diethyl phthalate	11.43	1.331	2.84	149	150	177	
60)	4-Chlorophenyl phenyl ether	11.53	1.342	2.94	204	141	206	
61)	4-Nitroaniline	11.61	1.352	3.02	138	65	92	
62)	2,4,6-Tribromophenol	11.89	1.384	3.30	330	332	141	
63)	PHENANTHRENE-D10	12.8	1.000	0.00	188	80	94	

#	Compound	t _R (min)	t _R /t _{R,I} (-)	t _R -t _{R,I} (min)	1 ⁰ m/z	2 ⁰ m/z	3 ⁰ m/z	4 ⁰ m/z
64)	4,6-Dinitro-2-methylphenol	11.67	0.912	-1.13	198	121	105	
65)	N-Nitrosodiphenylamine	11.69	0.913	-1.11	169	168	167	
66)	1,2-Diphenylhydrazine	11.74	0.917	-1.06	182	105	77	
67)	Azobenzene	11.74	0.917	-1.06	182	105	77	
68)	4-Bromophenyl phenyl ether	12.16	0.950	-0.64	248	250	77	
69)	1,3,5-Trinitrobenzene	12.08	0.944	-0.72	213	74	75	
70)	Phenacetin	12.11	0.946	-0.69	108	109	179	137
71)	Hexachlorobenzene	12.37	0.966	-0.43	249	282	286	
72)	4-Aminobiphenyl	12.51	0.977	-0.29	169	168	170	
73)	Pentachlorophenol **	12.6	0.984	-0.20	266	264	268	
75)	Pronamide	12.6	0.984	-0.20	173	174	145	
76)	Pentachloronitrobenzene	12.72	0.994	-0.08	237	249	295	
77)	Phenanthrene	12.83	1.002	0.03	178	176	179	
78)	Anthracene	12.83	1.002	0.03	178	176	179	
79)	di-N-butyl phthalate	13.62	1.064	0.82	149	150	104	
80)	Fluoranthene	14.65	1.145	1.85	202	200	203	
81)	Terphenyl-d14	15.28	1.194	2.48	244	122	212	
82)	CHRYSENE-D12	17.34	1.000	0.00	240	236	120	
83)	Benzidine	14.83	0.855	-2.51	184	185	92	
84)	Pyrene **	15.03	0.867	-2.31	202	200	203	
85)	p-Dimethylaminoazobenzene	15.57	0.898	-1.77	225	120	77	
86)	Butyl benzyl phthalate	16.23	0.936	-1.11	149	91	206	
88)	Benzo(a)anthracene	17.29	0.997	-0.05	228	226	229	
89)	3,3'-Dichlorobenzidine	17.25	0.995	-0.09	252	254	126	
90)	Chrysene	17.38	1.002	0.04	228	226	229	
92)	PERYLENE-D12	20.3	1.000	0.00	264	260	265	
91)	Bis(2-ethylhexyl)phthalate	17.42	0.858	-2.88	149	167	279	
93)	Di-n-octyl phthalate	18.66	0.919	-1.64	149	43	167	
95)	Benzo(b)fluoranthene	19.47	0.959	-0.83	252	253	126	
96)	7,12-Dimethylbenz(a)anthracene	19.5	0.961	-0.80	256	241	239	
97)	Benzo(k)fluoranthene	19.47	0.959	-0.83	252	253	126	
98)	Benzo(a)pyrene	20.16	0.993	-0.14	252	253	126	

#	Compound	t_R (min)	$t_R/t_{R,I}$ (-)	$t_R - t_{R,I}$ (min)	1^0 m/z	2^0 m/z	3^0 m/z	4^0 m/z
99)	3-Methylcholanthrene	21.04	1.036	0.74	268	252	253	269
100)	Dibenz(a,j)acridine	22.54	1.110	2.24	279	280	139	278
101)	Indeno(1,2,3-cd)pyrene	23.1	1.138	2.80	276	138	277	
102)	Dibenzo(a,h)anthracene	23.14	1.140	2.84	278	139	279	
103)	Benzo(ghi)perylene	23.92	1.178	3.62	276	138	277	

†: Absolute retention times (t_R) listed are from calibration BU061002.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e.* new, clipped, *etc.*), but the differential retention times ($t_R - t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

Table 1b. Summary of Retention Times[†] and Characteristic Ions for Polynuclear Aromatic Semi-Volatile Organics

#	Compound	t_R (min)	$t_R/t_{R,I}$ (-)	$t_R - t_{R,I}$ (min)	1 ⁰ m/z	2 ⁰ m/z	3 ⁰ m/z	4 ⁰ m/z
1)	1,4-DICHLOROBENZENE-D4	3.96	1.000	0.00	152	152		
2)	NAPHTHALENE-D8	5.21	1.000	0.00	136	68	108	
3)	Nitrobenzene-d5	4.52	0.868	-0.69	82	54	128	
4)	Naphthalene	5.23	1.004	0.02	128	127	129	
5)	2-Methylnaphthalene	5.88	1.129	0.67	141	141	115	
6)	ACENAPHTHALENE-D10	6.94	1.000	0.00	164	162	160	
7)	2-Fluorobiphenyl	6.23	0.898	-0.71	172	171	173	
8)	Acenaphthylene	6.78	0.977	-0.16	152	151	150	
9)	Acenaphthene **	6.97	1.004	0.03	154	153	76	
10)	Fluorene	7.49	1.079	0.55	166	165	167	
11)	PHENANTHRENE-D10	8.52	1.000	0.00	188	80	94	
12)	Phenanthrene	8.54	1.002	0.02	178	176	179	
13)	Anthracene	8.6	1.009	0.08	178	176	179	
14)	Fluoranthene	10.09	1.184	1.57	202	200	203	
15)	Terphenyl-D14	10.62	1.246	2.10	244	122	212	
16)	CHRYSENE-D12	12.5	1.000	0.00	240	236	120	
17)	Pyrene **	10.44	0.835	-2.06	202	101	200	
18)	Benzo(a)anthracene	12.46	0.997	-0.04	228	226	229	
19)	Chrysene	12.54	1.003	0.04	228	226	229	
20)	PERYLENE-D12	15.22	1.000	0.00	264	260	132	
21)	Benzo(b)fluoranthene	14.51	0.953	-0.71	252	253	126	
22)	Benzo(k)fluoranthene	14.56	0.957	-0.66	252	253	125	
23)	Benzo(a)pyrene	15.12	0.993	-0.10	252	253	126	
24)	Indeno(1,2,3-cd)pyrene	17.38	1.142	2.16	276	138	277	
25)	Dibenzo(ah)anthracene	17.39	1.143	2.17	278	139	279	
26)	Benzo(ghi)perylene	17.99	1.182	2.77	276	138	277	

[†]: Absolute retention times (t_R) listed are from calibration PF060829.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e.* new, clipped, *etc.*), but the differential retention times ($t_R - t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

Table 2a. Summary of Applicable Performance Compounds - Base/Neutral/Acid Analysis

COMPOUND	ISD	SSD
1,4-DICHLOROBENZENE-D4	✓	
2-Fluorophenol		✓
Phenol-d5		✓
NAPHTHALENE-D8	✓	
Nitrobenzene-d5		✓
ACENAPHTHALENE-D10	✓	
2-Fluorobiphenyl		✓
2,4,6-Tribromophenol		✓
PHENANTHRENE-D10	✓	
Terphenyl-d14		✓
CHRYSENE-D12	✓	
PERYLENE-D12	✓	

Key

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

Table 2b. Summary of Applicable Performance Compounds - Polynuclear Aromatic Analysis

COMPOUND	ISD	SSD
1,4-DICHLOROBENZENE-D4	✓	
NAPHTHALENE-D8	✓	
Nitrobenzene-d5		✓
ACENAPHTHALENE-D10	✓	
2-Fluorobiphenyl		✓
PHENANTHRENE-D10	✓	
CHRYSENE-D12	✓	
Terphenyl-d14		✓
PERYLENE-D12	✓	

Key

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

Table 2c. Recommended Minimum Relative Response Factor Criteria For Initial And Continuing Calibration Verification.

Semivolatile Compounds	Minimum Response Factor (RF) ^a
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010

Semivolatile Compounds	Minimum Response Factor (RF) ^a
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

^a The Project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed.

Table 3. GC/MS Operating Conditions - Base/Neutral/Acid (BNA) and Polynuclear Aromatic (PNA)
Semi-Volatile Organics Analysis[†]

Operating Parameter	BNA Analysis	PNA Analysis
Chromatographic Column	HP-5MS SV, $L = 30\text{ m}$, $ID = 0.25\text{ mm}$	HP-5MS SV, $L = 30\text{ m}$, $ID = 0.25\text{ mm}$
Carrier Gas	Helium (He) at 2 ml/min	Helium (He) at 2 ml/min
Temperature Program	<i>Variable-Instrument dependent</i>	<i>Variable-Instrument dependent</i>
Injector Temperature	250°C	250°C
Detector Temperature	300°C	300°C
Injection Volume	1-2 μl	1 μl
Mass Scanning Range	35 m/z - 500 m/z	35 m/z - 500 m/z
Mass Scanning Rate	1.8 Hz	1.4 Hz

Note: the above is subject to change based on GC and/or sample conditions.

Table 4. DFTPP Tune Evaluation Criteria

Mass	Ion Abundance Criteria
68	<2% of m/z 69
69	Present
70	<2% of m/z 69
197	<2% of m/z 198
198	Base peak or present
199	5-9% of m/z 198
365	>1% of Base Peak
441	<150% of m/z 443
442	Base peak or present
443	15-24% of m/z 442

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, or for an alternative carrier gas, provided method performance is not adversely affected.

Table 5a. Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
DFTPP	12-hour	Table 4	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	SPCC RF <0.050 CCC $\leq$ 20%	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Table 6	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	<RL	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated extraction glassware should result in a thorough re-cleaning of the affected glassware. If the method blank contamination for a batch is atypical (<i>i.e.</i> non phthalate esters), the blank should be re-extracted and re-analyzed. If additional sample exists, the samples associated with a failed, re-extracted blank

QC Item	Frequency	Acceptance Criteria	Corrective Action
			should also be re-extracted and re-analyzed.
Internal Standard	All samples	Section 7.5.5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate. Internal standards recoveries below 50% require re-analysis
Surrogate Standard	All samples	Table 6	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated. Two out three surrogates are to be within limits, as long as the third surrogate is above 10%.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 5b. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Tune Check	Prior to ICAL and prior To each 12-hour period of sample analysis	Specific ion abundance criteria of BFB or DFTPP from method.	Retune instrument and verify.	Flagging criteria is not appropriate.	No samples shall be analyzed without a valid tune.
Performance Check (Method 8270 only)	At the beginning of each 12-hour period, prior to analysis of samples.	Degradation $\leq 20\%$ for DDT. Benzidine and pentachlorophenol shall be present at their normal responses and shall not exceed a tailing factor of 2.	Correct problem, then repeat performance checks.	Flagging is not appropriate.	No sample shall be analyzed until performance check is within criteria. The DDT breakdown and Benzidine/Pentachlorophenol tailing factors are considered overall system checks to evaluate injector port inertness and column performance and are required regardless of the reported analyte list.
Initial calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	Each analyte must meet one of the three options below: <u>Option 1:</u> RSD for each analyte $\leq 15\%$; <u>Option 2:</u> linear least squares regression $r^2 \geq 0.99$; <u>Option 3:</u> non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging criteria is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. No samples shall be analyzed until ICAL has passed. If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements must also be met.
Retention time window position establishment	Once per ICAL and at the beginning of the	Position shall be set using the midpoint standard of the ICAL curve	NA.	NA.	Calculated for each analyte and surrogate.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
and surrogate	analytical sequence.	when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.			
Evaluation of relative retention times (RRT)	With each sample.	RRT of each reported analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA	After maintenance is performed which may affect retention times, RRTs may be updated based on the daily CCV. RRTs shall be compared with the most recently updated RRTs.
Initial Calibration Verification (ICV)	Once after each ICAL, analysis of a second source prior to sample analysis	All reported analytes within $\pm 20\%$ of true value.	Correct problem. Rerun ICV. If that fails, repeat ICAL.	Flagging is not appropriate.	No samples shall be analyzed until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within $\pm 20\%$ of true value. All reported analytes and surrogates within $\pm 50\%$ for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g. average RFs) these additional requirements must also be met.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.		
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time $\pm$ 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard. On days when ICAL is not performed, the daily initial CCV can be used.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is mandatory.	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	NA
Method blank (MB)	One per preparatory batch.	No analytes detected $> \frac{1}{2}$ LOQ or $> 1/10^{\text{th}}$ the amount measured in any sample or $1/10^{\text{th}}$ the regulatory limit, whichever is greater. Common contaminants, must not be detected $> \text{LOQ}$.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
				analyte(s) in all samples in the associated preparatory batch.	
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be	For the specific analyte(s) in the parent sample, apply J-flag if	MSD: Must contain all surrogates and all analytes to be reported. The data shall be evaluated to determine the source of difference.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes $\leq$ 20% (between MS and MSD or sample and MD).	taken.	acceptance criteria are not met and explain in the case narrative.	For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed..	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative..	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

DoD Appendix C LCS Limits
Method 8270 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
92-52-4	1,1-Biphenyl	40	117
95-94-3	1,2,4,5-Tetrachlorobenzene	37	119
120-82-1	1,2,4-Trichlorobenzene	34	118
95-50-1	1,2-Dichlorobenzene	33	117
528-29-0	1,2-Dinitrobenzene [1,2-DNB]	44	115
122-66-7	1,2-Diphenylhydrazine [Azobenzene]	41	125
99-35-4	1,3,5-Trinitrobenzene [1,3,5-TNB]	57	121
541-73-1	1,3-Dichlorobenzene	30	115
99-65-0	1,3-Dinitrobenzene [1,3-DNB]	43	127
106-46-7	1,4-Dichlorobenzene	31	115
100-25-4	1,4-Dinitrobenzene	37	132
130-15-4	1,4-Naphthoquinone	55	108
90-13-1	1-Chloronaphthalene	48	115
90-12-0	1-Methylnaphthalene	40	119
58-90-2	2,3,4,6-Tetrachlorophenol	44	125
935-95-5	2,3,5,6-Tetrachlorophenol	40	112
608-27-5	2,3-Dichloroaniline	44	121
95-95-4	2,4,5-Trichlorophenol	41	124
118-79-6	2,4,6-Tribromophenol	39	132
88-06-2	2,4,6-Trichlorophenol	39	126
120-83-2	2,4-Dichlorophenol	40	122
105-67-9	2,4-Dimethylphenol	30	127
121-14-2	2,4-Dinitrotoluene	48	126
87-65-0	2,6-Dichlorophenol	41	117
606-20-2	2,6-Dinitrotoluene	46	124
53-96-3	2-Acetylaminofluorene	54	134
91-58-7	2-Chloronaphthalene	41	114
95-57-8	2-Chlorophenol	34	121
321-60-8	2-Fluorobiphenyl	44	115
367-12-4	2-Fluorophenol	35	115

91-57-6	2-Methylnaphthalene	38	122
95-48-7	2-Methylphenol (o-Cresol)	32	122
88-74-4	2-Nitroaniline	44	127
119-75-5	2-Nitrodiphenylamine	53	123
88-75-5	2-Nitrophenol	36	123
109-06-8	2-Picoline [2-Methylpyridine]	27	103
91-94-1	3,3'-Dichlorobenzidine	22	121
56-49-5	3-Methylcholanthrene	56	134
99-09-2	3-Nitroaniline	33	119
65794-96-9	3/4-Methylphenol [m/p-Cresol]	34	119
534-52-1	4,6-Dinitro-2-methylphenol	29	132
101-55-3	4-Bromophenyl phenyl ether	46	124
59-50-7	4-Chloro-3-methylphenol	45	122
106-47-8	4-Chloroaniline [p-Chloroaniline]	17	106
7005-72-3	4-Chlorophenyl phenyl ether	45	121
106-44-5	4-Methylphenol [p-Cresol]	42	126
100-02-7	4-Nitrophenol	30	132
99-55-8	5-Nitro-o-toluidine [2-Amino-4-nitrotoluene]	23	117
57-97-6	7,12-Dimethylbenz(a)-anthracene	50	142
83-32-9	Acenaphthene	40	123
208-96-8	Acenaphthylene	32	132
98-86-2	Acetophenone	33	115
120-12-7	Anthracene	47	123
1912-24-9	Atrazine	47	127
103-33-3	Azobenzene	39	125
56-55-3	Benz(a)anthracene	49	126
50-32-8	Benzo(a)pyrene	45	129
205-99-2	Benzo(b)fluoranthene	45	132
191-24-2	Benzo(g,h,i)perylene	43	134
207-08-9	Benzo(k)fluoranthene	47	132
100-51-6	Benzyl alcohol	29	122
111-91-1	bis(2-Chloroethoxy)methane	36	121
111-44-4	Bis(2-chloroethyl) ether	31	120

39638-32-9	bis(2-Chloroisopropyl) ether	33	131
117-81-7	Bis(2-ethylhexyl) phthalate	51	133
103-23-1	bis(2-Ethylhexyl)adipate	61	121
85-68-7	Butyl benzyl phthalate	48	132
105-60-2	Caprolactam	46	117
86-74-8	Carbazole	50	123
510-15-6	Chlorobenzilate	49	150
218-01-9	Chrysene	50	124
84-74-2	Di-n-butyl phthalate	51	128
117-84-0	Di-n-octyl phthalate	45	140
2303-16-4	Diallate [cis or trans]	56	132
53-70-3	Dibenzo(a,h)anthracene	45	134
132-64-9	Dibenzofuran	44	120
84-66-2	Diethyl phthalate	50	124
60-51-5	Dimethoate	28	108
131-11-3	Dimethyl phthalate	48	124
60-11-7	Dimethylaminoazobenzene	64	134
88-85-7	Dinoseb	16	119
101-84-8	Diphenyl ether	78	114
122-39-4	Diphenylamine	48	111
62-50-0	Ethyl methanesulfonate	34	136
206-44-0	Fluoranthene	50	127
86-73-7	Fluorene	43	125
118-74-1	Hexachlorobenzene	45	122
87-68-3	Hexachlorobutadiene	32	123
67-72-1	Hexachloroethane	28	117
1888-71-7	Hexachloropropene	32	132
95-13-6	Indene	59	112
193-39-5	Indeno(1,2,3-cd)pyrene	45	133
465-73-6	Isodrin	56	132
78-59-1	Isophorone	30	122
120-58-1	Isosafrole	43	136
66-27-3	Methyl methanesulfonate	38	117
100-75-4	N-Nitorosopiperidine	60	119

924-16-3	N-Nitrosodi-n-butylamine	59	124
621-64-7	N-Nitrosodi-n-propylamine	36	120
55-18-5	N-nitrosodiethylamine	41	124
62-75-9	N-Nitrododimethylamine	23	120
86-30-6	N-Nitrosodiphenylamine	38	127
10595-95-6	n-Nitrosomethylethylamine	34	123
59-89-2	n-Nitrosomorpholine	50	133
930-55-2	n-Nitrosopyrrolidine	45	126
91-20-3	Naphthalene	35	123
98-95-3	Nitrobenzene	34	122
4165-60-0	Nitrobenzene-d5	37	122
56-57-5	Nitroquinoline-1-oxide	18	165
126-68-1	O,O,O-Triethyl phosphorothioate	59	124
593-45-3	Octadecane	44	131
608-93-5	Pentachlorobenzene	54	125
76-01-7	Pentachloroethane	39	102
87-86-5	Pentachlorophenol	25	133
82-68-8	Pentachloronitrobenzene	38	134
62-44-2	Phenacetin	57	133
85-01-8	Phenanthrene	50	121
108-95-2	Phenol	34	121
4165-62-2	Phenol-d5	33	122
23950-58-5	Pronamide	56	130
129-00-0	Pyrene	47	127
91-22-5	Quinoline	54	126
94-59-7	Safrole	47	129
1718-51-0	Terphenyl-d14	54	127
3689-24-5	Tetraethyl dithiopyrophosphate [Sulfotep]	52	137
297-97-2	Thionazine	62	127

DoD Appendix C LCS Limits
Method 8270 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
92-52-4	1,1-Biphenyl	49	115
95-94-3	1,2,4,5-Tetrachlorobenzene	35	121
120-82-1	1,2,4-Trichlorobenzene	29	116
95-50-1	1,2-Dichlorobenzene	32	111
528-29-0	1,2-Dinitrobenzene [1,2-DNB]	59	109
122-66-7	1,2-Diphenylhydrazine [Azobenzene]	49	122
99-35-4	1,3,5-Trinitrobenzene [1,3,5-TNB]	41	137
541-73-1	1,3-Dichlorobenzene	28	110
99-65-0	1,3-Dinitrobenzene [1,3-DNB]	49	128
106-46-7	1,4-Dichlorobenzene	29	112
90-13-1	1-Chloronaphthalene	58	111
90-12-0	1-Methylnaphthalene	41	119
134-32-7	1-Naphthylamine	24	124
58-90-2	2,3,4,6-Tetrachlorophenol	50	128
935-95-5	2,3,5,6-Tetrachlorophenol	50	121
608-27-5	2,3-Dichloroaniline	70	129
95-95-4	2,4,5-Trichlorophenol	53	123
118-79-6	2,4,6-Tribromophenol	43	140
88-06-2	2,4,6-Trichlorophenol	50	125
120-83-2	2,4-Dichlorophenol	47	121
105-67-9	2,4-Dimethylphenol	31	124
51-28-5	2,4-Dinitrophenol	23	143
121-14-2	2,4-Dinitrotoluene	57	128
87-65-0	2,6-Dichlorophenol	50	118
606-20-2	2,6-Dinitrotoluene	57	124
53-96-3	2-Acetylaminofluorene	60	138
91-58-7	2-Chloronaphthalene	40	116
95-57-8	2-Chlorophenol	38	117
93951-73-6	2-Chlorophenol-d4	54	106

321-60-8	2-Fluorobiphenyl	44	119
367-12-4	2-Fluorophenol	19	119
91-57-6	2-Methylnaphthalene	40	121
95-48-7	2-Methylphenol (o-Cresol)	30	117
88-74-4	2-Nitroaniline	55	127
119-75-5	2-Nitrodiphenylamine	64	131
88-75-5	2-Nitrophenol	47	123
109-06-8	2-Picoline [2-Methylpyridine]	34	109
91-94-1	3,3'-Dichlorobenzidine	27	129
56-49-5	3-Methylcholanthrene	56	133
99-09-2	3-Nitroaniline	41	128
65794-96-9	3/4-Methylphenol [m/p-Cresol]	29	110
534-52-1	4,6-Dinitro-2-methylphenol	44	137
101-55-3	4-Bromophenyl phenyl ether	55	124
59-50-7	4-Chloro-3-methylphenol	52	119
106-47-8	4-Chloroaniline [p-Chloroaniline]	33	117
7005-72-3	4-Chlorophenyl phenyl ether	53	121
106-44-5	4-Methylphenol [p-Cresol]	25	120
99-55-8	5-Nitro-o-toluidine [2-Amino-4-nitrotoluene]	38	126
57-97-6	7,12-Dimethylbenz(a)-anthracene	61	133
83-32-9	Acenaphthene	47	122
208-96-8	Acenaphthylene	41	130
98-86-2	Acetophenone	46	118
120-12-7	Anthracene	57	123
140-57-8	Aramite	34	132
1912-24-9	Atrazine	44	142
103-33-3	Azobenzene	61	116
56-55-3	Benz(a)anthracene	58	125
50-32-8	Benzo(a)pyrene	54	128
205-99-2	Benzo(b)fluoranthene	53	131
191-24-2	Benzo(g,h,i)perylene	50	134
207-08-9	Benzo(k)fluoranthene	57	129
100-51-6	Benzyl alcohol	31	112

111-91-1	bis(2-Chloroethoxy)methane	48	120
111-44-4	Bis(2-chloroethyl) ether	43	118
39638-32-9	bis(2-Chloroisopropyl) ether	37	130
117-81-7	Bis(2-ethylhexyl) phthalate	55	135
85-68-7	Butyl benzyl phthalate	53	134
86-74-8	Carbazole	60	122
510-15-6	Chlorobenzilate	58	150
218-01-9	Chrysene	59	123
124-18-5	Decane	29	105
84-74-2	Di-n-butyl phthalate	59	127
117-84-0	Di-n-octyl phthalate	51	140
2303-16-4	Diallate [cis or trans]	67	124
226-36-8	Dibenz(a,h)acridine	75	134
53-70-3	Dibenzo(a,h)anthracene	51	134
132-64-9	Dibenzofuran	53	118
84-66-2	Diethyl phthalate	56	125
131-11-3	Dimethyl phthalate	45	127
60-11-7	Dimethylaminoazobenzene	62	132
88-85-7	Dinoseb	61	126
101-84-8	Diphenyl ether	68	115
122-39-4	Diphenylamine	55	111
298-04-4	Disulfoton	55	130
62-50-0	Ethyl methanesulfonate	62	118
206-44-0	Fluoranthene	57	128
86-73-7	Fluorene	52	124
118-74-1	Hexachlorobenzene	53	125
87-68-3	Hexachlorobutadiene	22	124
67-72-1	Hexachloroethane	21	115
95-13-6	Indene	53	135
193-39-5	Indeno(1,2,3-cd)pyrene	52	134
465-73-6	Isodrin	68	128
78-59-1	Isophorone	42	124
120-58-1	Isosafrole	56	126
66-27-3	Methyl methanesulfonate	33	107

298-00-0	Methyl parathion	45	159
100-75-4	N-Nitrosopiperidine	56	121
924-16-3	N-Nitrosodi-n-butylamine	60	121
621-64-7	N-Nitrosodi-n-propylamine	49	119
55-18-5	N-nitrosodiethylamine	43	121
86-30-6	N-Nitrosodiphenylamine	51	123
10595-95-6	n-Nitrosomethylethylamine	41	117
59-89-2	n-Nitrosomorpholine	55	117
930-55-2	n-Nitrosopyrrolidine	48	113
91-20-3	Naphthalene	40	121
98-95-3	Nitrobenzene	45	121
4165-60-0	Nitrobenzene-d5	44	120
126-68-1	O,O,O-Triethyl phosphorothioate	66	119
95-53-4	o-Toluidine	30	110
593-45-3	Octadecane	50	128
56-38-2	Parathion	66	140
608-93-5	Pentachlorobenzene	59	123
76-01-7	Pentachloroethane	30	92
87-86-5	Pentachlorophenol	35	138
82-68-8	Pentachloronitrobenzene	54	135
62-44-2	Phenacetin	71	124
85-01-8	Phenanthrene	59	120
298-02-2	Phorate	38	139
23950-58-5	Pronamide	65	129
129-00-0	Pyrene	57	126
91-22-5	Quinoline	69	132
94-59-7	Safrole	61	119
1718-51-0	Terphenyl-d14	50	134
3689-24-5	Tetraethyl dithiopyrophosphate [Sulfotep]	61	133
297-97-2	Thionazine	72	132

LCS Limits
EPA 625.1 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
120-82-1	1,2,4-Trichlorobenzene	61	130
88-06-2	2,4,6-Trichlorophenol	69	130
120-83-2	2,4-Dichlorophenol	64	130
105-67-9	2,4-Dimethylphenol	58	130
51-28-5	2,4-Dinitrophenol	39	173
121-14-2	2,4-Dinitrotoluene	53	130
606-20-2	2,6-Dinitrotoluene	68	137
91-58-7	2-Chloronaphthalene	70	130
95-57-8	2-Chlorophenol	55	130
88-75-5	2-Nitrophenol	61	163
91-94-1	3,3'-Dichlorobenzidine	18	213
534-52-1	4,6-Dinitro-2-methylphenol	56	130
101-55-3	4-Bromophenyl phenyl ether	70	130
59-50-7	4-Chloro-3-methylphenol	68	130
7005-72-3	4-Chlorophenyl phenyl ether	57	145
83-32-9	Acenaphthene	70	130
208-96-8	Acenaphthylene	60	130
120-12-7	Anthracene	58	130
56-55-3	Benz(a)anthracene	42	133
50-32-8	Benzo(a)pyrene	32	148
205-99-2	Benzo(b)fluoranthene	42	140
191-24-2	Benzo(g,h,i)perylene	13	195
207-08-9	Benzo(k)fluoranthene	25	146
111-91-1	bis(2-Chloroethoxy)methane	52	164
111-44-4	Bis(2-chloroethyl) ether	52	130
39638-32-9	bis(2-Chloroisopropyl) ether	63	139
117-81-7	Bis(2-ethylhexyl) phthalate	43	137
85-68-7	Butyl benzyl phthalate	43	140
218-01-9	Chrysene	44	140

84-74-2	Di-n-butyl phthalate	52	130
117-84-0	Di-n-octyl phthalate	21	132
53-70-3	Dibenzo(a,h)anthracene	13	200
84-66-2	Diethyl phthalate	47	130
131-11-3	Dimethyl phthalate	50	130
206-44-0	Fluoranthene	47	130
86-73-7	Fluorene	70	130
118-74-1	Hexachlorobenzene	38	142
87-68-3	Hexachlorobutadiene	68	130
67-72-1	Hexachloroethane	55	130
193-39-5	Indeno(1,2,3-cd)pyrene	13	151
78-59-1	Isophorone	52	180
621-64-7	N-Nitrosodi-n-propylamine	59	170
91-20-3	Naphthalene	70	130
98-95-3	Nitrobenzene	54	158
85-01-8	Phenanthrene	67	130
129-00-0	Pyrene	70	130
100-02-7	4-Nitrophenol	35	130
87-86-5	Pentachlorophenol	42	152
108-95-2	Phenol	48	130

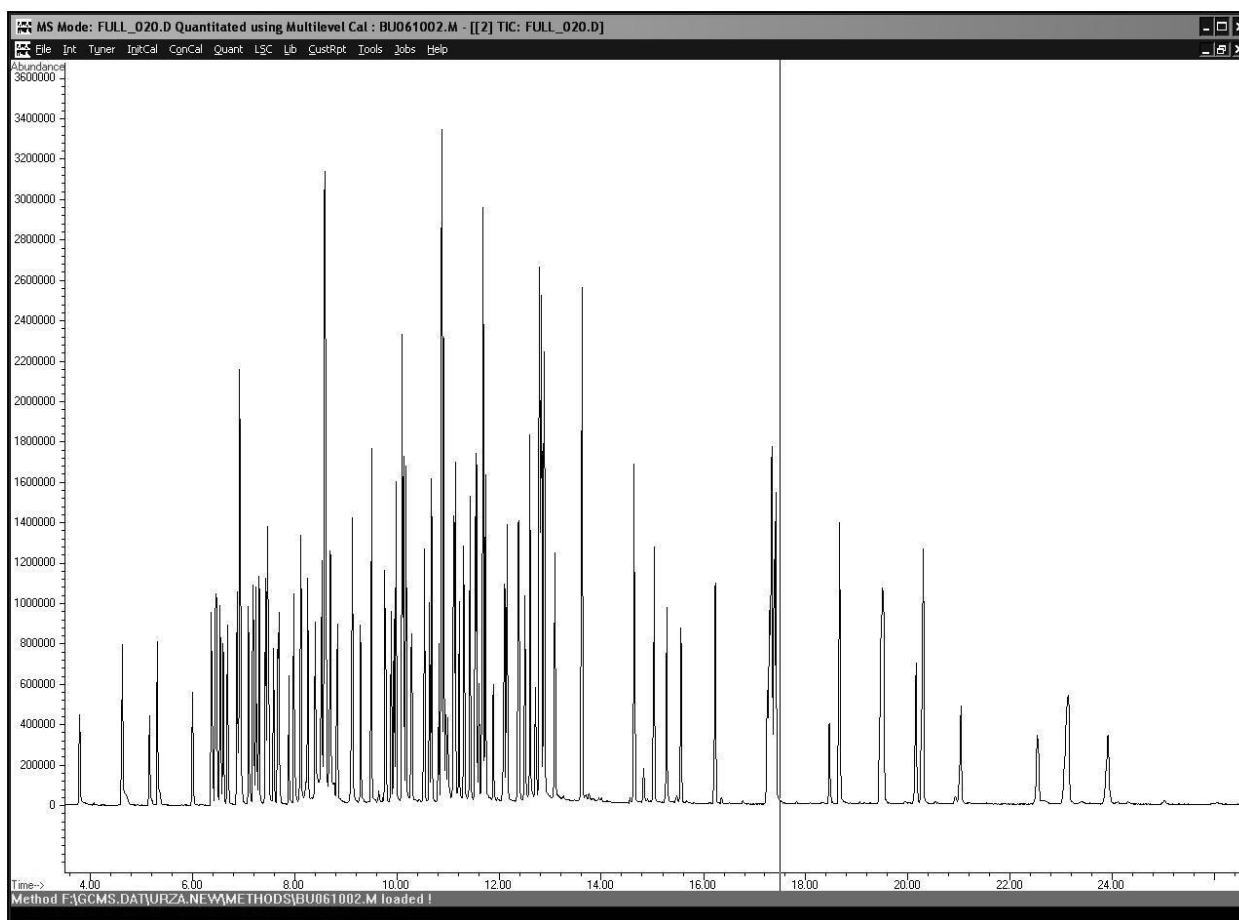
Table 6. Summary of Control Limits: Surrogate and Internal Standard Compounds Percent Recovery[†]

COMPOUND	Water Matrix		Solid Matrix	
	LCL (%)	UCL (%)	LCL (%)	UCL (%)
2-Fluorophenol	10.0	110.0	13.2	121.0
Phenol-d5	10.0	110.0	16.9	113.0
Nitrobenzene-d5	10.0	114.0	18.5	120.0
2-Fluorobiphenyl	10.0	116.0	10.0	115.0
2,4,6-Tribromophenol	10.0	123.0	13.0	122.0
Terphenyl-d14	10.0	141.0	10.3	137.0
1,4-Dichlorobenzene-D4	50.0	200.0	50.0	200.0
Naphthalene-D8	50.0	200.0	50.0	200.0
Acenaphthalene-D10	50.0	200.0	50.0	200.0
Phenanthrene-D10	50.0	200.0	50.0	200.0
Chrysene-D12	50.0	200.0	50.0	200.0
Perylene-D12	50.0	200.0	50.0	200.0

[†]: Results based on recovery data from 2020.

All target compounds must be included in the spike for DoD projects. DoD acceptance criteria is provided in the DoD QSM.

Figure 1. Example Total Ion Chromatogram for a Midpoint BNA Calibration Standard[†]



[†]: Data file FULL_020.D from calibration BU061002.M (20 ng/μL). GC/MS acquisition parameters are given by Table 3 for BNA Analysis.

STANDARD OPERATING PROCEDURE

*VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY
METHOD SW-846 8260C/ EPA 624.1*

APPROVALS:



03/08/2023

QA Officer

Date



03/08/2023

Technical Director

Date

Number	Description of Change	Date
001-011	Previous revisions not documented	
0012	Updated to comply with DoD QSM and ISO 17025 standards.	6/9/11
013	Updated to method 8260C	9/4/13
014	Updated to comply with DoD QSM 5.0 standards.	04/01/16
015	Updated to comply with DoD QSM 5.1 standards.	01/17/18
016	NY NELAC Audit Finding	03/13/19
017	DOD Audit Corrective Action	09/29/2020
018	2020 Internal Audit revisions	02/16/2021
019	NY NELAC Audit Finding	05/25/2022
020	Emergency SOP Amendment Form	03/08/2023
021		
022		

1.0 SCOPE AND APPLICATION

This SOP is used to determine volatile organic compounds (VOC) in a variety of matrices, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. See Table 1 for a list of compounds (along with their characteristic ions) that have been evaluated.

There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by SW-846 Methods 5030C (aqueous samples) and 5035A (solid, waste, and oil samples), are the most commonly used technique for volatile organic analytes. SW-846 Method 5000 provides general information on the selection of other introduction methods.

The practical quantitation limit (PQL) for an individual compound is instrument dependent and also dependent on the choice of the sample preparation/introduction method. Using standard quadrupole instrumentation and the purge-and-trap technique, limits should be approximately 50 µg/kg (wet weight) for solid samples and 1 µg/L for ground water. When lower reportable detection limits (RDLs) are required, the mass spectrometer (MS) can be set to selective ion monitoring (SIM) to achieve limits approximately 20 times lower than obtainable using the full scan method. Regardless of the sample matrix, PQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

Method Detection Limits (MDL) and Practical Quantitation Limits (PQL) are available in Merit's LIMS system.

This SOP is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF THE METHOD

VOC are introduced into the gas chromatograph by the purge-and-trap method or by other methods. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer interfaced to the gas chromatograph.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra

with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five point (or more) calibration curve.

The method includes specific calibration and quality control steps that supersede the general requirements provided in SW-846 Method 8000.

3.0 INTERFERENCES

Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds will be concentrated in the trap during the purge operation.

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to allow the system to be cleaned as well as to demonstrate the ultimate absence of cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

4.0 APPARATUS AND MATERIALS

Gas chromatograph/mass spectrometer system

- ◆ Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
- ◆ 20 m × 0.18 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 1-μm film thickness, or equivalent.
- ◆ Mass spectrometer capable of scanning from 35 to 260 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-bromofluorobenzene (BFB) which meets the criteria in Table 4.
- ◆ GC/MS interface - The capillary column is interfaced through a direct connection to the GC/MS system.

- ◆ Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

Purge-and-trap device.

Microsyringes - 2 to 500- μ L.

Balance - Analytical, capable of weighing 0.001 g, and top-loading, capable of weighing 0.1 g.

Glass bottles - 40-mL, with PTFE-lined screw-caps.

pH paper.

5.0 REAGENTS

Reagent grade organic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.

Organic-free reagent water - All references to water in this method refer to organic-free reagent water.

Stock standard solutions.

- ◆ Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.
- ◆ Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a high-concentration stock solution).
- ◆ Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.
- ◆ Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicate a problem.

Internal standard solutions - The internal standards used are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene- d_5 , and 1,4-dichlorobenzene- d_4 (see Table 2). Internal standards are used at a working concentration of 50 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 μ g/L (i.e. 10 μ L per 5000 μ L purge volume). For SIM (selective ion monitoring) analysis, internal standards are the same, but with concentrations at 0.4 ppb (μ g/L).

Calibration standards - A minimum of five calibration standards are prepared at different concentrations. The lowest calibration standard corresponds to a sample concentration at or below the standard reporting

limit. The remaining standards should represent the working range of the GC/MS system. Each standard should contain each analyte for quantitation by this method. For DoD projects, each standard shall contain all target compounds.

Surrogate standards - The surrogates used are toluene- d_8 , 4-bromofluorobenzene, and 1,2-dichloroethane- d_4 . Surrogate standards are used at a working concentration of 50 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 $\mu\text{g/L}$, or less. For SIM (selective ion monitoring) analysis, surrogate standards are the same, but with concentrations at 0.4 ppb ($\mu\text{g/L}$).

Matrix spike (MS), matrix spike duplicate (MSD) and laboratory control standards (LCS) - Matrix spiking solutions are prepared using the same standards as those used for the calibration. For DoD projects, matrix spiking solutions shall contain all target compounds.

- ◆ Matrix spiking mixes for individual analytes are created at 100 mg/L and spiked into samples at 50 $\mu\text{g/L}$ (*i.e.* 2.50 μL per 5000 μL purge volume).
- ◆ For SIM (selective ion monitoring) analysis, compounds of interest are spiked at concentrations of 0.4 ppb ($\mu\text{g/L}$).
- ◆ For 1-Dioxane, compounds of interest are spiked at concentrations of 50 ppb ($\mu\text{g/L}$).

Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

6.0 SAMPLE HANDLING AND PRESERVATION

Unanalyzed samples are refrigerated at 4 ± 2 degrees Celsius in sealed vials or containers.

Aqueous samples are preserved to a pH <2 with HCl and/or $\text{Na}_2\text{S}_2\text{O}_3$ (unless unpreserved requested) and collected in a 40 ml. Preserved samples must be analyzed within 14 days from sample collection; unpreserved samples must be analyzed within 7 days from sample collection.

Soil samples collected EncoreTM Samplers must be preserved within 48 hours and analyzed within 14 days. Soil samples collected in glass jars shall be kept refrigerated and analyzed within 14 days from sample collection. For additional information on sample collection, handling and preservation for soil samples see SOP #ORL-005.

7.0 PROCEDURE

Sample introduction.

- ◆ Direct injection - This method of introduction is used only rarely, generally when the compounds of interest exhibit poor purging efficiency. Quantitation in this case, if required, is generally subject to external standard calibration procedures (*cf.* Method 8000).
- ◆ Purge-and-trap - This is generally used for sample introduction for both soil and water samples. All samples, standards, spikes, and blanks are introduced into the GC/MS system in an identical manner (see Merit SOP# ORL-005).

GC/MS operating conditions - see Table 3 for routine operating conditions for VOC analysis.

- ◆ For SIM, the MS is put into the SIM mode. Based on compounds of interest, the time windows are set within the run (i.e. for internal standards, surrogate standards, compounds). For each time window, corresponding to a compound, a minimum of 3 ions are chosen for qualitative analysis. One ion (primary ion), generally the most abundant ion is used for quantitative analysis.

Initial calibration.

- ◆ Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for 4-bromofluorobenzene. Analysis does not begin until these criteria are met.
 - In the absence of any other manipulations, evaluate the mass spectrum of the peak apex or the scan immediately preceding or following from the total ion chromatogram for the BFB peak. This is the default approach used.
 - If the above evaluation is adversely affected by ion peak asymmetry, average the three highest intensity scans of the peak or average the mass spectrum ranging from the 10% initial peak intensity to the tailing 10% peak intensity level from the total ion chromatogram for the BFB peak.
 - If the above evaluation is adversely affected by background contamination, perform a background subtraction with a spectrum within 20 scans of the BFB peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.
 - The BFB mass intensity criteria in Table 4 are used as tuning acceptance criteria.
 - All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must use the identical mass spectrometer instrument conditions, Exception: for SIM, tune is run using full scan acquisition and subsequent samples are acquired using SIM.

- ◆ Purge and analyze each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary. The purge volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a midpoint calibration standard.
- ◆ Calculate response factors (*RFs*) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.
- ◆ Response Factor Criteria
 - It is recommended that a minimum response factor for the most common target analytes as noted in Table 2b, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration level is important in demonstrating the desired sensitivity. Due to the large number of compounds that may be analyzed, some compounds will fail to meet this criteria. In particular, poor performers such as ketones and 1,2-dibromo-3-chloropropane are likely to fail this criteria but have been demonstrated to perform adequately overall.
 - If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination in the purge-and-trap system, excessively high or low purge flow rates, and active sites in the column or chromatographic system. Replacing the calibration standards, clipping and/or replacing the column will likely solve this problem.
- ◆ Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. This is accomplished by setting the retention time extraction windows in the Chemstation software.
- ◆ Linearity of target analytes - If the %RSD of any target analytes is 20% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.

- Refer to SW-846 Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. The coefficient of determination for any regression fit should be ≥ 0.99 . In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters.
 - When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc.*
 - The method of linear regression analysis has the potential for a significant bias to the lower portion of a calibration curve, while the relative percent difference and the quadratic methods of calibration do not have this potential bias. When calculating the calibration curves using the linear regression model, a minimum quantitation check on the viability of the lowest calibration point should be performed by re-fitting the response from the low concentration calibration standard back into the curve. The recalculated concentration of the low calibration point should be within 30% of the standard's true concentration. Other recovery criteria may be applicable depending on the project's data quality objectives. For analytes which do not meet the minimum quantitation calibration re-fitting criteria reporting those analytes as estimated when the concentration is at or near the lowest calibration point may be appropriate.
 - The initial calibration curve should be verified immediately after performing the standard analyses using a second source standard at a concentration near the midpoint of the calibration range. The acceptance limits are 70-130% or project specific. Analytes that fail this criteria are considered estimated values.
 - The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e.* average RF or regression coefficients), and the appropriate calibration quality metric (*i.e.* %RSD or COD).
- ◆ GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

- ◆ Prior to the analysis of samples or calibration standards, purge the BFB standard into the GC/MS system. The resultant mass spectrum for BFB must meet the criteria given in Table 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the BFB.
- ◆ The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC/MS (50 µg/L; this represents 2.50 µL of the 100 mg/L calibration standard solution in a 5mL purge volume). A concentration of 0.1µg/L is analyzed for SIM procedures. The results from the calibration standard analysis must meet the verification acceptance criteria provided below. In addition the internal standards should be within 10s of those in the midpoint calibration standard and the responses should be 50-200% of those in the midpoint calibration standard.
- ◆ A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants. A method blank/wash sample is also run after calibration check/spike samples and prior to analytical samples in order to eliminate carryover contamination from the purge-and-trap system.
- ◆ Calibration Verification
 - A calibration verification must be made during every 12-hour analytical shift.
 - Each of the most common target analytes in the calibration verification standard should meet the minimum response factors as noted in Table 2b. This is the same check that is applied during the initial calibration and exceptions are noted above.
 - If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.
 - All target compounds of interest must be evaluated using a 20% variability criterion. If the percent drift for a compound is less than or equal to 20%, then the initial calibration for that compound is assumed to be valid. Due to the large numbers of compounds that may be analyzed by this method, some compounds will fail to meet the criteria. If the criterion is not met for more than 20% of the compounds included in the initial calibration, then corrective action must be taken prior to the analysis of samples. In cases where compounds fail, they may still be reported as non-detects if it can be demonstrated that there was adequate sensitivity to detect the compound at the applicable quantitation limit. For situations when a failed compound is present, the concentration is an estimated

value. Drift is defined as the normalized deviation of the measured from the spike value of a target component: $\%D = |C - C_{spike}| / C_{spike}$.

- Problems similar to those listed under initial calibration could affect the calibration verification. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The calibration verification criteria must be met before sample analysis begins.

GC/MS analysis of samples.

- ◆ Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.
- ◆ Use a 5 mL syringe to take a 5 mL aliquot from the sample vial. Be sure to eliminate any air bubbles from within the syringe.
- ◆ Add 5 µL of 50 mg/L internal/surrogate standard mixture are introduced to each sample through the autosampler. For SIM analysis, internal and surrogate standards are spiked at 0.1 µg/L.
- ◆ If the concentration for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.
- ◆ The Extracted Ion Current Profile (EICP) area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Table 5a and 5b). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.

Qualitative analysis.

- ◆ The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic

ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Figures 1a and 1b. Compounds are identified when the following criteria are met.

- Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound specific retention time.
- The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)
- Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
- Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
- Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.
- In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of continued uncertainty, the analyst should preferentially make a conservative judgment and accept an identified hit, allowing the potential for a false positive.

- ◆ For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:
 - Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
 - The relative intensities of the major ions should agree within $\pm 20\%$.
 - Molecular ions present in the reference spectrum should be present in the sample spectrum.
 - Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
 - Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Quantitative analysis.

- ◆ Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.
- ◆ The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1[C_s/C_i] + k_2[C_s/C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th} -order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv \langle \text{RF} \rangle$, while $k_0, k_2 \equiv 0$.
- ◆ The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the tentatively identified compound (TIC) areas for the nearest internal standard and target compound. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

- ◆ Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-xylene).

8.0 QUALITY CONTROL

All of the quality control items employed and evaluated are provided in Table 5a and 5b. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action. Control limits for surrogates and internal standards are listed in Table 6. The analyst will follow SOP # QA-007 and complete the appropriate review form upon completion of the analysis.

9.0 METHOD PERFORMANCE

The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis. Laboratory specific performance data is provided for Merit's LIMs system. Each sample batch contains a method blank, laboratory control sample and matrix spike samples. Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

Each instrument is assigned a maintenance logbook. All maintenance performed on the instrument must be recorded. Additionally, any modifications to the instrument settings shall be noted in the specific instrument logbook. Maintenance procedures provided in the equipment manual shall be followed. Maintenance may include, cleaning the MS source, clipping/replacing the column, or replacing the calibration standard.

Computer software and firmware can be found on Merit's network at F:\data\MERIT\EQUIPMENT\Instrument-Software Version List.200818.xls.

11.0 SAFETY

Eye protection and gloves must be worn while performing the analyses. Every laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples. The air system throughout the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.

A reference file of material safety data sheets (MSDSs) is available to all personnel. Specific attention shall be paid (but not limited) to:

- a. Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.
- b. Hydrochloric acid is corrosive. Extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations. Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 DEFINITIONS

4-Bromofluorobenzene (BFB), is used to verify that the GC/MS is properly tuned and ready for calibration and sample analyses. BFB is directly injected at 25-50 ng and precedes all other analyses. A twelve hour analysis time window is used before another BFB injection is required.

An Initial Calibration Verification standard (ICV) is analyzed before the analysis of samples as a check on the calibration curve. The ICV shall be of a second source, meaning a separate vendor and/or lot # shall be used to prepare this standard. A second source is needed to validate the integrity and concentration of the standards used for calibration.

An Initial Calibration Blank (ICB) is also analyzed before samples to confirm that the deionized water (DI H₂O) used for standards, blanks, and dilutions are free from contamination. An ICB for soil samples also includes organic free sand and/or methanol used for standard and QC preparation, as well as sample dilutions and volume adjustments; the control sand and methanol must also be documented as free from contamination.

A Calibration Check Verification standard (CCV) is analyzed at the beginning of each sequence (following the BFB injection) shift and every 12 hour shift thereafter. A CCV is made up from the same standards used for calibration and is used to ensure that the calibration and retention times are stable.

An analytical batch is defined as a group of samples (not to exceed 20 samples) analyzed per sequential run. Depending on client or program requirements, an analytical batch may or may not include matrix spikes as part of the 20 samples.

Internal standards (ISTD) are added to each sample, blank, spike, and check standard. The ISTDs used are Fluorobenzene, Chlorobenzene-d₅, and 1,4-Dichlorobenzene-d₄. The ISTD is used for internal calibration as a reference peak and to check purging efficiency.

Surrogate standards (SSTD) are also added to each sample, blank, spike, and check standard. The SSTDs used are Toluene-d₄, 4-Bromofluorobenzene, 1,2-Dichloroethane-d₄, and Dibromofluoromethane. The SSTD is used as matrix interference and as a method control check.

Method Blank (MB): An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

A Continuing Calibration Blank (CCB) is analyzed every 12 hour shift after the MB has been analyzed and before sample reanalyzes to ensure the system is still free from contamination.

Instrument blanks are analyzed whenever instrument contamination is a suspected possibility. The purpose of an IB is to prevent carry over from a standard, spike, or contaminated sample into another sample or blank. The acceptance criteria for an IB is the same as for a MB or CCB (for example: if an IB contains detections above acceptance criteria and a MB and/or sample following the IB exhibit the same contamination above acceptance criteria, then the instrument shall be considered contaminated). The samples and/or MBs shall be reanalyzed after the instrument is confirmed free from contamination.

Laboratory Control Spike (LCS): Milli-Q water (for water) and Organic-Free Soil (for soil) is spiked with all target compounds and carried through the complete sample preparation and analytical procedure. The control spike is used to document the ability of an analyst to generate acceptable precision and bias to verify the analytical system performance, and to document method accuracy for each matrix.

Matrix Spike (MS): An aliquot of sample spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Matrix Spike Duplicate (MSD): Intra-laboratory split samples spiked with all target compounds. The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

14.0 REFERENCES

Bellar, T., *Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

Department of Defense, Quality Systems Manual for Environmental Laboratories (DoD QSM), DoD Environmental Data Quality Workgroup, Department of Navy, Lead Service, ISO/IEC 17025:2005, ISO/IEC 17025:2017 and The NELAC Institute (TNI) Standards, Volume 1, September 2009, Version 5.3, May 7, 2019

U.S. EPA 40 CFR Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule*, October 26, 1984.

EPA SW-846, *Test Methods for Evaluation Solid Waste*, 3rd Edition, Update I dated 7/92, Update II dated 9/94, Update IIA dated 8/93, Update IIB dated 1/95, Update III dated 12/96, Update IV dated 1/08.

International Standards Organization (ISO), 2005. *General Requirements for the Competence of Testing and Calibration Laboratories*. ISO 17025.

National Environmental Laboratory Accreditation Conference (NELAC), 2003. *Standards, Chapters 1–6*, EPA/600/R-04/003.

EPA Method 624.1, December 2016

Table 1. Summary of Retention Times and Characteristic Ions for Volatile Organics

Compound List Report Ravnica

Method : F:\GCMS.DAT\RAVNICA.SN\METHODS\WR201119.M
 Title : Volatile Organics, SW-846 # 8260B
 Last Update : Thu Nov 19 18:19:17 2020
 Response via : Initial Calibration
 Total Cpnds : 88

PK#	Compound Name	QIon	Exp_RT	Rel_RT	Cal	#Qual	A/H	ID
1 I	PENTAFLUOROBENZENE (I)	168	4.04	1.000	A	2	A	B
2 S	1,2-DICHLOROETHANE-D4 (S)	65	4.19	1.039	A	2	A	B
3	1,1,2-Trichloro-1,2,2-trifluor	101	2.63	0.651	A	2	A	B
4	Diethyl ether (*)	74	2.41	0.596	A	2	A	B
5	Acetone (*)	43	2.66	0.660	A	2	A	B
6	Methyl iodide (iodomethane) (*)	142	2.70	0.669	A	2	A	B
7	Carbon disulfide (*)	76	2.76	0.684	A	2	A	B
8	Methyl Acetate	43	2.91	0.721	A	2	A	B
9	tert-Methyl butyl ether (MTBE)	73	3.17	0.784	A	3	A	B
10	Acrylonitrile (*)	53	3.15	0.780	A	2	A	B
11	2-Butanone (MEK) (*)	43	3.77	0.935	A	2	A	B
12	Dichlorodifluoromethane	85	1.26	0.311	QO	2	A	B
13	Chloromethane (SPCC)	50	1.34	0.332	A	2	A	B
14	Vinyl Chloride (CCC)	62	1.47	0.365	A	2	A	B
15	Bromomethane	94	1.75	0.432	A	2	A	B
16	Chloroethane	64	1.85	0.458	A	3	A	B
17	Acrolein	56	2.52	0.623	A	2	A	B
18	Trichlorofluoromethane	101	2.17	0.538	A	3	A	B
19	1,1-Dichloroethene (CCC/MS)	61	2.58	0.639	A	3	A	B
20	Methylene Chloride	84	2.97	0.736	A	3	A	B
21	trans-1,2-Dichloroethene	61	3.16	0.782	A	3	A	B
22	Hexane	57	3.33	0.825	A	2	A	B
23	Vinyl Acetate	43	3.32	0.823	A	2	A	B
24	1,1-Dichloroethane (SPCC)	63	3.42	0.848	A	2	A	B
25	cis-1,2-Dichloroethene	96	3.76	0.932	A	2	A	B
26	2,2-Dichloropropane	77	3.76	0.932	A	2	A	B
27	Tetrahydrofuran	42	3.92	0.970	A	2	A	B
28	Chloroform (CCC)	83	3.94	0.975	A	2	A	B
29	Bromochloromethane	130	3.90	0.965	A	3	A	B
30	1,1,1-Trichloroethane	97	4.04	1.000	A	2	A	B
31	1,1-Dichloropropene	75	4.11	1.018	A	2	A	B
32	Cyclohexane	42	4.06	1.005	A	3	A	B
33 I	1,4-DIFLUOROBENZENE (I)	114	4.40	1.000	A	2	A	B
34 S	TOLUENE-D8 (S)	98	5.11	1.160	A	2	A	B
35	4-Methyl-2-pentanone (MIBK) (*)	58	5.04	1.145	A	3	A	B
36	2-Hexanone (*)	58	5.43	1.232	A	3	A	B
37	2-chloroethylvinyl ether	63	4.90	1.113	A	2	A	B
38	Carbon Tetrachloride	117	4.12	0.936	A	2	A	B
39	Benzene (MS)	78	4.22	0.958	A	2	A	B
40	1,2-Dichloroethane	62	4.23	0.961	A	3	A	B
41 M	Trichloroethene (MS)	95	4.53	1.030	A	3	A	B
42	1,2-Dichloropropane (CCC)	63	4.64	1.055	A	2	A	B
43	Bromodichloromethane	83	4.77	1.083	A	3	A	B
44	Methyl Cyclohexane	55	4.63	1.051	A	3	A	B
45	Dibromomethane	174	4.71	1.069	A	3	A	B
46	cis-1,3-Dichloropropene	75	4.98	1.131	A	2	A	B
47 M	Toluene (CCC/MS)	91	5.14	1.167	A	2	A	B
48	trans-1,3-Dichloropropene	75	5.23	1.188	A	2	A	B

49		1,1,2-Trichloroethane	83	5.32	1.208	A	3	A	B
50		Tetrachloroethene	166	5.39	1.225	A	2	A	B
51	I	CHLOROBENZENE-D5 (I)	82	5.78	1.000	A	2	A	B
52	S	4-BROMOFLUOROBENZENE (S)	174	6.33	1.095	A	2	A	B
53		1,3-Dichloropropane	76	5.40	0.935	A	2	A	B
54		trans-1,4-Dichloro-2-butene	53	6.41	1.109	QO	3	A	B
55		Dibromochloromethane	129	5.51	0.954	A	2	A	B
56		1,2-Dibromoethane	107	5.57	0.965	A	2	A	B
57	M	Chlorobenzene (SPCC/MS)	112	5.79	1.003	A	2	A	B
58		1,1,1,2-Tetrachloroethane	131	5.83	1.009	A	3	A	B
59		Ethylbenzene (CCC)	91	5.84	1.010	A	2	A	B
60		p,m-Xylene	106	5.89	1.019	A	2	A	B
61		o-Xylene	91	6.08	1.052	A	2	A	B
62		Styrene	104	6.08	1.053	A	2	A	B
63		Isopropylbenzene	105	6.24	1.081	A	2	A	B
64		Bromoform (SPCC)	173	6.18	1.070	A	2	A	B
65		1,1,2,2-Tetrachloroethane (SPC)	83	6.38	1.104	A	3	A	B
66		1,2,3-Trichloropropane	110	6.41	1.110	A	3	A	B
67		n-Propylbenzene	91	6.44	1.114	A	2	A	B
68		Bromobenzene	156	6.41	1.109	A	2	A	B
69		1,3,5-Trimethylbenzene	120	6.52	1.128	A	2	A	B
70		2-Chlorotoluene	91	6.49	1.123	A	2	A	B
71		4-Chlorotoluene	126	6.54	1.132	A	2	A	B
72		tert-Butylbenzene	91	6.67	1.155	A	2	A	B
73		1,2,4-Trimethylbenzene	120	6.70	1.160	A	2	A	B
74	I	1,4-DICHLOROBENZENE-D4 (I)	152	6.88	1.000	A	2	A	B
75		sec-Butylbenzene	105	6.78	0.986	A	2	A	B
76		p-Isopropyltoluene	119	6.84	0.995	A	2	A	B
77		1,3-Dichlorobenzene	146	6.85	0.995	A	2	A	B
78		1,4-Dichlorobenzene	146	6.89	1.002	A	2	A	B
79		1,2-Dichlorobenzene	146	7.07	1.028	A	2	A	B
80		1,2,3-Trimethylbenzene	105	6.90	1.004	A	2	A	B
81		n-Butylbenzene	91	7.04	1.024	A	2	A	B
82		Hexachloroethane	201	7.19	1.046	A	2	A	B
83		1,2-Dibromo-3-Chloropropane	157	7.44	1.082	A	3	A	B
84		1,2,4-Trichlorobenzene	182	7.84	1.140	A	3	A	B
85		Hexachlorobutadiene	225	7.92	1.151	A	3	A	B
86		1,2,3-Trichlorobenzene	180	8.09	1.176	A	3	A	B
87		Naphthalene	128	7.97	1.159	A	3	A	B
88		2-Methylnaphthalene	142	8.52	1.239	A	2	A	B

Cal A = Average L = Linear LO = Linear w/origin Q = Quad QO = Quad w/origin

#Qual = number of qualifiers

A/H = Area or Height

ID R = R.T. B = R.T. & Q Q = Qvalue L = Largest A = All

 WR201119.M Fri Dec 18 09:41:56 2020

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

Table 2. Summary of Applicable Performance Compounds - Volatile Organics Analysis

COMPOUND	ISD	SSD
PENTAFLUOROBENZENE	✓	
1,2-DICHLOROETHANE-D4		✓
1,4-DIFLUOROBENZENE	✓	
TOLUENE-D8		✓
CHLOROBENZENE-D5	✓	
4-BROMOFLUOROBENZENE-		✓
1,4-DICHLOROBENZENE-D4	✓	

: For DoD projects, all target compounds will be included in the matrix spike and matrix spike duplicate

Key

ISD: Internal Standard Compound

SSD: Surrogate Standard Compound

Table 2b. Recommended Minimum Relative Response Factor Criteria For Initial And Continuing Calibration Verification.

Volatile Compounds	Minimum Response Factor (RF) ^a
Dichlorodifluoromethane	0.100
Chloromethane	0.100
Vinyl chloride	0.100
Bromomethane	0.100
Chloroethane	0.100
Trichlorofluoromethane	0.100
1,1-Dichloroethene	0.100
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100
Acetone	0.100
Carbon disulfide	0.100
Methyl Acetate	0.100
Methylene chloride	0.100
trans-1,2-Dichloroethene	0.100
cis-1,2-Dichloroethene	0.100
Methyl tert-Butyl Ether	0.100
1,1-Dichloroethane	0.200
2-Butanone	0.100
Chloroform	0.200
1,1,1-Trichloroethane	0.100
Cyclohexane	0.100
Carbon tetrachloride	0.100
Benzene	0.500
1,2-Dichloroethane	0.100
Trichloroethene	0.200
Methylcyclohexane	0.100
1,2-Dichloropropane	0.100
Bromodichloromethane	0.200
cis-1,3-Dichloropropene	0.200
trans-1,3-Dichloropropene	0.100
4-Methyl-2-pentanone	0.100
Toluene	0.400
1,1,2-Trichloroethane	0.100
Tetrachloroethene	0.200
2-Hexanone	0.100
Dibromochloromethane	0.100
1,2-Dibromoethane	0.100
Chlorobenzene	0.500

Volatile Compounds	Minimum Response Factor (RF) ^a
Ethylbenzene	0.100
meta-/para-Xylene	0.100
ortho-Xylene	0.300
Styrene	0.300
Bromoform	0.100
Isopropylbenzene	0.100
1,1,2,2-Tetrachloroethane	0.300
1,3-Dichlorobenzene	0.600
1,4-Dichlorobenzene	0.500
1,2-Dichlorobenzene	0.400
1,2-Dibromo-3-chloropropane	0.050
1,2,4-Trichlorobenzene	0.200

^a The Project-specific response factors obtained may be affected by the quantitation ion selected and when using possible alternate ions the actual response factors may be lower than those listed.

Table 3. GC/MS Operating Conditions - Volatile Organics Analysis

Operating Parameter	Volatiles Analysis
Chromatographic Column	DB 624, $L = 20\text{ m}$, $ID = 0.18\text{ mm}$
Carrier Gas	Helium (He)
Temperature Program	$T_0 = 30^\circ\text{C}$, hold 2.0 min $dT/dt_1 = 32^\circ\text{C/min}$ $T_1 = 195^\circ\text{C}$ $dT/dt_2 = 30^\circ\text{C/min}$ $T_2 = 235^\circ\text{C}$
Injector Temperature	150°C
Detector Temperature	300°C
Purge Volume	5 mL
Mass Scanning Range	$35\text{ m/z} - 260\text{ m/z}$
Mass Scanning Rate	2.0 Hz

Note: the above is subject to change based on GC and/or sample conditions.

Table 4. BFB Tune Evaluation Criteria

Target m/z	Relative m/z	LCL (%)	UCL (%)
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5.0	9.0
173	174	0	2.0
174	95	50	120
175	174	4.0	9.0
176	174	93	101
177	176	5.0	9.0

Abundance criteria are for a quadrupole mass spectrometer. 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, or for an alternative carrier gas, provided method performance is not adversely affected.

Table 5a. Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
BFB	12-hour	Table 4	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
Calibration Verification	12-hour	Table 2b	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Laboratory in-house Control Limits with no more than 4 Marginal Exceedances	A failed LCS should be re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-analyzed or QC data qualified.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	<RL	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) should result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard	All samples	Section 7.5.5	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch.

QC Item	Frequency	Acceptance Criteria	Corrective Action
			The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate
Surrogate Standard	All samples	Table 6	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract of re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

Table 5b. Quality Control Items, Frequency, and Corrective Action for DoD Projects

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Tune Check	Prior to ICAL and prior to each 12-hour period of sample analysis.	Specific ion abundance criteria of BFB or DFTPP from method.	Retune instrument and verify.	Flagging is not appropriate.	No samples shall be analyzed without a valid tune.
Initial calibration (ICAL) for all analytes (including surrogates)	At instrument set-up and after ICV or CCV failure, prior to sample analysis.	Each analyte must meet one of the three options below: Option 1: RSD for each analyte $\leq 15\%$; Option 2: linear least squares regression for each analyte: $r^2 \geq 0.99$; Option 3: non-linear least squares regression (quadratic) for each analyte: $r^2 \geq 0.99$.	Correct problem then repeat ICAL.	Flagging is not appropriate.	Minimum 5 levels for linear and 6 levels for quadratic. No samples shall be analyzed until ICAL has passed. If the specific version of a method requires additional evaluation (e.g., RFs or low calibration standard analysis and recovery criteria) these additional requirements must also be met.
Retention Time window position establishment	Once per ICAL and at the beginning of the analytical sequence.	Position shall be set using the midpoint standard of the ICAL curve when ICAL is performed. On days when ICAL is not performed, the initial CCV is used.	NA.	NA.	Calculated for each analyte and surrogate.
Evaluation of Relative Retention Times (RRT)	With each sample.	RRT of each reported analyte within ± 0.06 RRT units.	Correct problem, then rerun ICAL.	NA.	After maintenance is performed which may affect retention times, RRTs may be updated based on the daily CCV. RRTs shall be compared with the most recently updated RRTs.
Initial	Once after	All reported	Correct problem.	Flagging is not	No samples shall be analyzed

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Calibration Verification (ICV)	each ICAL, analysis of a second source prior to sample analysis	analytes within $\pm$ 20% of true value.	Rerun ICV. If that fails, repeat ICAL.	appropriate.	until calibration has been verified with a second source.
Continuing calibration verification (CCV)	Daily before sample analysis; after every 12 hours of analysis time; and at the end of the analytical batch run.	All reported analytes and surrogates within $\pm$ 20% of true value. All reported analytes and surrogates within $\pm$ 50% for end of analytical batch CCV.	Immediately analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails or if two consecutive CCVs cannot be run, perform corrective action(s) and repeat CCV and all associated samples since the last acceptable CCV. Alternately, recalibrate if necessary; then reanalyze all associated samples since the last acceptable CCV.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since last acceptable calibration verification.	Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed. If the specific version of a method requires additional evaluation (e.g, average RFs) these additional requirements must also be met.
Internal standards (IS)	Every field sample, standard, and QC sample.	Retention time $\pm$ 10 seconds from retention time of the midpoint standard in the ICAL; EICP area within -50% to +100% of ICAL midpoint standard.	Inspect mass spectrometer and GC for malfunctions and correct problem. Reanalysis of samples analyzed while system was malfunctioning is	If corrective action fails in field samples, data must be qualified and explained in the case narrative. Apply Q-flag	NA

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
		On days when ICAL is not performed, the daily initial CCV can be used.	mandatory.	to analytes associated with the non-compliant IS. Flagging criteria is not appropriate for failed standards.	
Method blank (MB)	One per preparatory batch.	No analytes detected > ½ LOQ or > 1/10 th the amount measured in any sample or 1/10 th the regulatory limit, whichever is greater. Common contaminants, must not be detected > LOQ.	Correct problem. If required, reprep and reanalyze MB and all QC samples and field samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Laboratory Control Sample (LCS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory	Must contain all surrogates and all analytes to be reported. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
				batch.	
Matrix Spike (MS)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified.	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	Must contain all surrogates and all analytes to be reported. For matrix evaluation only. If MS results are outside the limits, the data shall be evaluated to determine the source(s) of difference, i.e., matrix effect or analytical error.
Matrix spike duplicate (MSD) or Matrix duplicate (MD)	One per preparatory batch.	A laboratory must use the QSM Appendix C Limits for batch control if project limits are not specified. If the analyte(s) are not listed, use in-house LCS limits if project limits are not specified. MSD or MD: RPD of all analytes $\leq$ 20% (between MS and MSD or sample and MD).	Examine the project-specific requirements. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met and explain in the case narrative.	MSD: Must contain all surrogates and all analytes to be reported. The data shall be evaluated to determine the source of difference. For Sample/MD: RPD criteria only apply to analytes whose concentration in the sample is greater than or equal to the LOQ.
Surrogate spike	All field and QC samples.	QC acceptance criteria specified by project, if available; otherwise use QSM Appendix C limits or in-house LCS limits if analyte(s) are not listed..	Correct problem, then reprep and reanalyze all failed samples for all surrogates in the associated preparatory batch, if sufficient sample material is available. If obvious	Apply Q-flag to all associated analytes if acceptance criteria are not met and explain in the case narrative.	Alternative surrogates are recommended when there is obvious chromatographic interference.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
			chromatographic interference with surrogate is present, reanalysis may not be necessary, but the client must be notified prior to reporting data and the failures must be discussed in the Case Narrative.		

DoD Appendix C LCS Limits
Method 8260 Solid Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	125
71-55-6	1,1,1-Trichloroethane	73	130
79-34-5	1,1,2,2-Tetrachloroethane	70	124
79-00-5	1,1,2-Trichloroethane	78	121
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane [Freon-113]	66	136
75-34-3	1,1-Dichloroethane	76	125
75-35-4	1,1-Dichloroethene	70	131
563-58-6	1,1-Dichloropropene	76	125
87-61-6	1,2,3-Trichlorobenzene	66	130
96-18-4	1,2,3-Trichloropropane	73	125
526-73-8	1,2,3-Trimethylbenzene	82	118
120-82-1	1,2,4-Trichlorobenzene	67	129
95-63-6	1,2,4-Trimethylbenzene	75	123
96-12-8	1,2-Dibromo-3-chloropropane	61	132
106-93-4	1,2-Dibromoethane	78	122
95-50-1	1,2-Dichlorobenzene	78	121
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	71	136
540-59-0	1,2-Dichloroethene	78	122
78-87-5	1,2-Dichloropropane	76	123
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	64	132
108-70-3	1,3,5-Trichlorobenzene	71	128
108-67-8	1,3,5-Trimethylbenzene	73	124
541-73-1	1,3-Dichlorobenzene	77	121
142-28-9	1,3-Dichloropropane	77	121
542-75-6	1,3-Dichloropropene	77	126
106-46-7	1,4-Dichlorobenzene	75	120
105-05-5	1,4-Diethylbenzene	79	114

123-91-1	1,4-Dioxane	55	138
544-10-5	1-Chlorohexane	71	130
594-20-7	2,2-Dichloropropane	67	133
78-93-3	2-Butanone (MEK)	51	148
126-99-8	2-Chloro-1,3-butadiene	65	133
110-75-8	2-Chloroethyl vinyl ether	43	149
95-49-8	Chlorotoluene	75	122
591-78-6	2-Hexanone	53	145
79-46-9	2-Nitropropane	47	150
67-63-0	2-Propanol [Isopropyl alcohol]	60	140
460-00-4	4-Bromofluorobenzene	79	119
106-43-4	4-Chlorotoluene	72	124
108-10-1	4-Methyl-2-pentanone [MIBK]	65	135
67-64-1	Acetone	36	164
75-05-8	Acetonitrile	54	143
107-02-8	Acrolein [Propenal]	47	155
107-13-1	Acrylonitrile	65	134
107-05-1	Allyl chloride	68	135
71-43-2	Benzene	77	121
100-44-7	Benzyl chloride	64	120
108-86-1	Bromobenzene	78	121
74-97-5	Bromochloromethane	78	125
75-27-4	Bromodichloromethane	75	127
75-25-2	Bromoform	67	132
74-83-9	Bromomethane	53	143
75-15-0	Carbon disulfide	63	132
56-23-5	Carbon tetrachloride	70	135
108-90-7	Chlorobenzene	79	120
124-48-1	Chlorodibromomethane	74	126
75-00-3	Chloroethane	59	139
67-66-3	Chloroform	78	123
74-87-3	Chloromethane	50	136
156-59-2	cis-1,2-Dichloroethene	77	123

10061-01-5	cis-1,3-Dichloropropene	74	126
1476-11-5	cis-1,4-Dichloro-2-butene	69	143
110-82-7	Cyclohexane	67	131
108-94-1	Cyclohexanone	30	156
1868-53-7	Dibromofluoromethane	78	119
74-95-3	Dibromomethane	78	125
75-71-8	Dichlorodifluoromethane [Freon-12]	29	149
75-43-4	Dichlorofluoromethane	47	155
60-29-7	Diethyl ether	71	129
108-20-3	Diisopropyl ether	69	127
64-17-5	Ethanol	45	159
141-78-6	Ethyl acetate	52	139
97-63-2	Ethyl methacrylate	69	129
637-92-3	Ethyl tert-butyl ether	72	126
100-41-4	Ethylbenzene	76	122
462-06-6	Fluorobenzene	81	114
142-82-5	Heptane	49	138
87-68-3	Hexachlorobutadiene	61	135
67-72-1	Hexachloroethane	72	133
110-54-3	Hexane	45	142
74-88-4	Iodomethane	71	131
78-83-1	Isobutyl alcohol	60	135
108-21-4	Isopropyl acetate [Acetic acid]	58	131
98-82-8	Isopropylbenzene	68	134
179601-23-1	m/p-Xylene [3/4-Xylene]	77	124
126-98-7	Methacrylonitrile	66	132
79-20-9	Methyl acetate	53	144
80-62-6	Methyl methacrylate	63	134
1634-04-4	Methyl tert-butyl ether [MTBE]	73	125
108-87-2	Methylcyclohexane	66	133
75-09-2	Methylene chloride	70	128
123-86-4	n-Butyl acetate	62	128
71-36-3	n-Butyl alcohol	55	131

104-51-8	n-Butylbenzene	70	128
103-65-1	n-Propylbenzene	73	125
91-20-3	Naphthalene	62	129
95-47-6	o-Xylene	77	123
99-87-6	p-Isopropyltoluene [p-Cymene]	73	127
76-01-7	Pentachloroethane	69	135
107-12-0	Propionitrile [Ethyl cyanide]	68	134
135-98-8	sec-Butylbenzene	73	126
100-42-5	Styrene	76	124
994-05-8	tert-Amyl methyl ether [TAME]	73	126
75-65-0	tert-Butyl alcohol	68	133
98-06-6	tert-Butylbenzene	73	125
127-18-4	Tertachloroethene	73	128
109-99-9	Tetrahydrofuran	61	135
108-88-3	Toluene	77	121
2037-26-5	Toluene-d8	85	116
156-60-5	trans-1,2-Dichloroethene	74	125
10061-02-6	trans-1,3-Dichloropropene	71	130
110-57-6	trans-1,4-Dichloro-2-butene	62	136
79-01-6	Trichloroethene	77	123
75-69-4	Trichlorofluoromethane [Freon-11]	62	140
108-05-4	Vinyl acetate	50	151
75-01-4	Vinyl chloride	56	135
1330-20-7	Xylene [total]	78	124

DoD Appendix C LCS Limits
Method 8260 Water Matrix

CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
630-20-6	1,1,1,2-Tetrachloroethane	78	124
71-55-6	1,1,1-Trichloroethane	74	131
79-34-5	1,1,2,2-Tetrachloroethane	71	121
79-00-5	1,1,2-Trichloroethane	80	119
76-13-1	1,1,2-Trifluoro-1,2,2-trichloroethane	70	136

	[Freon-113]		
75-34-3	1,1-Dichloroethane	77	125
75-35-4	1,1-Dichloroethene	71	131
563-58-6	1,1-Dichloropropene	79	125
87-61-6	1,2,3-Trichlorobenzene	69	129
96-18-4	1,2,3-Trichloropropane	73	122
526-73-8	1,2,3-Trimethylbenzene	82	120
120-82-1	1,2,4-Trichlorobenzene	69	130
95-63-6	1,2,4-Trimethylbenzene	76	124
96-12-8	1,2-Dibromo-3-chloropropane	62	128
106-93-4	1,2-Dibromoethane	77	121
95-50-1	1,2-Dichlorobenzene	80	119
107-06-2	1,2-Dichloroethane	73	128
17060-07-0	1,2-Dichloroethane-d4	81	118
540-59-0	1,2-Dichloroethene	79	121
78-87-5	1,2-Dichloropropane	78	122
354-23-4	1,2-Dichlorotrifluoroethane [Freon 123a]	70	136
108-70-3	1,3,5-Trichlorobenzene	75	130
108-67-8	1,3,5-Trimethylbenzene	75	124
106-99-0	1,3-Butadiene	43	158
541-73-1	1,3-Dichlorobenzene	80	119
142-28-9	1,3-Dichloropropane	80	119
542-75-6	1,3-Dichloropropene	77	123
106-46-7	1,4-Dichlorobenzene	79	118
105-05-5	1,4-Diethylbenzene	79	118
123-91-1	1,4-Dioxane	59	139
544-10-5	1-Chlorohexane	76	124
540-84-1	2,2,4-Trimethylpentane [Isooctane]	58	132
594-20-7	2,2-Dichloropropane	60	139
75-85-4	2-Butanol	66	120
78-93-3	2-Butanone (MEK)	56	143
126-99-8	2-Chloro-1,3-butadiene	65	135

110-75-8	2-Chloroethyl vinyl ether	51	139
95-49-8	Chlorotoluene	79	122
591-78-6	2-Hexanone	57	139
91-57-6	2-Methylnaphthalene	17	142
79-46-9	2-Nitropropane	49	136
67-63-0	2-Propanol [Isopropyl alcohol]	56	142
624-95-3	3,3-Dimethyl-1-butanol	49	133
460-00-4	4-Bromofluorobenzene	85	114
106-43-4	4-Chlorotoluene	78	122
108-10-1	4-Methyl-2-pentanone [MIBK]	67	130
67-64-1	Acetone	39	160
75-05-8	Acetonitrile	50	142
107-02-8	Acrolein [Propenal]	39	155
107-13-1	Acrylonitrile	63	135
107-05-1	Allyl chloride	68	130
71-43-2	Benzene	79	120
100-44-7	Benzyl chloride	42	138
108-86-1	Bromobenzene	80	120
74-97-5	Bromochloromethane	78	123
75-27-4	Bromodichloromethane	79	125
75-25-2	Bromoform	66	130
74-83-9	Bromomethane	53	141
75-15-0	Carbon disulfide	64	133
56-23-5	Carbon tetrachloride	72	136
108-90-7	Chlorobenzene	82	118
124-48-1	Chlorodibromomethane	74	126
75-45-6	Chlorodifluoromethane	40	129
75-00-3	Chloroethane	60	138
67-66-3	Chloroform	79	124
74-87-3	Chloromethane	50	139
156-59-2	cis-1,2-Dichloroethene	78	123
10061-01-5	cis-1,3-Dichloropropene	75	124
1476-11-5	cis-1,4-Dichloro-2-butene	57	146

110-82-7	Cyclohexane	71	130
1868-53-7	Dibromofluoromethane	80	119
74-95-3	Dibromomethane	79	123
75-71-8	Dichlorodifluoromethane [Freon-12]	32	152
75-43-4	Dichlorofluoromethane	72	131
60-29-7	Diethyl ether	68	129
108-20-3	Diisopropyl ether	67	128
64-17-5	Ethanol	48	151
141-78-6	Ethyl acetate	55	138
97-63-2	Ethyl methacrylate	72	126
637-92-3	Ethyl tert-butyl ether	70	127
100-41-4	Ethylbenzene	79	121
462-06-6	Fluorobenzene	80	116
142-82-5	Heptane	49	140
87-68-3	Hexachlorobutadiene	66	134
67-72-1	Hexachloroethane	72	134
110-54-3	Hexane	48	143
74-88-4	Iodomethane	69	131
78-83-1	Isobutyl alcohol	63	133
108-21-4	Isopropyl acetate [Acetic acid]	63	133
98-82-8	Isopropylbenzene	72	131
179601-23-1	m/p-Xylene [3/4-Xylene]	80	121
126-98-7	Methacrylonitrile	63	133
79-20-9	Methyl acetate	56	136
80-62-6	Methyl methacrylate	67	128
1634-04-4	Methyl tert-butyl ether [MTBE]	71	124
108-87-2	Methylcyclohexane	72	132
75-09-2	Methylene chloride	74	124
123-86-4	n-Butyl acetate	69	125
71-36-3	n-Butyl alcohol	59	131
104-51-8	n-Butylbenzene	75	128
109-60-4	n-Propyl acetate	76	126
103-65-1	n-Propylbenzene	76	126

91-20-3	Naphthalene	61	128
95-47-6	o-Xylene	78	122
99-87-6	p-Isopropyltoluene [p-Cymene]	77	127
76-01-7	Pentachloroethane	69	133
109-66-0	Pentane	16	134
107-12-0	Propionitrile [Ethyl cyanide]	64	136
135-98-8	sec-Butylbenzene	77	126
100-42-5	Styrene	78	123
994-05-8	tert-Amyl methyl ether [TAME]	68	128
75-65-0	tert-Butyl alcohol	68	129
762-75-4	tert-Butyl formate	65	132
98-06-6	tert-Butylbenzene	78	124
127-18-4	Tertachloroethene	74	129
109-99-9	Tetrahydrofuran	57	133
108-88-3	Toluene	80	121
2037-26-5	Toluene-d8	89	112
156-60-5	trans-1,2-Dichloroethene	75	124
10061-02-6	trans-1,3-Dichloropropene	73	127
110-57-6	trans-1,4-Dichloro-2-butene	43	140
79-01-6	Trichloroethene	79	123
75-69-4	Trichlorofluoromethane [Freon-11]	65	141
108-05-4	Vinyl acetate	54	146
75-01-4	Vinyl chloride	58	137
1330-20-7	Xylene [total]	79	121

LCS Limits
EPA 624.1 Water Matrix

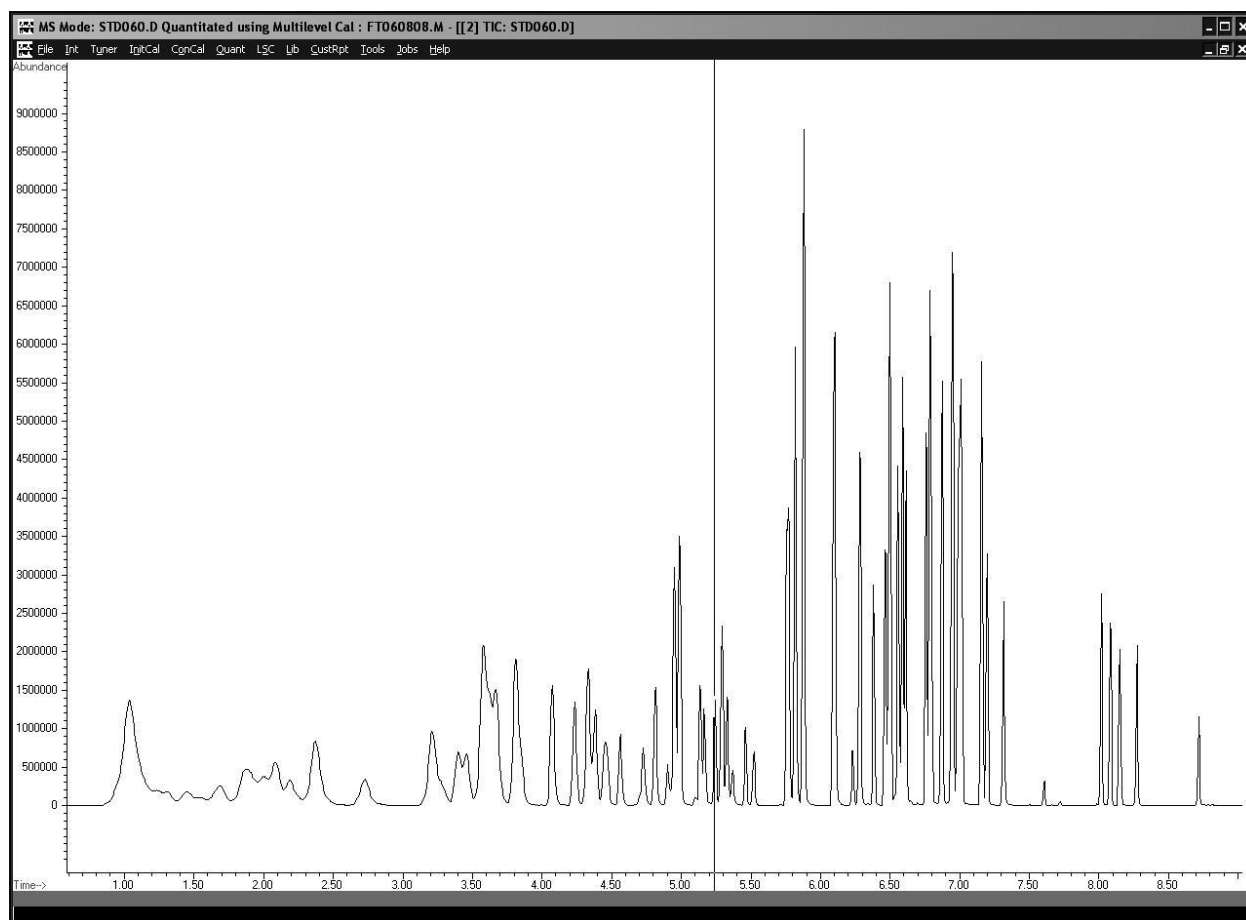
CAS ID	ANALYTE	LOWER CONTROL LIMIT (LCL)	UPPER CONTROL LIMIT (UCL)
71-55-6	1,1,1-Trichloroethane	70	130
79-34-5	1,1,2,2-Tetrachloroethane	60	140
79-00-5	1,1,2-Trichloroethane	70	130
75-34-3	1,1-Dichloroethane	70	130
75-35-4	1,1-Dichloroethene	50	150
95-50-1	1,2-Dichlorobenzene	65	135
107-06-2	1,2-Dichloroethane	70	130
78-87-5	1,2-Dichloropropane	35	165
541-73-1	1,3-Dichlorobenzene	70	130
106-46-7	1,4-Dichlorobenzene	65	135
110-75-8	2-Chloroethyl vinyl ether	0	225
107-02-8	Acrolein [Propenal]	60	140
107-13-1	Acrylonitrile	60	140
71-43-2	Benzene	65	135
75-27-4	Bromodichloromethane	65	135
75-25-2	Bromoform	70	130
74-83-9	Bromomethane	15	185
56-23-5	Carbon tetrachloride	70	130
108-90-7	Chlorobenzene	65	135
124-48-1	Chlorodibromomethane	70	135
75-00-3	Chloroethane	40	160
67-66-3	Chloroform	70	135
74-87-3	Chloromethane	0	205
10061-01-5	cis-1,3-Dichloropropene	25	175
100-41-4	Ethylbenzene	60	140
75-09-2	Methylene chloride	60	140
127-18-4	Tetrachloroethene	70	130
108-88-3	Toluene	70	130
156-60-5	trans-1,2-Dichloroethene	70	130

10061-02-6	trans-1,3-Dichloropropene	50	150
79-01-6	Trichloroethene	65	135
75-69-4	Trichlorofluoromethane [Freon-11]	50	150
75-01-4	Vinyl chloride	5	195

Table 6. Summary of Control Limits: Surrogate and Internal Standard Compounds Percent Recovery[†]

COMPOUND	Water Matrix		Solid Matrix	
	LCL (%)	UCL (%)	LCL (%)	UCL (%)
1,2-DICHLOROETHANE-D4	72.0	125.0	71.0	124.0
TOLUENE-D8	89.0	112.0	83.0	120.0
4-BROMOFLUOROBENZENE	80.0	124.0	81.0	124.0
Pentafluorobenzene	50.0	200.0	50.0	200.0
1,4-Difluorobenzene	50.0	200.0	50.0	200.0
Chlorobenzene-D5	50.0	200.0	50.0	200.0
1,4-Dichlorobenzene-D4	50.0	200.0	50.0	200.0

[†]: Results based on recovery data from 2020.

Figure 1. Example Total Ion Chromatogram for a Midpoint VOA Calibration Standard[†]

[†]: Data file Std060.D (60 µg/L). GC/MS acquisition parameters are given by Table 4.

TGI – GROUNDWATER AND SOIL SAMPLING EQUIPMENT DECONTAMINATION

Rev: 0

Rev Date: February 23, 2017



VERSION CONTROL

Revision No	Revision Date	Page No(s)	Description	Reviewed by
0	February 23, 2017	ALL	Conversion from SOP to TGI	Cassandra McCloud / Pete Frederick

APPROVAL SIGNATURES

Prepared by:



Date: 02/23/2017

Derrick Maurer

Technical Expert Reviewed by:



Date: 02/23/2017

Cassandra McCloud (Technical Expert)

1 INTRODUCTION

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

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In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, state-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM.

2 SCOPE AND APPLICATION

Decontamination is performed on sampling equipment prior to sample collection to ensure that the sampling equipment that contacts a sample, or monitoring equipment that is brought into contact with environmental media to be sampled, is free from analytes of interest and/or constituents that could interfere with laboratory analysis for analytes of interest. Sampling equipment must be appropriately cleaned prior to use for sampling or coming into contact with environmental media to be sampled, and following completion of the sampling event prior to shipment or storage. The effectiveness of the decontamination procedure should be verified by collecting and analyzing equipment blank samples.

The sampling equipment cleaning procedures described herein includes pre-field, in the field, and post-field cleaning of sampling equipment which may be conducted at an established equipment decontamination area (EDA) on site, as appropriate and necessary. Sampling equipment that may require decontamination at a given site includes: soil sampling tools; groundwater, sediment, and surface-water sampling devices; water testing instruments; down-hole instruments; and other activity-specific sampling equipment. Non-disposable equipment will be cleaned before collecting each sample, between each

sample collected, and prior to placing sampling equipment in protective cases, or containers for transport. Cleaning procedures for sampling equipment should be monitored by collecting equipment blank samples as required in project work plans, field sampling plans, quality assurance project plans (QAPP), or other pertinent project documents. Dedicated and/or single-use (i.e., not to be re-used) sampling equipment will not require decontamination.

3 PERSONNEL QUALIFICATIONS

Arcadis field sampling personnel will have completed or are in the process of completing site-specific training as well as having current health and safety training as required by Arcadis, client, or regulations, such as 40-hour HAZWOPER training and/or OSHA HAZWOPER site supervisor training. Arcadis personnel will also have current training as specified in the Health and Safety Plan (HASP) which may include first aid, cardiopulmonary resuscitation (CPR), Blood Borne Pathogens (BBP) as needed. In addition, Arcadis field sampling personnel will be knowledgeable in the relevant processes, procedures, and Technical Guidance Instructions (TGIs) and possess the demonstrated required skills and experience necessary to successfully complete the desired field work. The project health and safety plan (HASP) and other documents will identify other training requirements or access control requirements.

4 EQUIPMENT LIST

The equipment required for equipment decontamination is presented below:

- Health and safety equipment, including appropriate PPE, as required in the site Health and Safety Plan (HASP)
- Deionized water that meets that analytical criteria for deionized water with no detectable constituents above the reporting limits for the methods to be used and analytes being analyzed for. Deionized water is used for inorganics, and organic-free water for VOCs, SVOCs, pesticides, etc.
- Non-phosphate detergent such as Alconox or, if sampling for phosphorus or phosphorus-containing compounds, Liquinox (or equivalent).
- Tap water
- Rinsate collection plastic containers
- DOT-approved waste shipping container(s), as specified in the work plan, field sampling plan, or regulatory requirements if decontamination waste is to be shipped for disposal
- Brushes
- Large heavy-duty garbage bags
- Spray bottles
- (Optional) – Isopropyl alcohol (free of ketones) or methanol. These can be wipes or diluted with water (usually 1part isopropyl/methanol to 10 parts water) if a spray is needed.
- Airtight, sealable plastic baggies, such as Ziploc-type
- Plastic sheeting

5 CAUTIONS

Rinse equipment thoroughly and allow the equipment to dry before re-use or storage to prevent introducing solvent into sample medium. If manual drying of equipment is required, use clean lint-free material to wipe the equipment dry. Ensure all rinsate materials do not adversely affect sample collection efficiency or analytical results.

Store decontaminated equipment in a clean, dry environment. Do not store near combustion engine exhausts. Properly containerize equipment to ensure cross-contamination doesn't happen from other uncontaminated surfaces or equipment.

If equipment is damaged to the extent that decontamination is uncertain due to cracks, gouges, crevices, or dents, the equipment should not be used and should be discarded or submitted for repair prior to use for sample collection.

A proper shipping determination regarding hazardous materials will be performed by a DOT-trained individual for cleaning materials shipped by Arcadis.

Caution should be exercised to avoid contact with the pump casing and water in the container while the pump is running (do not use metal drums or garbage cans) to avoid electric shock.

6 HEALTH AND SAFETY CONSIDERATIONS

Review the safety data sheets (SDS) for the cleaning agents and materials used in decontamination. If solvent is used during decontamination, use appropriate PPE and work in a well-ventilated area and stand upwind while applying solvent to equipment. Apply solvent in a manner that minimizes potential for exposure to workers and bystanders. Follow health and safety procedures outlined in the HASP.

7 PROCEDURE

A designated area will be established to clean sampling equipment in the field prior to and following sample collection. Equipment cleaning areas will be set up within or adjacent to the specific work area, but not at a location that expose equipment to contamination (i.e. exposed to combustion engine exhaust). Detergent solutions will be prepared in clean containers for use in equipment decontamination. Decontaminated equipment should be handled by workers wearing clean gloves, properly changed to prevent cross-contamination.

Cleaning Sampling Equipment

1. Wash the equipment/pump with potable water.
2. Wash with detergent solution (Alconox, Liquinox or equivalent) to remove all visible particulate matter and any residual oils or grease.
3. If equipment is very dirty, precleaning gross debris with a brush and tap water may be necessary.
4. If non-aqueous phase liquids are present, the use of isopropyl alcohol (free of ketones) or methanol is recommended. Cloth wipes or diluted solution can be used to remove the non-aqueous phase liquids that are hard to remove with detergent solution in step 2. Consult with project manager if

non-aqueous phase liquids are present onsite and design an appropriate decontamination procedure that includes step 4.

5. Rinse with deionized water.

Decontaminating Submersible Pumps

Submersible pumps may be used during well development, groundwater sampling, or other investigative activities. The pumps must be cleaned and flushed before and between uses. This cleaning process will consist of an external detergent solution wash and tap water rinse, a flush of detergent solution through the pump, followed by a flush of potable water through the pump. Flushing will be accomplished by using an appropriate container filled with detergent solution and another container filled with potable water. The pump should be flushed with deionized water as the last step prior to use. The pump will run long enough to effectively flush the pump housing and hose (unless new, disposable hose is used). Disconnect the pump from the power source before handling. The pump and hose should be placed on or in clean polyethylene sheeting to avoid contact with the ground surface.

8 WASTE MANAGEMENT

Equipment decontamination rinsate will be managed in conjunction with all other waste produced during the field sampling effort. Waste management procedures are outlined in the work plan or Waste Management Plan (WMP).

9 DATA RECORDING AND MANAGEMENT

Equipment cleaning and decontamination will be noted in the field notebook for project documentation. Information will include the type of equipment cleaned, the decontamination location, specific procedures utilized, solvents and/or cleaning agents used, source of water, and deviations or omissions from this TGI.

Unusual field conditions should be noted if there is potential to impact the efficacy of the decontamination or subsequent sample collection.

An inventory of the solvents brought on site and used and removed from the site will be maintained in the project documentation. Records will be maintained for solvents used in decontamination, including lot number and expiration date.

Containers with decontamination fluids will be labeled.

10 QUALITY ASSURANCE

Equipment blanks should be collected to verify that the decontamination procedures are effective in minimizing potential for cross contamination. The equipment blank is prepared by pouring deionized water (or organic-free water, for organic analyses) over the clean and dry tools and collecting the water into appropriate sample containers. Equipment blanks should be analyzed for the same set of parameters that are performed on the field samples collected with the equipment that was cleaned as specified in the sampling and analysis plan. Equipment blanks are collected per equipment set, which represents all of the tools needed to collect a specific sample.

11 REFERENCES

USEPA Region 9 - Field Sampling Guidance #1230, Sampling Equipment Decontamination.

USEPA Region 1 - Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells.



TGI – Sample Chain of Custody

Rev: 3

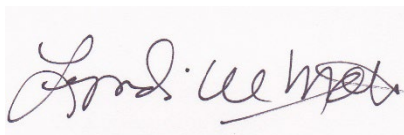
Rev Date: March 28, 2022

Version Control

Issue	Revision No.	Date Issued	Page No.	Description	Reviewed By
	0	April 19, 2017	All	Re-write to COC only	Richard Murphy
	1	May 23, 2017	4,7,9	Add: Guidance on use of previous version of TGI. Add: Info on COCs for multiple shipping containers Modify: Move letter i. to letter m. and change to “when appropriate”	Peter Frederick
	2	April 29, 2020	4, 11	Remove obsolete link	Lyndi Mott
	3	December 28, 2022	All	Updated Arcadis format Added to 6c. Collection time between COC and container must match. Added to 6o. Add name of overnight courier when relinquishing samples. Updated reference documents and added internet links.	Lyndi Mott

Approval Signatures

Prepared by:

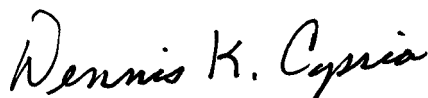


3/28/2022

Lyndi Mott (Preparer)

Date

Reviewed by:

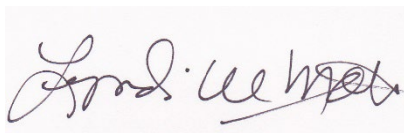


3/28/2022

Dennis Capria (Chain of Custody Reviewer)

Date

Reviewed by:



12/22/2021

Lyndi Mott (Subject Matter Expert)

Date

1 Introduction

This Technical Guidance Instruction (TGI) provides the procedure for Arcadis field personnel for required documentation during the collection of environmental field samples and transfer of custody to a laboratory. It provides direction for completion of the Chain of Custody form that must accompany collected field samples for analysis by a laboratory.

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

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3 Scope and Application

This TGI describes the general Chain of Custody (COC) procedures and guidance instructions for samples collected from project sites that are relinquished from Arcadis' possession.

COC is defined as the maintenance of an unbroken record of possession of an item from the time of its collection through some analytical or testing procedure. COC is typically documented by a written record of the collection, possession, and handling of samples collected from a project location. Each sample will be tracked by a documented record that efficiently documents the individuals who were responsible for the sample during each successive transfer of that sample to various recipients beyond Arcadis' possession. This information can be used to legally establish the integrity of the samples and therefore the analytical results derived from the samples. This

information can be used in addition to other records and documentation regarding the samples, such as field forms, field logs, and photographs.

A sample is considered under custody if:

- It is in your possession; or
- It is in your view, after being in your possession; or
- It was in your possession and then you then locked it up to prevent tampering; or
- It is in a designated secure area.

Continued use of previous version of TGI:

Although not recommended, Arcadis program-, project-, and client-teams may be able to use the previous version of this TGI provided that it meets all of the quality expectations of Arcadis and client and meets applicable regulatory requirements. It is up to the program, project, and/or client-team leader to determine whether it is appropriate to adopt the current TGI or to continue using the previous version.

However, all new work not associated with the previous version of this TGI must be performed with the current version of the TGI.

When adopting this new TGI, users of the previous versions must be aware that specific handling, packing, and shipping procedures and guidance has been removed and that those should be addressed within program or project plans (e.g., Quality Assurance Project Plans (QAPP), Work Plans, Sampling and Analysis Plans (SAPs), etc.) or in a more detailed TGI specific to that sampling activity, whether related to media, constituent/analyte, client, state, etc.

In addition, adopting this new TGI will require users to refer to the Arcadis Department of Transportation (DOT) Safety Program for procedures and guidance on the determination and handling, packing, and shipping of samples that are or may be considered hazardous materials.

4 Personnel Qualifications

Arcadis personnel performing work under the purview of this TGI will have received appropriate training and have field experience regarding the collection of samples from project locations. Arcadis personnel will have all other applicable and appropriate training relevant to the sampling work and project site.

5 Equipment List

The following list provides materials that may be required for each COC. Project reporting and documentation requirements must be reviewed with the CPM prior to execution of work. Additional materials, tools, equipment, etc. may be required, and project staff are required to verify with the CPM and/or Technical Expert what specific equipment is required to complete the COC.

- Indelible ink pen (preferably either black or blue ink);
- COC form (**Appendix A**) from either Arcadis, laboratory receiving and analyzing the samples, or other applicable and appropriate entity for the work performed;
- When appropriate, such as for litigation or expert testimony work, custody seals or tape.

6 Cautions

One way in which the law tries to ensure the integrity of evidence is by requiring proof of the chain of custody by the party who is seeking to introduce a particular piece of evidence.

A proper chain of custody requires three types of affirmations: (1) affirmation that a sample is what it purports to be (for example, soil collected from a specified location and depth); (2) affirmation of continuous possession by each individual who has had possession of the sample from the time it is collected until the time it is analyzed or held by a laboratory; and (3) affirmation by each person who has had possession that sample remained in substantially the same condition and not contaminated or affected by outside influences from the moment one person took possession until the moment that person released the evidence into the custody of another (for example, affirmation that the sample was stored in a secure location where no one but the person in custody had access to it).

Proving chain of custody is necessary to "lay a foundation" for the samples in question, by showing the absence of alteration, substitution, or change of condition.

Ensure that appropriate sample containers with applicable preservatives, coolers, and packing material are planned for and provided at the site at the time of sample collection.

Understand the offsite transfer requirements of the samples for the facility at which samples are collected.

If overnight courier service is required schedule pick-up or know where the drop-off service center is located and the hours of operation.

An Arcadis employee appropriately trained at the correct level of internal hazardous materials/DOT)shipping must complete an Arcadis shipping determination to address applicable DOT and International Air Transport Association (IATA) shipping requirements. Review the applicable Arcadis procedures and guidance instructions for sample packaging, and labeling. Prior to using air transportation, confirm air shipment is acceptable under DOT and IATA regulations.

The person relinquishing possession of the samples or other member of the project team should contact the final recipient of the samples to confirm receipt and review any special provisions on the COC or questions that they may have.

7 Health and Safety Considerations

Follow the health and safety procedures outlined in the project/site Health and Safety Plan (HASP) as well as other applicable H&S requirements, such as:

- Arcadis Hazardous Material/DOT handling, packaging, and shipping training
- Project site-specific H&S training
- Client-specific H&S training
- Constituent-specific H&S training
- Media-specific H&S training

8 Procedure

Collected samples must be uniquely identified, and properly documented, containerized, labeled with unique identifier, possessed in a secure manner during remainder of sampling event, packaged, and shipped to recipient laboratory.

Sample Identification

The method of sample identification depends on the type of measurement or analyses performed. In some cases, in-situ measurements of existing conditions and/or sample location must be made during sample collection.

These data will be recorded directly on field forms, logbooks, or other project record data sheets used to permanently retain this information for the project file. Examples of location identification information includes: latitude/longitudinal measurements, compass directions, well number, building number, floor number, room name, or proximity to a site feature unique to the site. Examples of in-situ measurements are pH, temperature, conductivity, flow measurement, or physical condition of the media being sampled. Physical samples collected are identified by a unique identifying number or code on a sample tag or label. These physical samples are removed from the sample location and transported to a laboratory for analyses.

In some cases, before samples are placed into individual containers and labeled as individual samples, samples may be separated into portions depending upon the analytical methods and required duplicate or triplicate analyses to be performed.

When completing a COC for samples, personnel must complete the following:

1. Written COCs must be completed with indelible ink (preferably either black or blue colored ink).
2. Written COCs must be completed using legible printed writing, and not cursive writing.
3. All entry fields on the COC form must be completed. If information is not applicable for a specific entry field, personnel will either put "N/A" or use a strike-out line or dash like "-----" to indicate no applicable information is needed for that field.
4. Use of quotation marks or lines/down arrows to represent repetitive/duplicative text in similar fields.
5. Regardless of the type or specific COC form, the following pertinent information must be provided on the COC form:
 - a. Arcadis project number
 - b. Arcadis project name
 - c. Project location, including street address, city, state, building number, providing as much detail as appropriate
 - d. Recipient laboratory contact and sample receiving shipping location information
 - e. Entities'/persons' contact information for who will be receiving analytical results
 - f. Name of sampler, i.e., person collecting sample and relinquishing possession of samples to the next entity in the chain of custody
 - g. Date of sample collection
 - h. If appropriate for the sample media, contaminant/constituent of concern, or analytical method, document time of sample collection using standard military time
 - i. Sample analytical method(s)

- j. Turnaround time required for analyses and/or reporting
- k. Instructions to laboratory regarding handling, timing, analyses, etc. as applicable and appropriate.
- l. Printed name and signature of the individual person who collected the samples and relinquishing possession of the samples
- m. If appropriate or when documentation of the specific sample collection method will influence how the laboratory handles, prepares, or analyzes the samples, document the sample collection methodology used for collecting the samples (e.g., ASTM D5755)

6. The following additional specific information will be entered on the COC form, regardless of what type of COC is being used:

- a. Unique Sample Identifier – The sample identifier (ID) must be unique to the individual sample it is applied to. The information in which the sample ID conveys is determined by the CPM, Technical Expert, and/or other project team members in advance of sample collection so that sample identification is consistently applied for the project. The sample nomenclature may be dictated by a specific client, program, or project database and require unique identification for each sample collected for the project. Consult with the CPM and/or Technical Expert for additional information regarding sample identification.

The sample ID could convey specific information regarding the sample to aid personnel in recognizing what the sample represents, or they may be arbitrary so as to facilitate the anonymity of the sample location, media, constituent of concern, project site, etc.

Examples of unique identifiers include:

- 1. Well locations, grid points, or soil boring identification numbers (e.g., MW-3, X-20, SB-30). When the depth interval is included, the complete sample ID would be “SB-30 (0.5-1.0) where the depth interval is in feet. Please note it is very important that the use of hyphens in sample names and depth units (i.e., feet or inches) remain consistent for all samples entered on the chain of custody form. DO NOT use the apostrophe or quotes in the sample ID.
 - 2. Sample names may also use the abbreviations “FB,” “TB,” “FD” and “DUP” as prefixes or suffixes to indicate that the sample is a field blank, trip blank, or field duplicate, respectively.
- b. List the date of sample collection. All indicated dates must be formatted using either mm/dd/yy (e.g., 03/07/09) or mm/dd/yyyy (e.g., 03/07/2009).
 - c. List the local time that the sample was collected. The time value should be presented using military format. For example, 3:15 P.M. should be entered as 15:15. The time listed on the COC form must match the sample collection time on the sample container(s).
 - d. Samples should be indicated to be either “Grab” or “Composite”. Grab samples are collected from only one unique location at one specific point in time.
 - e. Composite samples are a group of individual samples that are combined for analysis in their totality. Composite samples need to be documented if they are either collected from a number of different locations over a broader area to be representative of the entire area being sampled, or if they are representative of a single location over an extended period of time.

- f. If used, preservatives for the individual sample will be noted.
 - g. The requested analytical method(s) that the samples are being analyzed for must be indicated. As much detail, as necessary, should be presented to allow the analytical laboratory to properly analyze the samples. For example, polychlorinated biphenyl (PCB) analyses may be represented by entering “EPA Method 8082 – PCBs” or “EPA PLM 600-R93-116.” In cases where multiple analytical methods and/or analytical parameters are required for an individual sample, each method should be indicated for the sample (e.g., EPA 8082/8260/8270 or EPA PLM/400-point count).
 - h. If there are project-specific sample analytes to be reported, they should be specifically listed for each individual sample (e.g., 40 CFR 264 Appendix IX).
 - i. The total number of containers for each analytical method requested should be documented. This information may be included under the parameter or as a total for the sample.
 - j. When necessary, note which samples should be used for site specific matrix spikes in the Remarks or Comments field.
 - k. Indicate special project-specific requirements pertinent to the handling, shipping, or analyses. These requirements may be on a per sample basis such as “extract and hold sample until notified,” or may be used to inform the laboratory of special reporting requirements for the entire sample delivery group (SDG).
 - l. Indicate turnaround time (TAT) required for samples on COC. If individual samples have differing TATs, the different TATs for each sample or groups of samples must be clearly indicated.
 - m. Provide contact name and phone number in the event that problems are encountered when samples are received at the laboratory. The person relinquishing possession of the samples or other member of the project team should contact the final recipient of the samples to confirm receipt and review any special provisions on the COC or questions that they may have.
 - n. If available, attach the Laboratory Task Order or Work Authorization forms.
 - o. The “Relinquished By” field must contain the signature of the Arcadis person who relinquished custody of the samples to the next entity in the chain of custody, which may be another person, the shipping courier, or the analytical laboratory. If a courier, enter the shipping courier in the “Received by” such as FedEx. The date/time relinquished should be when the person signs the COC and seals the cooler or shipping container for pick-up by the shipping courier.
 - p. Dates and times must be indicated using the following format:
 - 1) Date: either mm/dd/yy e.g., 01/01/17 OR mm/dd/yyyy e.g., 01/01/2017
 - 2) Time: use military format, e.g., 9:30 a.m. is 0930 and 9:30 p.m. is 2130
 - q. The “Received By” section is signed by sample courier or laboratory representative who received the samples from the sampler. The laboratory will sign upon laboratory receipt from the overnight courier service.
7. When more than one page of the COC form is required to complete the total number of samples, use as many sheets as necessary to accurately and clearly, document the samples and information. Some COCs may have a standard first page/cover page, and subsequent pages may not contain all the detailed fields as

the first page/cover page. Ensure that any subsequent pages convey all of the necessary and pertinent information for each individual sample as required in this procedure document.

8. Pages of the COC must retain a page count of the total number of pages; e.g., Page 1 of 3, Page 2 of 3, Page 3 of 3.
9. Upon completing the COC forms, forward the original signed COC with the sample package. Ensure that the original COC form is secured with the sample package so that it remains with the physical samples for the duration of transport and handling to its final destination and ensure that the COC form will not be become damaged or rendered unreadable due to sample breakage/leakage if stored inside the sample shipping container or outside influences if COC is stored in an outside plastic pouch to the container.
10. If you've collected enough samples that would require more than one container to ship them all to the same laboratory or location, then each separate/individual container that contains any number of samples must have a separate COC representing only those samples contained within that specific container. For example, if you have 3 total shipping containers for all of your samples, you must have a total of 3 separate, individual COCs for each of the 3 containers representing only those samples in their representative container. Thus, every container holding samples must have its own, individual COC.
11. If electronic chain of custody (eCOC) forms are utilized, ensure that the requirements of this procedure and guidance instructions are followed to the extent possible. Verify that proper signature and COC procedures are maintained with the CPM and/or Technical Expert when using eCOC.

9 Waste Management

Not Applicable.

10 Data Recording and Management

The original signed COC shall be submitted with the samples. Copies of COC records will be transmitted to the CPM or designee at the end of each day unless otherwise directed by the CPM. The sampling team leader retains copies of the chain of custody forms for filing in the project file. Record retention shall be in accordance with client- and project-specific requirements and Arcadis policies, the most stringent will apply.

The option to use the Electronic Chain of Custody (eCOC) form in conjunction with the appropriate sample application(s) may be available through the FieldNow® program but is currently limited to a select list of approved analytical laboratories. Use of the eCOC application is intended to reduce common transcription errors both by field staff and laboratory staff on a conventional handwritten paper COC. Once the eCOC form is completed and approved on the field tablet by field staff, a PDF version of the form is automatically emailed to each assigned team member. In addition, a dedicated or mobile printer is recommended for printing a hard copy of the completed eCOC to be included in each sample cooler to meet laboratory requirements.

11 Quality Assurance

COC forms will be legibly completed in accordance with this procedure and guidance instruction document, as well as other applicable and appropriate project documents such as SAP, Quality QAPP, Work Plan, or other project guidance documents.

COC records will be reviewed by the CPM or their appropriate designee for completeness and accuracy to the applicable requirements. Non-conformances will be noted and corrected in a timely manner on the copies retained by Arcadis as well as contacting the ultimate receiving entity for correction to the originally signed COC in their possession.

12 References

Arcadis Transportation Safety Program requirements, procedures, and guidance instructions.

EPA Samplers' Guide – Contract Laboratory Program Guidance for Field Samplers, EPA document EPA-540-R014-013 October 2014 https://www.epa.gov/sites/default/files/2015-03/documents/samplers_guide.pdf.

EPA Region III – Sample Submission Procedures for the Office of Analytical Services and Quality Assurance (OASQA) Laboratory Branch revision 14.0 October 18, 2018, <https://www.epa.gov/sites/default/files/2018-12/documents/sample-submission-procedures-rev14.pdf>.

EPA Region IV Science and Ecosystem Support Division Operating Procedure for Sample and Evidence Management May 25, 2016, <https://www.epa.gov/sites/default/files/2015-06/documents/Sample-and-Evidence-Management.pdf>.

Attachment A

Chain of Custody and Laboratory Analysis Request Form

		ID#	CHAIN OF CUSTODY & LABORATORY ANALYSIS REQUEST FORM										Lab Work Order #	
			Page ____ of ____											
Send Results to:	Contact & Company Name:	Telephone:	Preservative										Keys Preservation Key: A. H ₂ SO ₄ B. HCL C. HNO ₃ D. NaOH E. None F. Other: _____ G. Other: _____ H. Other: _____ Matrix Key: SO - Soil W - Water T - Tissue SE - Sediment SL - Sludge Containment Information Key 1. 40 ml Vial 2. 1 L Amber 3. 250 ml Plastic 4. 500 ml Plastic 5. Encore 6. 2 oz. Glass 7. 4 oz. Glass 8. 8 oz. Glass 9. Other: _____ 10. Other: _____ A - Air NL - NAPL/Oil SW - Sample Wipe Other: _____	
	Address:	Fax:	Filtered (✓)											
	City State Zip	E-mail Address:	# of Containers											
	Project Name/Location (City, State):		Project #:	Container Information										
Sampler's Printed Name:		Sampler's Signature		PARAMETER ANALYSIS & METHOD										
SAMPLE ID	Collection Date Time	Type (✓) Comp Grab	Matrix										REMARKS	
Special Instructions/Comments														
☐ Special QA/QC Instructions (✓)														
Laboratory Information and Receipt				Relinquished By		Received By		Relinquished By		Laboratory Received By				
Last Name:		Cooler Custody Seal (✓)		Printed Name:		Printed Name:		Printed Name:		Printed Name:				
		☐ Intact ☐ Not Intact		Signature:		Signature:		Signature:		Signature:				
Specify Turnaround Requirements:		Sample Receipt		Firm:		Firm:		Firm:		Firm:				
Shipping Tracking #:		Condition/Cooler Temp: _____		Date/Time:		Date/Time:		Date/Time:		Date/Time:				

SOP – Sample Chain of Custody Rev1_May 23, 2017

Arcadis U.S., Inc.
630 Plaza Drive, Suite 200
Highlands Ranch
Colorado 80129
Phone: 720 344 3500
Fax: 720 344 3535
www.arcadis.com

TGI – Soil Drilling and Sample Collection

Rev: #2

Rev Date: April 8, 2022

Version Control

Issue	Revision No.	Date Issued	Page No.	Description	Reviewed By
	0	October 11, 2018	All	Updated and re-written as a TGI	Marc Killingstad
	1	May 12, 2020	None	Review – no changes necessary	Marc Killingstad
	2	April 8, 2022	All	Updated to new format and minor content (e.g., PFAS)	Chris Shepherd/Marc Killingstad

Approval Signatures

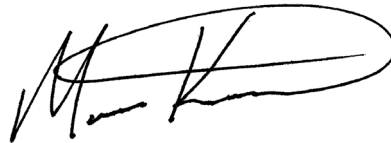
Prepared by:

4/8/2022

Chris Shepherd (Preparer)

Date

Reviewed by:



4/8/2022

Marc Killingstad (Subject Matter Expert)

Date

1 Introduction

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

This document is not considered to be all inclusive nor does it apply to any and all projects. It is the CPM's responsibility to determine the proper scope and personnel required for each project. There may be project- and/or client- and/or state-specific requirements that may be more or less stringent than what is described herein. The CPM is responsible for informing Arcadis and/or Subcontractor personnel of omissions and/or deviations from this document that may be required for the project. In turn, project staff are required to inform the CPM if or when there is a deviation or omission from work performed as compared to what is described herein.

In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, state-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM. All deviations or omissions should be documented.

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

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3 Scope and Application

This Technical Guidance Instruction (TGI) describes general drilling procedures and the methods to be used to field screen and collect soil samples for laboratory analysis in unconsolidated or weakly consolidated sediments. For soil description procedures, please refer to the *TGI - Soil Description*. For monitoring well installation in granular aquifers, please refer to the *TGI - Monitoring Well Installation*. For per- and polyfluoroalkyl substances (PFASs) drilling and soil sampling procedures, please refer to: *TGI – PFAS-Specific Drilling and Monitoring Well Installation*, *TGI – Per- and Polyfluoroalkyl Substances (PFAS) Field Sampling Guide*, and *TGI – Equipment and Reagent Blank Sample Collection for PFAS Analysis*.

Overburden (unconsolidated sediments) drilling is commonly performed using the hollow-stem auger drilling method. Other drilling methods suitable for overburden drilling, which are sometimes necessary due to site-specific geologic conditions, include: direct-push, drive-and-wash, spun casing, rotasonic, dual-rotary (Barber Rig), and fluid/mud rotary with core barrel or roller bit. Direct-push techniques (e.g., Geoprobe or cone penetrometer) and hand tools may also be used. Drilling within consolidated materials such as fractured rock is commonly performed using water-rotary (coring or tri-cone roller bit), air rotary or rotasonic methods. For guidance when drilling in consolidated materials (i.e., bedrock), please refer to the *TGI – Bedrock Core Collection and Description*.

The drilling method to be used at a given site will be selected based on site-specific consideration of anticipated drilling depths, targeted chemicals, site or regional geologic knowledge, types of sampling to be conducted, required sample quality and volume, and cost.

Field screening of soil samples is commonly performed using a photoionization detector (PID) and/or a flame ionization detector (FID). These instruments are used to measure relative concentrations of volatile organic compounds (VOCs) for the selection of samples for further laboratory or field analysis. Field screening for dense non-aqueous phase liquids (DNAPL) may be performed using hydrophobic dye (Oil Red O or Sudan IV), which is pertinent at chlorinated solvent sites.

Collection of soil samples for laboratory analysis may be performed using a variety of techniques including grab samples, undisturbed cores, and composite or homogenized samples. Samples may require homogenization across a given depth interval, or several discrete grabs (usually five) may be combined into a composite sample. Samples for VOC analysis will not be homogenized or composited and are collected as discrete grab samples.

No oils or grease will be used on equipment introduced into the boring (e.g., drill rod, casing, or sampling tools). Some lubricants (e.g., vegetable oil-based lubricants) may be acceptable, if the constituents won't interfere with the analyses.

4 Personnel Qualifications

Arcadis field personnel will have completed or are in the process of completing site-specific training as well as having current health and safety training as required by Arcadis, client, or state/federal regulations, such as 40-hour HAZWOPER training and/or OSHA HAZWOPER site supervisor training. Arcadis personnel will also have current training as identified in the site-specific Health and Safety Plan (HASP) which may include first aid,

cardiopulmonary resuscitation (CPR), Blood Borne Pathogens (BBP) as needed. The HASP will also identify any access control requirements.

Prior to mobilizing to the field, Arcadis field personnel will review and be thoroughly familiar with relevant site-specific documents including but not limited to the task-specific work plan or field implementation plan (FIP), Quality Assurance Project Plan (QAPP), HASP, historical information, and other relevant site documents.

Arcadis field personnel will be knowledgeable in the relevant processes, procedures, and TGIs and possess the demonstrated required skills and experience necessary to successfully complete the desired field work. Personnel responsible for overseeing drilling operations will have at least 16 hours of prior training overseeing drilling activities with an experienced geologist, environmental scientist, or engineer with at least 2 years of prior experience.

Arcadis personnel directing, supervising, or leading soil sampling activities will have a minimum of 1 year of previous environmental soil sampling experience. Field employees with less than 6 months of experience will be accompanied by a supervisor (as described above) to ensure that proper sample collection techniques are employed.

Additionally, the Arcadis field team will review and be thoroughly familiar with documentation provided by equipment manufacturers and become familiar with the operation of (i.e., hands-on experience) all equipment that will be used in the field prior to mobilization.

5 Equipment List

The following materials will be available, as required, during soil boring drilling, field screening, and sampling activities:

- Site-specific HASP and health and safety documents identified in the HASP
- FIP/work plan that includes site map with proposed boring locations, field sampling plan (with corresponding depths, sample analyses, sample volume required, and sample holding time), and previous boring logs (as available)
- Appropriate personal protective equipment (PPE), as specified in the HASP
- Including but not limited to disposable chemical resistant gloves and Level D PPE
- Traffic cones, delineators, and caution tape as appropriate for securing the work area as specified in the Traffic Safety Plan (TSP)
- Photoionization detector (PID), flame ionization detector (FID) or other air/soil screening equipment, as needed, in accordance with the HASP or workplan
- Sampling equipment:
- Drilling equipment required by *ASTM D1586*, when performing split-spoon sampling including clean sample sleeves
- Disposable plastic liners, when drilling with direct-push equipment
- Stainless steel hand auger and stainless-steel spade if using manual methods
- Appropriate soil sampling equipment (e.g., stainless steel spatulas/spoons/bowls, knife)
- Sealable plastic bags (e.g., Ziploc®)

- Air-tight sample containers and 8-oz. glass Mason jars or driller's jars
- Aluminum foil
- Appropriate sample blanks (trip blank supplied by the laboratory), as specified in the FSP
- Soil sample containers and labels (supplied by the laboratory) appropriate for the analytical method(s) with preservative, as needed (parameter-specific)
- Sample labels
- Indelible ink pens
- Engineer's ruler or survey rod
- Plastic sheeting (e.g., Weatherall Visqueen)
- Appropriate transport containers (coolers) with ice and appropriate labeling, packing, and shipping materials
- Decontamination equipment (buckets, distilled or deionized water, cleansers appropriate for removing expected chemicals of concern, paper towels) in accordance with the *TGI for Groundwater and Soil Sampling Equipment Decontamination*
- Forms/notes:
 - Tablet with digital forms, etc., if appropriate
 - Appropriate soil boring log (**Attachment 1**)
 - Chain-of-custody forms
 - Field notebook
 - Digital camera (or smart phone with camera)
- Drums or other containers appropriate for soil and decontamination water, as specified by the site investigation-derived waste (IDW) management plan, and appropriate drum labels

6 Cautions

Prior to beginning field work, underground utilities in the vicinity of the drilling areas will be delineated by the drilling contractor or an independent underground utility locator service in accordance with the work plan, client requirements, and Arcadis guidance. See appropriate guidance for proper utility clearance protocol. Work will be performed in accordance with the Arcadis *Utility Location and Clearance Health and Safety Standard* and the *Utilities and Structures Checklist* will be completed before beginning any intrusive work.

Prior to beginning field work, the project technical team will ensure that all field logistics (e.g., access issues, health and safety issues, communication network, schedules, etc.) and task objectives are clearly understood by all team members. An internal call with the project technical team to review the FIP/work plan scope and objectives is strongly recommended prior to mobilization to ensure that the field work will be effectively and efficiently executed.

Some regulatory agencies have specific requirements regarding borehole abandonment and grout mixtures. Determine whether the oversight agency has any such requirements prior to finalizing the

drilling plan.

If DNAPL is known or expected to exist at the site, refer to the project specific documents (e.g., DNAPL Contingency Plan) for additional details regarding drilling to reduce the potential for inadvertent DNAPL remobilization.

Similarly, if light non-aqueous phase liquid (LNAPL) is known or expected to be present as “perched” layers above the water table, refer to the DNAPL Contingency Plan. Follow the general provisions and concepts in the DNAPL contingency plan during drilling above the water table at known or expected LNAPL sites.

Avoid using drilling fluids or materials that could impact groundwater or soil quality, or could be incompatible with the subsurface conditions. Water used for drilling, decontamination of drilling/sampling equipment, or grouting boreholes upon completion will be of a quality acceptable for project objectives. Testing of water supply will be considered.

Specifications of materials used for backfilling the borehole will be obtained, reviewed and approved to meet project quality objectives. Bentonite is not recommended where DNAPL is likely to be present or in groundwater with high salinity. In these situations, neat cement grout is preferred.

Store and/or stage empty and full sample containers and coolers out of direct sunlight. Sample container threads should be wiped down with a clean, nonabrasive material (e.g., paper towels) to better ensure the sample container is properly sealed. Be careful not to over-tighten lids with Teflon® liners or septa. Over-tightening can impair the integrity of the seal and can cause the glass to shatter and create a risk for hand injuries.

NOTE: Field logs and some forms are considered to be legal documents. All field logs and forms will therefore be filled out in indelible ink. Do not use permanent marker or felt-tipped pens for labels on sample container or sample coolers. Permanent markers could introduce volatile constituents into the samples.

NOTE: An Arcadis employee that is appropriately trained at the correct level of internal hazardous materials/DOT (Department of Transportation) shipping must complete an Arcadis shipping determination to address applicable DOT and IATA (International Air Transport Association) shipping requirements. Review the applicable Arcadis procedures and guidance instructions for sample packaging and labeling. Prior to using air transportation, confirm air shipment is acceptable under DOT and IATA regulations.

7 Health and Safety Considerations

The HASP will be followed, as appropriate, to ensure the safety of field personnel. Review all site-specific and procedural hazards as they are provided in the HASP, and review Job Safety Analysis (JSA) documents in the field each day prior to beginning work.

Prior to drilling, utility clearance must be performed (see Section 5). Appropriate personal protective equipment (PPE) will be worn at all times in line with the task and the site-specific HASP.

Working outside at sites with suspected contamination may expose field personnel to hazardous materials such as contaminated groundwater or NAPL (e.g., oil). Other potential hazards include biological hazards (e.g., stinging insects, ticks in long grass/weeds, etc.), and potentially the use of sharp cutting tools (scissors, knife). Only use non-toxic peppermint oil spray for stinging insect nests. Review client-specific health and safety requirements, which may preclude the use of fixed/folding-blade knives

and use appropriate hand protection.

If thunder or lightning is present, discontinue drilling and sampling until 30 minutes have passed after the last occurrence of thunder or lightning.

8 Procedure

The procedures for drilling and the methods to be used to field screen and collect soil samples for laboratory analysis are presented below:

8.1 Drilling Procedures

8.1.1 Hollow-Stem Auger, Drive-and-Wash, Spun Casing, Fluid/Mud Rotary, Rotasonic, and Dual-Rotary Drilling Methods

1. Find/identify boring location, establish work zone, and set up sampling equipment decontamination area.
 - a. Verify utilities were cleared (see Section 5) and use soft dig technique to clear borehole, if applicable
 - b. Clean sampling equipment in accordance with the FIP/work plan prior to drilling
2. Advance boring to target depth:
 - a. Collect soil samples at appropriate interval as specified in the FIP/work plan (or equivalent) using the appropriate tooling (e.g., split-barrel sampler) and sample containers
 - i. Split-barrel or drive-ahead samples are obtained during drilling
 - ii. A common sampling method that produces high-quality soil samples with relatively little soil disturbance is described in *ASTM D1586 – Standard Test Method for Standard Penetration Test (SPT) and Split-Barrel Sampling of Soils* (ASTM D1586).
 - b. Always change disposable gloves before handling the sampling equipment
 - c. Collect, document, and store samples for laboratory analysis as specified in the FIP/work plan (or equivalent; see below for additional details on sample collection procedures)
 - d. Field screen samples as specified in the FIP/work plan (or equivalent; see below for additional details on field screening procedures)
 - e. Rotasonic drilling produces soil cores that, for the most part, are relatively undisturbed, but note that when drilling in consolidated or finer-grained sediment the vibratory action during core barrel advancement may create secondary fractures or breaks. The core is retrieved by vibrating the soil/rock into a separate core bag, typically in 5-foot or 10-foot increments. The soil cores may consolidate or expand during retrieval, depending on soils, etc.
 - f. Dual-rotary removes cuttings by compressed air or water/mud and allow only a

- general assessment of geology unless separate coring tools and techniques are used
- g. Decontaminate equipment between samples in accordance with the FIP/work plan (or equivalent)
3. Describe each soil sample as outlined in the appropriate project records (refer to the description procedures outlined in the *TGI - Soil Description*)
- a. Record descriptions on the soil boring log (**Attachment 1**) and/or field notebook
 - b. When possible, photo document the samples (e.g., soil cores, split-barrels)
 - c. During soil boring advancement, document all drilling events in field notebook, including blow counts (i.e., the number of blows from a soil sampling drive weight [140 pounds] required to drive the split-barrel sampler in 6-inch increments) and work stoppages
 - d. Blow counts will not be available if rotasonic, dual-rotary, or direct-push methods are used; however, if standard penetration testing is required during rotasonic drilling, an automatic drop hammer may be used in conjunction with the method to switch from core barrel advancement to standard penetration testing
 - e. If soils are screened with a PID/FID or another instrument, document the measurement in accordance with the work plan
4. The drilling contractor will be responsible for obtaining accurate and representative samples, informing the supervising Arcadis geologist of changes in drilling pressure, drilling penetration rates, and keeping a separate general log of soils encountered, including blow counts
- a. The term “samples” means soil materials from particular depth intervals, whether or not portions of these materials are submitted for laboratory analyses
 - b. Records will also be kept of occurrences of premature refusal due to boulders, construction materials that may have been used as fill, etc.
 - c. Where a boring cannot be advanced to the desired depth, the boring will be abandoned, and an additional boring will be advanced at an adjacent location to obtain the required sample in accordance with the work plan
 - d. Where it is desirable to avoid leaving vertical connections between depth intervals (e.g., if DNAPL or perched LNAPL are known or expected to exist at the site), the borehole will be sealed using cement and/or bentonite (see **Section 5** above)
 - e. Multiple refusals may lead to a decision by the supervising geologist to abandon that sampling location

8.1.2 Direct-Push Method

The direct-push drilling method may also be used to complete soil borings. Examples of this technique include Geoprobe®, Diedrich Environmental Soil Probe (ESP) System, or AMS PowerProbe.

Environmental probe systems typically use a hydraulically operated percussion hammer.

Depending on the equipment used, the hammer delivers 140- to 350-foot pounds of energy with each blow. The hammer provides the force needed to penetrate very stiff to medium dense soil formations. The hammer simultaneously advances an outer steel casing that contains a dual tube liner for sampling soil

(dual tube sampling system).

The outside diameter (OD) of the outer casing ranges from 2.25 to 6 inches and the OD of the inner sampling tube diameter ranges from 1.4 to 4.5 inches. The outer casing isolates overlying soil and permits the unit to continue to probe at depth. The dual tube sampling system provides a borehole that may be tremie-grouted from the bottom up. Alternatively, a single rod system may be used that does not provide a cased boring and which limits tremie-grouting from the bottom up.

Direct-push drilling can generally achieve target depths 100 feet or less depending on the site geology. The known or expected site conditions (e.g., presence of NAPL) will be evaluated when selecting the type of direct-push sampling system to be employed.

1. Find/identify boring location, establish work zone, and set up sampling equipment decontamination area
 - a. Verify utilities were cleared (see Section 5) and use soft dig technique to clear borehole, if applicable
 - b. Clean sampling equipment in accordance with the FIP/work plan prior to drilling
2. Advance soil boring to target depth.
 - a. Collect soil samples at appropriate interval as specified in the FIP/work plan (or equivalent) using clean/disposable sampling equipment (plastic liners)
 - b. Always change disposable gloves before handling the sampling equipment
 - c. Collect, document, and store samples for laboratory analysis as specified in the FIP/work plan (or equivalent; see below for additional details on sample collection procedures)
 - d. Field screen samples as specified in the FIP/work plan (or equivalent; see below for additional details on field screening procedures)
3. Decontaminate equipment between samples in accordance with the FIP/work plan (or equivalent)
4. Describe samples in accordance with the procedures outlined in **Step 3** under ***Hollow-Stem Auger, Drive-and-Wash, Spun Casing, Fluid/Mud Rotary, Rotasonic, and Dual-Rotary Drilling Methods*** above (refer to the description procedures outlined in the *TGI - Soil Description*)

8.1.3 Manual Methods

Manual methods may also be used to complete shallow soil borings. Examples of this technique include using a spade, spoon, scoop, hand auger, or slide hammer. Manual methods are typically used to collect surface soil samples (0 to 6 inches) or to complete soil borings/collect soil samples from a depth of 5 feet or less.

1. Find/identify boring location, establish work zone, and set up sampling equipment decontamination area
2. Clear the ground surface of brush, root mat, grass, leaves, or other debris
3. Use a spade, spoon, scoop, hand auger, or slide hammer to collect a sample of the required depth interval
4. Use an engineer's ruler or survey rod to verify that the sample is collected to the correct depth and

record the top and bottom depths from the ground surface

5. To collect samples below the surface interval, remove the surface interval first; then collect the deeper interval
 - a. To prevent the hole from collapsing, it may be necessary to remove a wider section from the surface or use cut polyvinyl chloride (PVC) pipe to maintain the opening
 - b. Collect soil samples at appropriate interval as specified in the FIP/work plan (or equivalent) and transfer to the appropriate, laboratory-supplied container
 - c. Collect, document, and store samples for laboratory analysis as specified in the FIP/work plan (or equivalent; see below for additional details on sample collection procedures)
 - d. Field screen samples as specified in the FIP/work plan (or equivalent; see below for additional details on field screening procedures)
6. Decontaminate equipment between samples in accordance with the FIP/work plan (or equivalent)
7. Describe samples in accordance with the procedures outlined in **Step 3** under ***Hollow-Stem Auger, Drive-and-Wash, Spun Casing, Fluid/Mud Rotary, Rotasonic, and Dual-Rotary Drilling Methods*** above (refer to the description procedures outlined in the *TGI - Soil Description*)

8.2 Field Screening Procedures

8.2.1 PID and FID Screening

Soils are typically field screened with a PID or FID for a relative measure of the total VOCs at sites where VOCs are known or suspected to exist. PIDs and FIDs require calibration in accordance with the work plan(s) and manufacturer's specifications and PIDs should be calibrated based on the target chemicals. The PID employs an ultraviolet lamp to measure VOCs and the ionization energy (IE) of the site constituents need to be considered when selecting the type of lamp (e.g., 10.6 eV, 11.7 eV) that will be used. In general, any compound with an IE lower than that of the lamp photons can be measured. The FID has a wide linear range and responds to almost all VOCs.

Field screening is performed using one (or both) of the following two methods:

1. Upon opening the sampler, the soil is split open and the PID or FID probe is placed in the opening and covered with a clean, gloved hand. Such readings will be obtained at several locations along the length of the sample.
2. A portion of the collected soil is placed in a jar, which is covered with aluminum foil, sealed, and allowed to warm to room temperature (see below). After warming, the cover is removed, the foil is pierced with the PID or FID probe, and a reading is obtained.

Prior to usage, the PID or FID must be calibrated according to the manufacturer's specifications at a minimum frequency of once per day prior to collecting PID or FID readings. The PID will be calibrated to a benzene-related compound (isobutylene) or other appropriate gas, while the FID will be calibrated to methane. The time, date, and calibration procedure must be clearly documented in the field notebook and/or the calibration form.

If at any time the PID or FID results appear erratic or inconsistent with field observations, then the instrument will be recalibrated.

If calibration is difficult to achieve, then the PID's lamp will be checked for dirt or moisture and cleaned, or technical assistance will be required. Maintenance and calibration records will be kept as part of the field quality assurance program.

Initial PID readings will be recorded on the soil boring log (**Attachment 1**) and/or in the field notes. The soil sample will be separated from the slough material (if any) by using disposable gloves and a pre-cleaned stainless-steel spoon or tool.

For the second method, a representative portion of the sample will be placed in a pre-cleaned air-tight container (as quickly as possible to avoid loss of VOCs), filling the container half full to allow for the accumulation of vapors above the soil. An aluminum foil seal will be placed between the glass and cap and the cap will be screwed on tightly. Unless the screening will be performed immediately after the sample is placed in the container, the sample containers will be stored in a cooler chilled to approximately 4°C until screening can be performed.

The headspace of the container will be measured using a PID or FID as follows:

1. Samples will be taken to a warm workspace and allowed to equilibrate to room temperature for at least one hour.
2. Prior to measuring the soil vapor headspace concentration, the container will be shaken.
3. The headspace of the sample will then be measured directly from the container by piercing the aluminum foil seal with the probe of the PID or FID and measuring the relative concentration of VOCs in the headspace of the soil sample. The initial (peak) reading must be recorded.

8.2.2 NAPL Screening

To screen for the potential presence of non-aqueous phase liquid (NAPL) in soil, drilling procedures must allow for high-quality porous media samples to be taken. Split-barrel samplers or direct-push samplers will be collected continuously ahead of the auger, drill casing/rods, or probe rods. Upon opening each split-barrel sampler or direct-push plastic liner sleeve, the soil will immediately be evaluated for the presence of visible NAPL and odors. If suspected NAPL is immediately visible in the sample, its depth will be noted.

Additionally, the soil will be screened for the presence of organic vapors using a PID or FID, in accordance with the work plan, if applicable. During screening, the soil will be split open using a clean spatula or knife and the PID or FID probe will be placed in the opening and covered with a clean, gloved hand (**Method 1** above). Such readings will be obtained along the entire length of the sample. Alternatively, **Method 2** for PID/FID screening (outlined above) may also be performed. If the PID or FID examination reveals the presence of organic vapors above 100 parts per million (ppm), the sample will undergo further detailed evaluation for visible NAPL.

The assessment for NAPL will include the following tests/observations:

- Evaluation for Visible NAPL Sheen or Free-Phase NAPL in Soil Sampler
 - NAPL sheen will be a colorful iridescent appearance on the soil sample
 - NAPL may also appear as droplets or continuous accumulations of liquid with a color typically ranging from yellow to brown to black, depending on the type of NAPL
 - Creosote DNAPL (associated with wood-treating sites) and coal tar DNAPL (associated with manufactured gas plant [MGP] sites) are typically black and have a characteristic, pungent odor
 - Pure chlorinated solvents may be colorless in the absence of hydrophobic dye. Solvents mixed

with oils may appear brown

- Particular care will be taken to fully describe any sheens observed, staining, discoloration, droplets (blebs), or NAPL saturation
- Soil-Water Pan Test
 - A portion of the selected soil interval with the highest PID or FID reading above 100 ppm will be placed in a disposable polyethylene dish along with a small volume of potable or distilled water
 - The dish will be gently tilted back and forth to mix the soil and water, and the surface of the water will be viewed in natural light to observe the development of a sheen, if any
 - A small quantity of Oil Red O or Sudan IV hydrophobic dye powder should be added in accordance with the work plan, and the soil and dye will be manually mixed for approximately 30 to 60 seconds and smeared in the dish to create a paste-like consistency
 - A positive test result will be indicated by a sheen on the surface of the water and/or a bright red color imparted to the soil following mixing with dye
- Soil-Water Shake Test
 - A small quantity of soil (up to 15 cc) will be placed in a clear, colorless, jar containing an equal volume of potable or distilled water (40-mL vials are well suited to this purpose, but not required)
 - After the soil settles into the water, the surface of the water will be evaluated for a visible sheen under natural light
 - The jar will be closed and gently shaken for approximately 10 to 20 seconds
 - Again, the surface of the water will be evaluated for a visible sheen or a temporary layer of foam
 - A small quantity (approximately 0.5 to 1 cc) of Oil Red O or Sudan IV powder will be placed in the jar in accordance with the work plan
 - The sheen layer, if present, will be evaluated for a reaction to the dye (change to bright red color)
 - The jar will be closed and gently shaken for approximately 10 to 20 seconds
 - The contents in the closed jar will be examined under natural light for visible bright red dyed liquid inside the jar

- A positive test result will be indicated by the presence of a visible sheen or foam on the surface of water, a reaction between the dye and the sheen layer upon first addition of the dye powder, a bright red coating on the inside of the vial (particularly above the water line), or red-dyed droplets within the soil

NOTE: If NAPL is obviously present upon opening the soil sampler or evaluating the soil sample within the split-spoon sampler or direct-push liner sleeve, it is not necessary to perform a soil-water pan test or soil-water shake test. In addition, it is not necessary to perform both a soil-water pan test and a soil-water shake test; either test method is acceptable. The pan test may be preferred in some circumstances because the presence of a sheen may be easier to see on a wider surface. Further, these tests will only be performed if specified in the work plan(s).

NOTE: When using hydrophobic dye in the tests above, color will be assessed outdoors under natural light during the period between sunrise and sunset, regardless of the degree of cloud cover. The hydrophobic dye Safety Data Sheets (SDS) will be incorporated into the HASP and reviewed prior to use and the dyes will be carefully handled and disposed in accordance with regulations, if applicable.

8.3 Soil Sample Collection for Laboratory Procedures

If not specifically identified in the FIP/work plan, soil samples will be selected for laboratory analysis based on:

1. Their position in relation to identified source areas
2. The visual presence of source residues (e.g., NAPL or staining)
3. The relative levels of total VOCs based on field screening measurements
4. The judgment of the field coordinator
5. Moisture content or relative position with regard to apparent groundwater table/saturation

Samples designated for laboratory analysis will be placed in the appropriate containers.

Sample containers for VOC analysis will be filled first immediately following soil core retrieval to reduce loss of VOCs.

If samples will be collected for other analyses, a sufficient amount of the remaining soil will then be homogenized as described below and sample containers will be filled for other parameters.

VOC samples will be collected as discrete samples using a small diameter core sampler (e.g., En Core® Sampler, Terra Core™ Sampler).

The En Core® Sampler is a disposable volumetric sampling device that collects, stores and delivers soil samples without in-field chemical preservation. The En Core® Sampler requires the use of a reusable T-handle.

The Terra Core™ Sampler is a one-time use transfer tool, designed to collect soil samples and transfer them to the appropriate containers for in-field chemical preservation (e.g., methanol).

The small diameter core samplers will be used according to the manufacturer's instructions (e.g., Ennovative Technologies). Some regulatory agencies have specific requirements regarding VOC sample

collection. Determine whether the oversight agency has specific requirements prior to commencing sampling and collect samples at appropriate interval as specified in the FIP/work plan (or equivalent). Samples may require homogenization across a given depth interval, or several discrete grabs (usually five) may be combined into a composite sample.

NOTE: *Samples for VOC and PFAS analysis will NOT be homogenized or composited and will be collected as discrete samples as described above.*

The procedure for mixing samples is provided below.

1. Mix the materials in a stainless steel (or appropriate non-reactive material) bowl using a stainless-steel spoon (or disposable equivalents)
 - a. When dealing with large sample quantities, use disposable plastic sheeting and a shovel or trowel
 - b. **NOTE:** *When preparing samples for metals analyses, do not use disposable aluminum (or metal tools or trays other than stainless steel), as it may influence the analytical results*
2. Flatten the pile by pressing the top without further mixing
3. Divide the circular pile by into four equal quarters by dividing out two diameters at right angles
4. Mix each quarter individually using appropriate non-reactive bowls, spoons and/or sheeting
5. Mix two quarters (as described above) to form halves, then mix the two halves to form a composite or homogenized sample
6. Place composite or homogenized sample into specified containers
7. Remaining material will be disposed of in accordance with project requirements and applicable regulations
8. Sample containers will be labeled with sample identification number, date, and time of collection and placed on ice in a cooler (target 4° Celsius)
9. Samples selected for laboratory analysis will be documented (chain-of-custody forms), handled, packed, and shipped in accordance with the procedures outlined in the FIP/work plan (or equivalent).

8.4 Soil Boring Abandonment

All soil borings need to be abandoned in accordance with ***TGI for Monitoring Well and Soil Boring Decommissioning***. See Attachment E of the TGI for specifics.

9 Waste Management

Investigative-Derived Waste (IDW) generated during drilling activities, including soil and excess drilling fluids (if used), and decontamination liquids, will be stored on site in appropriately labeled containers and disposed of properly. Disposable materials will be stored and disposed of separately. Containers must be labeled at the time of collection and will include date, location(s), site name, city, state, and description of matrix contained (e.g., soil, PPE). Waste will be managed in accordance with the ***TGI – Investigation-Derived Waste Handling and Storage***, the procedures identified in the FIP/work plan or QAPP as well as

state-, federal- or client-specific requirements. Be certain that waste containers are properly labeled and documented in the field log.

10 Data Recording and Management

Digital data collection is the Arcadis standard using available FieldNow® applications that enable real-time, paperless data collection, entry, and automated reporting. Paper forms should only be used as backup to FieldNow® digital data collection and/or as necessary to collect data not captured by available FieldNow® applications. The Field Now® digital form applications follow a standardized approach, correlate to most TGIs and are available to all projects accessible with a PC or capable mobile device. Once the digital forms are saved within FieldNow®, the data is instantly available for review on a web interface. This facilitates review by project management team members and SMEs enabling error or anomalous data detection for correction while the staff are still in the field. Continual improvements of FieldNow® applications are ongoing, and revisions are made as necessary in response to feedback from users and subject matter experts.

Management of the original documents from the field will be completed in accordance with the site- specific QAPP.

In general, drilling activities will be documented on appropriate field/log forms as well as in a proper field notebook. All field data will be recorded digitally or with indelible ink. Field forms, logs/notes (including daily field and calibration logs), digital records, and chain-of-custody records will be maintained by the field team lead. Any deviations or omissions from this TGI should be documented.

Initial field logs and chain-of-custody records will be transmitted to the Arcadis CPM and Technical Lead at the end of each day unless otherwise directed by the CPM. The field teamleader retains copies of the field documentation.

Additionally, all documents (and photographs) will be scanned and electronically filed in the appropriate project directory for easy access. Pertinent information will include personnel present on site, times of arrival and departure, significant weather conditions, timing of drilling activities, soil descriptions, soil boring information, and quantities of materials used.

In addition, the locations of soil borings will be documented photographically and in a site sketch. If appropriate, a measuring wheel or engineer's tape will be used to determine approximate distances between important site features.

Records generated as a result of this TGI will be controlled and maintained in the project record files in accordance with project requirements.

11 Quality Assurance

Quality assurance procedures shall be conducted in accordance with the Arcadis Quality Management System or the site-specific QAPP.

All drilling equipment and associated tools (including augers, drill rods, sampling equipment, wrenches, and any other equipment or tools) that may have come in contact with soil will be cleaned in accordance with the procedures outlined in the appropriate TGI.

Field-derived quality assurance blanks will be collected as specified in the FIP/work plan and/or site- specific QAPP, depending on the project quality objectives. Typically, field rinse blanks (equipment blanks) will be collected when non-dedicated equipment (e.g., split-spoon sampler, stainless steel spoon) is used during soil sampling. Field rinse blanks will be used to confirm that decontamination procedures are sufficient and samples are representative of site conditions. Trip blanks for VOCs, which aid in the detection of contaminants from other media, sources, or the container itself, will be kept with the coolers and the sample containers throughout the sampling activities and during transport to the laboratory.

Operate all monitoring instrumentation in accordance with manufacturer's instructions and calibration procedures. Calibrate instruments at the beginning of each day and verify the calibration at the end of each day. Record all calibration activities in the field notebook.

12 References

ASTM D1586 - *Standard Test Method for Standard Penetration Test (SPT) and Split-Barrel Sampling of Soils*. ASTM International. West Conshohocken, Pennsylvania.

13 Attachments

Attachment 1. Soil Boring Log Form

Attachment 1

Soil Boring Log Form

ARCADIS

[illegible]

Boring ID: _____ Project Name: _____ Page: _____ / _____

[illegible]

BORING LOG



Boring ID: _____ Project Name: _____ Page: _____ / _____

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Arcadis U.S., Inc.
630 Plaza Drive, Suite 200
Highlands Ranch
Colorado 80129
Phone: 720 344 3500
Fax: 720 344 3535
www.arcadis.com

TGI – Vertical Aquifer Profile (VAP) Sampling

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Version Control

Issue	Revision No.	Date Issued	Page No.	Description	Reviewed By
	0	June 22, 2018	All	Original SOP	Joe Quinnan
	1	May 11, 2020	Multiple	Added content to Personnel Qualifications, references to Geoprobe SP-16 and SP-22, Attachment 3, and updated references /formatting	Marc Killingstad
	2	June 15, 2022	Multiple	Combined with PFAS-specific VAP TGI and dye/tracer procedures.	Patrick Curry

Approval Signatures

Prepared by:



6/15/2022

Patrick Curry (Preparer)

Date

Reviewed by:



6/15/2022

Marc Killingstad (Subject Matter Expert)

Date

1 Introduction

This Arcadis Technical Guidance Instruction (TGI) describes proper vertical aquifer profile (VAP) sampling procedures using a variety of methods and approaches. This document has been developed to emphasize drilling and sampling procedures used to collect groundwater samples from boreholes installed via direct push technology (DPT), hollow stem auger (HSA), and rotary-sonic (sonic) methods and includes the use of visible tracer in drilling fluid to obtain representative samples during vertical profiling.

2 Intended Use and Responsibilities

This document describes general and/or specific procedures, methods, actions, steps, and considerations to be used and observed by Arcadis staff when performing work, tasks, or actions under the scope and relevancy of this document. This document may describe expectations, requirements, guidance, recommendations, and/or instructions pertinent to the service, work task, or activity it covers.

It is the responsibility of the Arcadis Certified Project Manager (CPM) to provide this document to the persons conducting services that fall under the scope and purpose of this procedure, instruction, and/or guidance. The Arcadis CPM will also ensure that the persons conducting the work falling under this document are appropriately trained and familiar with its content. The persons conducting the work under this document are required to meet the minimum competency requirements outlined herein, and inquire to the CPM regarding any questions, misunderstanding, or discrepancy related to the work under this document.

This document is not considered to be all inclusive nor does it apply to all projects. It is the CPM's responsibility to determine the proper scope and personnel required for each project. There may be project- and/or client- and/or state-specific requirements that may be more or less stringent than what is described herein. The CPM is responsible for informing Arcadis and/or Subcontractor personnel of omissions and/or deviations from this document that may be required for the project. In turn, project staff are required to inform the CPM if or when there is a deviation or omission from work performed as compared to what is described herein.

In following this document to execute the scope of work for a project, it may be necessary for staff to make professional judgment decisions to meet the project's scope of work based upon site conditions, staffing expertise, regulation-specific requirements, health and safety concerns, etc. Staff are required to consult with the CPM when or if a deviation or omission from this document is required that has not already been previously approved by the CPM. Upon approval by the CPM, the staff can perform the deviation or omission as confirmed by the CPM.

3 Scope and Application

Vertical aquifer profile (VAP) borings are typically advanced via DPT, HSA, or sonic drilling techniques to collect single or multiple depth-discrete groundwater samples using low-flow or grab sampling methodologies. This can be combined with retrieval of continuous soil cores and lithologic logging, as well as collection of single or multiple depth-discrete dry and saturated soil samples.

When possible, co-locate or bias VAP groundwater sampling intervals towards potential discrete transport zones (and target slow advection zones when feasible) as indicated by soil logging observations or permeability measurements (e.g., point slug tests, Geoprobe® hydraulic profiling tool [HPT] [preferred],

Waterloo APS™ [alternate]). Permeability measurements coupled with contaminant concentration allows estimation of relative flux and mass discharge to evaluate potential risk to downgradient receptors. In the absence of permeability measurements, field soil lithological logging observations may be used to interpret hydrostratigraphy and select sampling intervals.

The intent of this TGI is to provide VAP instructions including specific considerations for per- and polyfluoroalkyl substances (PFAS) due to their unique chemical and physical properties, low detection limits, and regulatory standards. It also covers field procedures for using nontoxic fluorescent tracer (e.g., fluorescein dye) in drilling fluid during drilling to assist in determining when sufficient purging has been performed prior to collecting screening-level groundwater samples during the drilling process. Screening level groundwater samples may be obtained by evacuating water from the drill casing or from intervals of geologic formations isolated by inflatable packers. This procedure improves the quality of screening-level groundwater samples by providing a technical basis to determine when purging has sufficiently removed drill water prior to collecting screening-level groundwater samples.

Multiple VAP samples can be collected through temporary wells, drilling rod tooling (e.g., Geoprobe® Screen Point 16 [SP-16]/Screen Point 22 [SP-22] Groundwater Samplers or SP-60 Sonic Groundwater Sampler or Cascade's Sonic Push-Ahead or Packer Isolation Groundwater Profilers) or via combined hydraulic profiling and sampling tools (e.g., Geoprobe® HPT-Groundwater Sampling System [HPT-GWS] or Waterloo APS™). They can be analyzed quickly via on-site mobile lab or expedited off-site fixed lab analysis to provide adaptive high-resolution quantitative groundwater concentration data. The vertical frequency of groundwater sampling within a formation will be determined relative to the scale of variability demonstrated in site hydrostratigraphy and outlined in the FIP/Work Plan. Thin aquifers with transport zones only tens of feet thick (or less) can be sampled at intervals as close as 3 to 5 feet. In aquifers with transport zones substantially thicker (e.g., more than 50 feet), sample spacing of 5 to 20 feet may be adequate. It is important to note that field data be evaluated to verify that sampling intervals provide sufficient resolution to meet data quality objectives (DQOs) (See **Section 7**).

4 Personnel Qualifications

In general, VAP activities will be performed by persons who have been trained in proper drilling and sampling procedures under the guidance of an experienced field geologist, engineer, or technician. Arcadis personnel overseeing, directing, or supervising VAP activities shall have previous related experience (minimum of 2 years) in drilling and groundwater sampling. Drilling subcontractors will need current applicable drilling licenses.

Arcadis field personnel will have completed or are in the process of completing site-specific training as well as having current health and safety training as required by Arcadis, client, or regulations, such as 40-hour HAZWOPER training and/or OSHA HAZWOPER site supervisor training. Arcadis personnel will also have current training as identified in the site-specific Health and Safety Plan (HASP) which may include first aid, cardiopulmonary resuscitation (CPR), Blood Borne Pathogens (BBP) as needed. The HASP will also identify any access control requirements.

Prior to mobilization, the field team will review and be thoroughly familiar with relevant site-specific documents including but not limited to the task-specific work plan or field implementation plan (FIP)/field sampling plan, Quality Assurance Project Plan (QAPP), HASP, historical information, and other relevant site documents.

Arcadis field sampling personnel will be knowledgeable in the relevant processes, procedures, and TGIs and possess the demonstrated required skills and experience necessary to successfully complete the desired field work. Additionally, the field team will review and be thoroughly familiar with documentation provided by equipment manufacturers and become familiar with the operation of (i.e., hands-on experience) all equipment that will be used in the field prior to mobilization.

5 Equipment List

The following equipment and materials must be available for VAP sampling

- Site plan with proposed sampling locations
- Relevant work plan (or equivalent)
- Health and Safety Plan (HASP)
- Field Tablet with appropriate Fulcrum app for logging groundwater sampling.
- NOTE: *As of June 2022, several digital logging applications are available through the FieldNow™ program and the Fulcrum app. A future revision of this TGI, likely in early 2023, will emphasize digital logging methods and groundwater sampling. FieldNow™ is discussed further in Section 10.*
- Appropriate health and safety equipment, as specified in the site HASP
 - Drilling Equipment
 - Drill rig (to be provided by drilling subcontractor). Type (e.g., roto-sonic, direct push) to be determined based on site-specific details
 - Traffic cones, delineators, caution tape, and/or fencing as appropriate for securing the work area, if not provided by the drillers

NOTE: *Prior to mobilizing to the site, Arcadis personnel will contact the drilling subcontractor or in-house driller (as appropriate) to confirm that appropriate sampling equipment will be provided in quantities capable of achieving estimated target depths. Typical equipment/materials provided by the driller could include*

- Acetate or plastic liners
 - Appropriate length of drilling rods and tooling
 - Drilling and sampling equipment decontamination materials,
 - Decontamination pad materials, if required. See **Section 6.3** below for more information
- Sampling Equipment
 - Appropriate groundwater sampling equipment (e.g., disposable bailers for volumetric sampling, peristaltic pump for shallow groundwater sampling, submersible bladder pump for deeper sampling). Refer to *the TGI – Low-Flow Groundwater Purging and Sampling Procedures for Monitoring Wells* (Arcadis 2020a) for necessary equipment
 - Direct push groundwater samplers (e.g., Geoprobe® SP-22) or roto-sonic sampling devices (e.g., Cascade Push Ahead/Packer Isolation Groundwater Profiler or Geoprobe® SP-60 Sonic Groundwater Sampler) (to be provided by drilling subcontractor)
 - Appropriate soil sampling equipment (e.g., stainless steel spatulas, knife, metal trowel)

- Dedicated plastic sheeting (preferably high-density polyethylene [HDPE]) or other clean surface to prevent sample contact with the ground
- Multi-parameter water quality probe (e.g., conductivity, temperature, pH, dissolved oxygen, oxidation reduction potential, and turbidity meter)
- Water level meter
- Appropriate sample containers and labels
 - Labeled sample bottles: see the *TGI – Poly- and Perfluorinated Alkyl Substances (PFAS) Field Sampling Guidance* (Arcadis 2017a) for PFAS-specific considerations
 - Ziplock-style bags to hold ice and samples
 - Appropriate blanks (field reagent blanks supplied by the laboratory)
 - Packing and shipping materials
 - Chain-of-Custody (COC) Forms; see the *Sample Chain of Custody* for reference (Arcadis 2017b)
 - Appropriate transport bottles (coolers) with ice and appropriate labeling, no blue ice
- Decontamination Equipment
 - Equipment cleaning materials: see the *TGI – Poly- and Perfluorinated Alkyl Substances (PFAS) Field Sampling Guidance* (Arcadis 2017a) or the *TGI – Groundwater and Soil Sampling Equipment Decontamination* (Arcadis 2020b) as applicable
 - Drum labels as required for investigation derived waste handling: see the *TGI – Investigation-Derived Waste Handling and Storage* for details (Arcadis 2017c)
- Documentation/Field Notes
 - Electronic data collection device (smart phone or tablet) as applicable
 - Pens, pencils, and/or Sharpie® brand pens for writing
 - Digital camera
 - Any other appropriate field forms
- Tracer Equipment (as needed)
 - Sodium fluorescein (also known as fluorescein or uranine dye) tracer (to be added to drilling water to produce a vibrant yellow-green color); 38 grams of dye will be added to each 500 gallons of drilling water (potable water) to achieve target applied tracer concentration of 20 milligrams per liter (mg/L)
 - Bottles for retaining dyed drilling water samples and preparing visual dye standards (clear, colorless, 40 mL unpreserved VOA bottles or equivalent)
 - Graduated cylinders (50 mL and 1 L)
 - Scale for measuring mass of dye to the nearest 1 gram
 - Bottles for groundwater samples to be analyzed for tracer dye (if necessary) and chemicals of concern (COCs)

- Poly storage tank (typically 550-to-1,000-gallon capacity)
- Potable water source
- Generator
- Utility pump for mixing dye
- Pump for groundwater purging and sampling
- Flashlight or other portable lighting device
- Blue ice (for tracer dye samples)

6 Cautions

Field activities associated with borehole advancement and VAP groundwater sampling will be performed in accordance with the HASP, a copy of which will be present on site during such activities. Field staff (including subcontractors) will be aware of and understand the associated physical and health hazards.

6.1 Utility Clearance

The appropriate drilling authorities will be contacted and a site visit for public utility line clearance at the proposed boring locations will be conducted at least 72 hours prior to work commencing. As applicable, utility maps will be reviewed during field reconnaissance of the proposed investigation locations to determine if any are co-located with public utility lines. Arcadis will also contract an independent geophysical survey company to verify that proposed boring locations are not co-located with existing underground utility/substructure features, as necessary. Arcadis will clear locations with soft dig methods to assess the presence of underground utilities as necessary.

See the *Utility Location and Clearance Arcadis Health and Safety Standard* (Arcadis 2020c) for reference.

6.2 PFAS-Specific General Sampling Considerations

This section provides a summary of methods and procedures applicable to the collection of environmental samples for field screening or laboratory analysis during PFAS site characterization activities. In general, sampling techniques used for PFAS site characterization are consistent with conventional sampling techniques used in the environmental industry, but special consideration is made regarding PFAS-containing materials and cross-contamination potential. For example, Teflon™ and other fluoropolymer containing materials are found in pumps, tubing, and sample storage containers and, therefore, will be avoided if possible (Department of Environment Regulation [DER], Western Australia 2016; New Hampshire Department of Environmental Services [NHDES] 2016). Certain field documentation materials such as waterproof paper or field books, adhesive paper products, and some writing utensils (grouped as non-Sharpie® markers) are also prohibited items during PFAS sampling (DER 2016; NHDES 2016).

Attachment 1 (Tables 1 and 2) provides recommendations for PFAS Site Investigation equipment. Table 1 provides a summary of materials that have been approved for site investigation; this list is expected to grow longer as industry experience increases. Table 2 provides a summary of field equipment and materials that have available testing information and/or industry knowledge regarding PFAS cross-

contamination potential, and it is recommended that these materials be prohibited for sample collection. For materials that are suspected of containing and/or retaining PFAS, these recommendations are considered preliminary and subject to change.

Given the extremely low detection limits associated with PFAS analysis and the many potential sources of trace levels of PFAS, field personnel are typically advised to err on the side of caution by strictly following field wear guidelines and decontamination procedures as specified in the *TGI - Poly- and Perfluorinated Alkyl Substances (PFAS) Field Sampling Guidance* (Arcadis 2022). The most important consideration during PFAS related VAP sampling is to prevent contact between sample media and suspect PFAS sources.

6.3 PFAS-Specific Groundwater Sampling

The potential presence of material containing PFAS in equipment that may come into contact with the target water sample must be evaluated as part of the sample planning process to maintain sample integrity. For example, low-flow sampling with a peristaltic pump will be conducted using silicone or HDPE tubing; Teflon™ tubing is prohibited (DER 2016). If a bladder pump is used to collect samples, the bladder and other internal parts (e.g., check balls, O-rings, compression fittings) will not contain Teflon™, and bladder and O-rings will be changed between samples (DER 2016).

Note that if high concentrations of PFAS related to Class B firefighting foams are expected in a groundwater sample, it has been recommended to collect and shake a small portion of the sample at the time of sample collection (USACE 2016; Arcadis 2017a). If foaming is noted within the sample, it indicates elevated concentrations of PFAS may be present and the sample will be proactively diluted at the laboratory prior to analysis, and the foaming will be noted on the sample COC form. It is recommended to collect sampling equipment blanks following foam observation to confirm the effectiveness of decontamination procedures.

6.4 Use of Tracer in Drilling Fluid

Field staff (including subcontractors) will be aware of tracer hazards and understand the associated health hazards. Please be sure to read the SDS (included as Attachment 2) for fluorescein dye. Note that some individuals can experience a mild allergic reaction to skin contact with fluorescein. Protective gloves will be worn during dye handling and mixing activities, and rinse bottles will be readily available for washing affected areas in case of accidental contact.

7 Health and Safety Considerations

To ensure the safety of the field personnel, field activities associated with VAP will be performed in accordance with a site-specific HASP, a copy of which will be present on site during such activities. Review all site-specific and procedural hazards as they are provided in the HASP and review relevant Job Safety Analysis (JSA) documents in the field each day prior to beginning work.

Appropriate personal protective equipment (PPE) will be always worn in line with the task and the site-specific HASP. Verify staff has required health and safety training and personal protection

equipment in accordance with the HASP and JSAs. At a minimum, all staff will have level D PPE with chemical resistant gloves.

8 Procedure

The specific procedure for advancing VAP borings will be developed after careful review and consideration of project DQOs and clearly detailed in the FIP/Work Plan. Typically, VAP borings are conducted in boreholes adjacent to soil borings previously completed to develop stratigraphic and relative permeability profiles of the aquifer to determine sampling depth intervals that target transport zones. Prior boreholes typically consist of soil borings with detailed soil descriptions or Geoprobe® HPT borings. The primary advantage of completing stratigraphic/permeability profiles in advance of VAP sampling is to gain an understanding of hydrofacies trends to ensure that the most appropriate intervals and sampling methods are used. For sonic or HSA drilling, VAP samples are typically collected from the same borehole as soil samples. In the absence of a co-located boring, sample depth intervals can be determined based upon lithologic logging of soil cores, either from a separate adjacent borehole or from the same borehole. HPT drilling will be completed consistent with the *TGI – Geoprobe Hydraulic Profiling Tool (HPT)* (Arcadis 2022a), and soil lithologic logging will be performed in accordance with *TGI – Soil Description* (Arcadis 2022b).

NOTE: Waterloo APS™ can be utilized as an alternative to HPT to provide permeability profiles, but it is more time consuming than HPT; therefore, it is not considered the preferred tool for permeability profiling.

8.1 Direct Push Vertical Aquifer Profile Sampling

Direct push tooling is ideal for shallow unconsolidated aquifers and requires minimal water for drilling, reducing the potential for sample dilution/cross-contamination. For sites with shallow groundwater in unconsolidated formations (e.g., at less than 100 feet bgs), the typical approach is to collect VAP groundwater samples nominally every 5 to 10 feet with a bias to the more permeable transport zones.

When a zone of interest is identified, either by using permeability measurements (preferred) or logging soil, a screen point sampling device such as Geoprobe® SP-16 or SP-22 (see **Attachment 3**) can be driven to the target interval and the screen opened to collect a groundwater sample. In poorly sorted aquifers with appreciable amounts of silt, VAP sampling from an adjacent borehole after completing initial permeability profiling (e.g., Geoprobe® HPT or point slug tests) is typically more efficient and cost effective. In the absence of permeability profiling tools (e.g., HPT), VAP sampling can be performed based on soil lithological observations alone, either from a separate borehole or in the same borehole. However, VAP sample collection can be more efficient when conducted from an adjacent borehole, particularly if a bottom-up sampling approach is used. See Section 8.1.1.

Combined permeability profiling and sampling tools such as the Geoprobe® HPT-GWS (or Waterloo APS™ as an alternate) can be used to collect groundwater samples based on permeability measurements from the same borehole at deeper depths where the process is more cost-effective; otherwise at shallower depths, separate permeability profiling prior to VAP sampling is preferred. This is most effective in well-sorted sand and gravel when small volumes are required for analysis, since these tools provide limited volumes for purging and sample collection. Use of these combined tools (HPT-GWS or Waterloo APS™) for PFAS sites is not recommended because low detection and regulatory thresholds for PFASs require more extensive purging to decontaminate the sampling equipment (i.e., insufficient data are available to confirm the volume of purging required to eliminate cross-contamination with PFAS).

It is recommended that DPT drilling for VAP sampling be completed using a dual-tube drilling approach. An outer casing is advanced with the screen point sampling device to limit the potential for cross-contamination between sampling intervals. Pre-calculated volume purging and monitoring for water quality parameter stabilization can be performed consistent with low-flow sampling to help determine when purge water is representative of the groundwater formation.

There are two general methods for completing VAP sampling: bottom-up and top-down. With bottom-up sampling, a greater purge volume is required to ensure a representative groundwater sample; however, the overall time savings is significant relative to top-down sampling, where more time is required per borehole to lower the tooling, retract it, and decontaminate it between subsequent sampling intervals. However, the top-down method minimizes any potential for cross-contamination and is the preferred approach for PFAS projects due to the low detection limits and regulatory levels associated with PFASs.

8.1.1 Bottom-Up VAP Sampling

Bottom-up VAP sampling involves advancing dual-tube direct push casing to the deepest target depth with either a solid drive tip (without collecting soil cores) or acetate liners for collection of continuous soil cores to provide a lithological log for the entire boring. This is followed by lowering the groundwater sampling screen through the outer casing to the bottom of the borehole and collecting multiple VAP groundwater samples at different depths as the casing and screen is retracted up the borehole.

Using this approach, the external casing is retracted to allow borehole collapse around the sampling screen while isolating it from the section above that is still covered by the external casing.

NOTE: Bottom-up VAP sampling is not recommended when there is a potential for dense non-aqueous phase liquid (DNAPL), the highest concentrations are expected to be at the bottom of the formation, or the borehole goes through multiple confining units. Bottom-up is not recommended for PFAS sampling due to potential cross-contamination concerns associated with lack of decontamination between sample intervals.

The advantages of this approach are: (1) when combined with soil core collection, groundwater sampling depth intervals can be pre-selected based on lithologic observations to target the transport zones, especially in the absence of any co-located permeability measurements, and (2) the entire process is much more time-efficient per borehole as the sampling equipment is not pulled, decontaminated, and then drilled to the next interval. However, additional purging (i.e., 3 to 5 casing volumes) is required to assure a representative groundwater sample. Bottom-up sampling also does not allow for post-grouting of the borehole since when the groundwater sampling device is pulled up to the next VAP sampling interval, the sidewalls of the open borehole below collapse.

8.1.2 Top-Down VAP Sampling

Top-down VAP sampling involves advancing dual-tube direct push casing with either a solid drive tip (without collecting soil cores) or a plastic liner for soil core retrieval from target depth interval followed by lowering the screen point sampling screen to target depth and pulling up the outer casing to expose the screen. After purging and sample collection, the screen point device is pulled back up and decontaminated. A solid drive tip or plastic liner is lowered back into the borehole and the entire assembly is then advanced to the next depth interval. Thus, top-down sampling requires pulling the tooling after each sample interval, decontaminating the tooling, re-setting the groundwater sampler, and advancing the tooling to the next planned interval.

The advantages of this approach are that it allows grouting of the borehole from the bottom of the borehole and

reduces the potential for cross-contamination from adjacent sampling intervals.

The primary disadvantage is that the entire process is much less time-efficient per borehole since the tooling must be retracted and re-advanced every time.

NOTE: *Top-down is the preferred method for PFAS VAP sampling.*

8.2 Sonic Drilling VAP Sampling

For sites with deep unconsolidated aquifers, bedrock/weathered bedrock, or otherwise challenging drilling conditions (e.g., presence of dense tills, caliche, cobbles), sonic drilling will be necessary to complete VAP. Like direct push, groundwater profilers can be used with sonic rigs to collect multiple depth-discrete groundwater samples biased towards transport zones based on soil lithological cores. The configuration of individual samplers varies based on their manufacturer by different drilling contractors (e.g., Cascade Push Ahead/Packer Isolation Groundwater Profiler or Geoprobe® SP-60).

The overall strategy of sonic drilling VAP sampling is consistent with direct push VAP sampling; however, drilling with sonic or some rotary methods can require the introduction of drilling fluid/water that can potentially affect the integrity of the groundwater sample. If possible, sonic drilling for VAP borings will be conducted without the use of drilling water. If, for example, the geology is known for flowing sands or VAP is required deep below the water table, drilling water will be used to keep the core barrel free inside the outer drill casing. In this case it is recommended that a visible dye be used to spike the drilling water to assist with purging of the VAP interval. The VAP interval is then purged until the visible dye is no longer visible, or less the 10% of the starting concentration. For more on drilling with visible dye, see Section 8.2.3. Sonic VAP sampling is typically performed in a top-down manner using either a push ahead sampling device or a packer system.

8.2.1 Push-Ahead Groundwater Profiler

Push-ahead groundwater sampling devices are available through Cascade Drilling and other sonic drillers and consists of a stainless-steel sheathed “screen” threaded to the base of the sonic drill rod. The device is driven ahead of the sonic casing into the undisturbed formation to the prescribed sample depth interval. Once the point is at the specified interval, the threaded portion between the profiler and rod is partially unthreaded to expose the water ports to allow native formation water to enter the profiler. A groundwater sample is then obtained using either a stainless-steel bailer or pump with tubing depending on the DQOs. The interval is typically purged until relatively free of fine-grained material.

The disadvantage of using this device is that groundwater samples are obtained from undisturbed native formation with unknown soil lithology, so sampling is conducted “blind”. Therefore, it is recommended that a pre-existing lithological log from an adjacent borehole is used to determine sampling depth intervals.

8.2.2 Packer Isolation Groundwater Profiler

Packer Isolation groundwater profilers (e.g., Packer Isolation groundwater profiler from Cascade, Geoprobe® SP-60 Sonic Groundwater Profiler) work by driving the casing over the soil core, retrieving the soil core barrel, and then lowering a stainless screen and packer assembly to the base of the sonic casing. The sonic outer casing is then extracted to expose the screen to the formation, and the packer is inflated within the casing above the screen to isolate the screened interval from any water that might be above the packer in the sonic casing. A groundwater sample can then be collected from the screen.

The biggest advantage of this device is that groundwater sampling depth intervals can be determined based on lithological logs obtained from the same borehole.

A disadvantage is that a large volume of purge water may need to be removed to clear the borehole of water introduced from above.

8.2.3 Drilling with Visible Dye

Potable water is commonly used as a drilling fluid during drilling to remove cuttings of geologic materials from the borehole (e.g., coring or roller-bit rotary drilling), cool the drill bit (e.g., sonic drilling), and/or maintain sufficient hydraulic pressure within the drilling tools to prevent heaving of aquifer solids into the drill casing(s).

Typically, if groundwater sampling is performed during drilling, the purge volume to be removed is at least as much as was lost during drilling. However, accurately determining the volume of water lost to the formation, or to specific intervals of the borehole, is not always feasible or possible.

To ensure that groundwater samples accurately represent groundwater quality of the surrounding formation and are not significantly influenced by unrecovered drilling fluid, fluorescein dye can be added to the drilling water to visually confirm when unimpacted native groundwater enters the borehole and can be sampled.

The target concentration of dye is approximately 20 mg/L, which is greater than two (2) orders of magnitude above its visual threshold (approximately 0.1 mg/L) and over five (5) orders of magnitude above its typical laboratory detection limit (less than 0.001 mg/L). Once the drilling tool has been advanced to the prescribed depth for groundwater sampling, water will be pumped from the borehole until the discharge water is relatively clear of fluorescein. The goal of purging is to reach the clarity of a prepared visual standard, indicating that the discharge water is comprised of at least 95 percent formation water and less than 5 percent drilling water. Groundwater samples will then be collected for COC analysis.

If the visual standard is still not reached after a reasonable period and volume of purging, then COC sampling can still be performed, provided that samples of the dyed drilling water and groundwater are also sent for fluorescein analysis. The fluorescein data can then be used to calculate a correction factor to be applied to COC analytical results.

8.2.3.1 Set-Up Procedures

a. Dye Batch Preparation

- Prior to initiating drilling activities, measure the proper mass of powdered dye for mixing with drilling water - 38 grams of fluorescein (provided by Ozark Underground Laboratory) will be added to every 500 gallons of water to yield an average tracer concentration of approximately 20 mg/L.
- If the drilling water “batch” is larger or smaller than 500 gallons, the same ratio of dye to drilling water will be used.
- Measure the mass of dye using a scale with an accuracy of +/- 1 gram.
- Add the dye to the drilling water batch tank while also adding the potable water to provide agitation to assist in mixing the dye.
- A utility pump is also recommended to mix the tracer with the drilling water by recirculating water in the tank for at least 15 minutes.

- Place 40 mL of the dyed drilling water into a 50 mL graduated cylinder for use in preparing the visual standard discussed below.
- Collect four (4) additional 40 mL unpreserved VOA vials of drilling water from each batch of drilling water – label all four of these vials “DW1” for the first batch of drilling water, “DW2” for the second batch, etc. These samples will be archived for potential use in preparing other standards with other dilutions (optional) or for submittal for laboratory analysis, if necessary.

b. Preparation of Visual Standard: A visual standard will be prepared for each batch of dyed drilling water, as follows.

- Pour the 40 mL volume of dyed drilling water from the 50 mL graduated cylinder into a 1 L graduated cylinder.
- Add 760 mL of un-dyed potable water (from the same potable water source used to prepare the dyed drilling water) to the 1 L graduated cylinder to produce 800 mL of “visual standard”.
- Fill one 40-mL unpreserved VOA vial with visual standard solution and label this “VS1” for the visual standard from the first batch of drilling water, “VS2” for the visual standard from the second batch of drilling water, etc.
- These visual standards represent a 95% dilution of the drill water and will provide a visual standard to verify that sufficient purging has been performed to remove at least 95% of the drilling water from a given interval, indicating that the purge water consists of at least 95% formation water.
- Discard the remaining fluid within the graduated cylinder using an appropriate container.
- Photograph the “DW” samples and the “VS” sample from each batch of drilling water with adequate, consistent light, against a white background.
- Keep all the dyed drilling water (“DW”) samples and visual standard (“VS”) samples in a cooler to keep them dark as the dye will degrade with exposure to light.

8.2.3.2 Drilling Procedures

- Fresh drilling water from the dyed drilling water batch tank will be used during drilling operations. In general, a positive head will be maintained during drilling, which should prevent dilution of the drilling water by formation water. However, any water upwelling from the casing during drilling will be contained in a tub positioned over the borehole. As needed, recovered water in the tub will be pumped to a frac tank.
- The drilling water source will be sampled for chlorine and pH at the start of the project. Chlorine, if present in detectable quantities, will consume fluorescein; therefore, wait a period of at least four (4) hours between dye addition and sampling (and use) of the drilling fluid. Below pH values of about 5, fluorescein will have reduced fluorescence. Depending on the source of the drilling fluid and project objectives, the source water may also be sampled for COCs and fluorescein.
- In open sunlight, fluorescein photodegrades rapidly. If the tracer batch tank is translucent, use 1-millimeter (mm) thick black plastic to cover the tank during the day to minimize photodegradation of the tracer batch water.
- After tracer addition, each batch of drilling fluid will be sampled at least once for fluorescein.
- At the end of the day, any excess tracer batch water can be stored for use on the following day, or it may be disposed of as investigation derived waste. Alternatively, fluorescein concentrations can be reduced to below

visible concentrations with granular activated carbon, UV-oxidation, chemical oxidants, or direct exposure to sunlight for several days.

- The field geologist will record the amount of drilling water lost to the formation during drilling of each sampling depth interval.
- At the end of the project, any excess tracer batch water can be disposed of as investigation derived waste. Alternatively, fluorescein concentrations can be reduced to below visible concentrations with granular activated carbon, UV-oxidation, chemical oxidants, or direct exposure to sunlight for several days. Depending on project and regulatory requirements, excess batch water with fluorescein concentrations below the visible limit could be discharged to a sanitary sewer or other discharge location.

8.2.3.3 Purging and Sampling Procedures

- After a groundwater sampling interval is reached, purging and screening-level groundwater sampling will be performed.
- The target sample interval will be purged using a pump, and during purging, purge water will be periodically collected in a 40-mL unpreserved VOA vial and compared to the visual standard ("VS" sample) prepared from the drilling water used to drill that depth interval.
- If the purge water contains significant suspended particulates/turbidity, it may be necessary to allow particulates to settle before comparing the purge water sample to the visual standard.
- Purging will continue until one of the following two conditions is met:
 - 1) Purge water clarity (in terms of remaining dye content) matches or exceeds the clarity of the visual standard, indicating that the purge water consists of at least 95% formation water.
 - a. In this case, the purge water sample and the associated visual standard will be photographed against a white background to document that the purging goal has been reached.

OR

- 2) A different practical purging limit has been reached, based on purge volume or time
 - a. In this case, the purge water sample and the associated visual standard will be photographed against a white background to document the degree of purge water visual clarity that was attained
 - b. Also, a sample of the purge water will be collected in a 40 mL unpreserved VOA; this sample and one of the vials of dyed drilling water will be submitted to Ozark Underground Laboratories for quantitative analysis of fluorescein. These samples will be shipped in a cooler with reusable "Blue Ice" rather than wet ice. The analytical results for fluorescein will be used to calculate a COC correction factor, as discussed below (see Section 8.2.3.4).
- After purging has been completed, screening-level groundwater samples will be collected from the discharge end of the pump tubing for COC analysis in accordance with the approved work plan.

8.2.3.4 Calculation of Correction Factor

- If the purge water does not reach the goal indicated by the visual standard (“VS” sample), a sample of the drilling water and a sample of the purge water (obtained immediately prior to sampling for COC analysis) will be sent for laboratory analysis of fluorescein.
- Representative COC concentrations in groundwater (C_{gw}) can then be calculated as:

$$C_{gw} = C_m [F_d / (F_d - F_s)]$$

where: C_m = measured COC concentration, as reported by the lab

F_d = fluorescein concentration in drilling water

F_s = fluorescein concentration in groundwater sample

- The term $[F_d / (F_d - F_s)]$ is the COC correction factor.

8.3 Boring Abandonment

Upon completion, each top-down borehole is backfilled with bentonite grout from the terminal end of the boring upward. The top portion of each boring is sealed with asphalt or concrete to match the existing grade. Each bottom-up borehole is typically abandoned by the collapse as the rods are retraced.

Borehole abandonment requirements in some geographies dictate top-down sampling; this should be verified in advance of work and outlined in the FIP/Work Plan. See also *TGI for Monitoring Well and Borehole Decommissioning*.

9 Waste Management

Investigation derived waste (IDW) (e.g., soil cuttings and decontamination water generated during cleaning procedures) will be collected and contained on site in appropriate containers: see the *TGI – Investigation- Derived Waste Handling and Storage* for details (Arcadis 2020d). All IDW generated during field activities will be placed in Department of Transportation approved containers, sealed, and labeled. Containerized IDW will be stored on site until it is profiled and subsequently transported to an approved facility for disposal or recycling.

Personal protective equipment (e.g., gloves, disposable clothing, disposable equipment) resulting from personnel cleaning procedures and soil sampling activities will be placed in plastic bags. These bags will be transferred into appropriately labeled containers for appropriate disposal.

Waste manifests for all IDW suspected to have come into contact with PFAS will clearly note the potential presence of PFAS.

Additional IDW sampling and management details will be provided in the site-specific FIP/Work Plan/QAPP addendum and will be consistent with applicable client and state requirements.

10 Data Recording and Management

Digital data collection is the Arcadis standard using available FieldNow® applications that enable real-time, paperless data collection, entry, and automated reporting. Paper forms should only be used as backup to FieldNow® digital data collection and/or as necessary to collect data not captured by available FieldNow® applications. The Field Now® digital form applications follow a standardized approach, correlate to most TGIs and are available to all projects accessible with a PC or capable mobile device. Once the digital forms are saved within FieldNow®, the data is instantly available for review on a web interface. This facilitates review by project management team members and SMEs enabling error or anomalous data detection for correction while the staff are still in the field. Continual improvements of FieldNow® applications are ongoing, and revisions are made as necessary in response to feedback from users and subject matter experts.

The supervising field lead will be responsible for documenting drilling events and for recording all relevant information in a clear and concise format. The record of drilling events will include (at a minimum):

- Start and finish drilling dates
- Project name and location
- Project number, client, and site location
- VAP boring number and depths
- Depth to water
- Type of VAP performed and associated tools
- Core barrel size
- Names of contractor's drillers, inspectors, or other people onsite
- Weather conditions

Field staff will ensure COC Forms are properly completed and will verify which analytes (including PFAS analytes) are required for analysis and note on the COC.

Waterproof field books must not be used for field notes. Instead, it's recommended that field notes be on loose paper on Masonite, plastic, or aluminum clip boards and/or electronic data collection tablets (as required). Other requirements for field notes include:

- Keep field notes, writing implements, and electronic data collection tablets away from samples and sampling materials; and,
- Do not write on sampling bottles unless they are closed.

11 Quality Assurance

In general, the following quality assurance and quality control (QA/QC) samples will be collected:

- Equipment blanks
- Field duplicates
- Field (i.e., reagent) blanks

- Matrix spike/matrix spike duplicate

Details on QC sampling requirements (e.g., frequency of collection, types of QA/QC samples) are provided in the QAPP and/or FIP/Work Plan. Additionally, detailed procedures related to equipment and field (i.e., reagent) blank sample collection are outlined in the *TGI for Equipment and Reagent Blank Sample Collection for PFAS Analysis*.

In general, equipment blanks should be collected from every piece of downhole equipment that could come into contact with soil or groundwater during sample collection. This includes the profiling tools (e.g., Geoprobe® SP-16, Geoprobe® SP-22, Geoprobe® SP-60, Cascade Packer Isolation Groundwater Profiler).

To avoid cross-contamination during drilling and sampling, reusable equipment such as hand tools will be cleaned using a non-phosphate soap free of VOCs, double-rinsed in potable water, and allowed to air dry prior to re-use. Drive casings and other drilling equipment will be steam cleaned or replaced with new equipment between boreholes. The drilling equipment will be cleaned in an area designated by the supervising engineer or geologist that is located outside of the work zone.

Prior to initiating field activities, water sources to be used during drilling activities will be sampled to verify those sources are PFAS-free to the extent possible.

Refer to quality control requirements for the project to ensure that appropriate quality assurance and quality control (QA/QC) samples are collected. When collecting QA/QC samples, the same guidelines apply as when collecting regular samples – specifically that:

- Samples will be collected in laboratory-supplied HDPE bottles
- Bottle caps must remain in the hand of the sampler until replaced on the bottle
- Labels must be completed after the caps have been placed back on each bottle
- Samples must be stored in appropriate transport bottles (coolers) with ice (Ziplock-type bags for use as ice containers) with appropriate labeling
- Do not use blue ice except for shipping fluorescein samples
- Store PFAS samples in a separate cooler from other types of samples

11.1 Equipment Blanks (if relevant)

QA/QC sampling typically includes daily collection of equipment blanks using the laboratory-supplied water, or in the case of PFAS sampling, “PFAS-free” water. For peristaltic pump tubing, laboratory supplied water will be poured into a clean HDPE sample bottle and then pumped through new HDPE tubing using the peristaltic pump (with new silicone tubing). Equipment blanks will also be collected from the water used by drillers, as well as any downhole tooling to ensure absence of any cross-contamination. Drilling water sources must be submitted for analysis of all COCs before work commences for VAP as discussed above. See also *TGI for Poly- and Perfluorinated Alkyl Substances (PFAS) Potable Water Sampling Guidance*.

11.2 Field Duplicates

QA/QC sampling typically includes the collection of one field duplicate for every 10 or 20 samples collected. Each duplicate sample will be collected immediately after the initial sample of which it is a duplicate into a separate laboratory-provided sample bottle. Do not indicate to the laboratory which sample the duplicate replicates (i.e., it will be given a blind reference on the COC and sample name such as “Dup 1”).

11.3 Field Blanks

QA/QC sampling for typically includes the submission of one laboratory supplied field blank per day. The reagent field blank sample is brought to the site in a laboratory-supplied sample bottle. Field staff transfer the laboratory-supplied reagent blank to an empty sample bottle. This reagent fieldblank will be placed in the same cooler as the other PFAS samples.

11.4 Matrix Spikes (optional in some cases)

QA/QC sampling includes submitting a sample to be used as a matrix spike if the project requires it. If a separate sample bottle is required, an additional sample will be collected immediately after the initial sample of which it is a duplicate into a separate laboratory-supplied sample bottle.

11.5 Laboratory Analytical QA/QC

- Internal laboratory QA/QC will consist of one laboratory blank and one laboratory control sample (or blank spike) per batch of samples, and additional QA/QCs as indicated by the laboratory QA/QC procedures. Isotope dilution will be used for quantification with isotope-labeled surrogate standards, as available.
- For groundwater and surface water samples, extract the entire groundwater and surface water sample and at least two sampling bottle solvent rinsates for analysis to increase sample accuracy. Avoid sub-sampling an aliquot of the sample bottle.
- Soil samples will be analyzed in their entirety or thoroughly homogenized before extraction and analysis.
- As part of the internal QA/QC, relative percent difference will be calculated between samples and corresponding field or laboratory duplicates. The laboratory quality assurance portion of the laboratory certificates will be reviewed to verify that all calculations/recoveries were within acceptable limits as established by the laboratory method.
- In January 2017, the U.S. Department of Defense and U.S. Department of Energy Quality Systems Manual (QSM) 5.1 (U.S. Department of Defense 2017) was finalized and introduced laboratory guidance for the measurement of PFAS in matrices other than drinking water. This guidance is not a detailed procedural method such as an U.S. Environmental Protection Agency method, but it does recommend best practices around the analysis of PFAS. Laboratories are not required to comply with QSM 5.1 until 2019, although the recommendations around PFAS analysis are similar to what most laboratories are already implementing. Arcadis recommends that any request for PFAS analysis in

groundwater or soil should specifically reference the need to comply with Table B-15 in the QSM 5.1 (i.e., Per- and Polyfluoroalkyl Substances (PFAS) Using Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) With Isotope Dilution or Internal Standard Quantification in Matrices Other Than Drinking Water); however, this list can be modified to support project specific deliverables.

12 References

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ATTACHMENT 1

Table 1 and Table 2: PFAS Investigation Material Recommendations



Table 1: Summary of Acceptable Sampling Equipment and Materials for PFAS Site Investigations

Sampling Materials	Additional Considerations	References
Water Sampling Materials		
High density polyethylene (HDPE) or silicone tubing materials	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
HDPE HydraSleeves™	Low density polyethylene (LDPE) HydraSleeves™ are not recommended	USACE 2016; MassDEP 2017
Drilling and Soil Sampling Materials		
PFAS-free drilling fluids	--	DER 2016
PFAS-free makeup water	Confirm PFAS-free water source via laboratory analysis prior to investigation	--
Acetate liners	For use in soil sampling	USACE 2016
Sample Containers and Storage		
HDPE sample containers with HDPE lined lids for soil and water samples	Laboratory should provide; whole bottle analysis of aqueous samples combined with a solvent rinse of bottle is recommended	DER 2016, MassDEP 2017
Ice contained in plastic (polyethylene) bags (double bagged)	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Field Documentation		
Sharpie®	--	NHDES 2016; USACE 2016; MassDEP 2017
Ball point pens	--	MassDEP 2017
Standard paper and paper labels	--	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Decontamination		
Water-only decontamination	Confirm PFAS-free water source via laboratory analysis prior to investigation	DER 2016
Alconox®, Liquinox® or Citranox® followed by deionized water or PFAS-free water rinse	Alconox® known to contain trace levels of 1,4-dioxane	NHDES 2016; USACE 2016; MassDEP 2017
Methanol, isopropanol, or acetone	Special health and safety precautions are necessary	UNEP 2015; USACE 2016

Note: This list is considered preliminary and additional materials may be added as additional information becomes available. Project teams are expected to follow a methodical evaluation process of materials to be used and confirm acceptance prior to implementation of field activities.

Table 2: Summary of Equipment and Materials Not Recommended for PFAS Site Investigations.

Sampling Materials	Known PFAS-Containing Materials	Suspected PFAS-Containing Materials	Materials with Potential to Retain PFASs	References
Water Sampling Materials				
Teflon® or polytetrafluoroethylene (PTFE)-containing or coated field equipment (e.g., tubing, bailers, tape, plumbing paste)	x			DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Passive diffusion bags			x	MassDEP 2017
LDPE HydraSleeves™			x	USACE 2016; MassDEP 2017
Water particle filters			x	MassDEP 2017
Drilling and Soil Sampling Materials				
Aluminum foil			x	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Drilling fluid containing PFASs	x	x		DER 2016
Sample Containers and Storage				
Glass sample containers with lined lids			x	DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
LDPE containers and lined lids			x	USACE 2016
Teflon® or PTFE- lined lids on containers (e.g., sample containers, rinsate water storage containers)	x			DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Reusable chemical or gel ice packs (e.g., BlueIce®)		x		DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Field Documentation				
Self-sticking notes and similar office products (e.g., 3M Post-it-notes)		x		DER 2016; USACE 2016; NHDES 2016; MassDEP 2017
Waterproof paper, notebooks, and labels	x			DER 2016, MassDEP 2017
Non-Sharpie® markers		x		NHDES 2016
Decontamination				
Some detergents and decontamination solutions (e.g., Decon 90® Decontamination Solution)	x	x		DER 2016; NHDES 2016; MassDEP 2017

Note: For materials that are suspected of containing PFASs, or have the potential to retain PFASs, project specific considerations may provide adequate justification for use during the field event. For example, further evaluation may be conducted in the form of pre-field equipment blank sample analysis.

ATTACHMENT 2

Safety Data Sheet (SDS) Fluorescein





SAFETY DATA SHEET (SDS)
REVISION DATE: 03/03/2016

HUE CORPORATION

Color your everything, may your Hue come true

SECTION I. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

PRODUCT IDENTIFIER:

PRODUCT NAME **HUE URANINE CONC** (Also known as Fluorescein)
 PRODUCT NUMBER 1-C8-073PC
 COLOR INDEX NAME ACID YELLOW 073
 COLOR INDEX NO 45350
 C. A. S. # 518-47-8
 CHEMICAL FAMILY..... XANTHENE

INTENDED USE OF THE PRODUCT:

FELT TIP, MARKER INKS, WATER BASED COATINGS AND LEAK DETECTION

NAME, ADDRESS AND TELEPHONE OF RESPONSIBLE PARTY:

HUE CORPORATION	TELEPHONE	714-389-3130
P.O. BOX 509	FAX	714-389-9731
TUSTIN, CA 92781	EMAIL	SUPPORT@HUECORPORATION.COM

EMERGENCY TELEPHONE NUMBER:

CHEMTREC (USA)	1-800-424-9300
CHEMTREC (OUTSIDE USA)	1-703-527-3887

SECTION 2. HAZARD(S) IDENTIFICATION

CLASSIFICATION OF THE SUBSTANCE OR MIXTURE:

GHS-US
 ACUTE TOX. - INHALATION (CATEGORY 5)
 EYE DAM./IRRITATION (CATEGORY 2B)
 SKIN CORR./IRRITATION (CATEGORY 3)

GHS LABELING:

HAZARD PICTOGRAMS (GHS-US): NO SYMBOL

SIGNAL WORD WARNING

HAZARD STATEMENT(S) H333 - MAY BE HARMFUL IF INHALED
 H320 - CAUSES EYE IRRITATION
 H316 - CAUSES MILD SKIN IRRITATION

PRECAUTIONARY STATEMENTS P305 + 351 + P338 - IF IN EYES: RINSE CAUTIOUSLY WITH WATER FOR SEVERAL MINUTES. REMOVE CONTACT LENSES IF PRESENT AND EASY

TO DO. CONTINUE RINSING.
 P337 + P313 - IF EYE IRRITATION OCCURS/PERSISTS:
 GET MEDICAL ADVICE AND ATTENTION.
 P261 - AVOID BREATHING DUST/FUMES/GAS/MIST/VAPORS/SPRAY
 P264 - WASH FACE THOROUGHLY AFTER HANDLING.
 P322 + P313 - IF SKIN IRRITATION OCCURS: GET MEDICAL ADVICE/
 ATTENTION.
 P304 + 312 - IF INHALED: CALL A POISON CENTER/DOCTOR/PHYSICIAN
 IF YOU FEEL UNWELL

OTHER HAZARDS	NO DATA AVAILABLE
UNKNOWN ACUTE TOXICITY	NO DATA AVAILABLE

SECTION 3. COMPOSITION / INFORMATION ON INGREDIENTS

DESCRIPTION OF MIXTURE: PROPRIETARY MIXTURE OF DYES.

SUBSTANCE:

NAME	C.A.S.#	WEIGHT 100%	GHS-US CLASSIFICATION
ACID YELLOW 073	518-47-8	100%	ACUTE TOX. - INHALATION (CATEGORY 5) EYE DAM./IRRITATION (CATEGORY 2B) SKIN CORR./IRRITATION (CATEGORY 3)

SECTION 4. FIRST AID MEASURES

FIRST AID MEASURES GENERAL:

INHALATION: REMOVE TO FRESH AIR. IF BREATHING IS DIFFICULT, GIVE OXYGEN AND GET IMMEDIATE MEDICAL ATTENTION.

SKIN: WASH WITH MILD SOAP AND WATER. IF IRRITATION OCCURS GET MEDICAL ATTENTION. IF CLOTHING IS CONTAMINATED, RE-MOVE AND WASH BEFORE REUSE.

EYES: FLUSH EYES WITH WATER FOR AT LEAST 15 MINUTES, HOLDING EYELIDS APART FOR THOROUGH IRRIGATION. GET IMMEDIATE MEDICAL ATTENTION.

INGESTION: INDUCE VOMITING - SEEK IMMEDIATE MEDICAL ATTENTION.

MOST IMPORTANT SYMPTOMS AND EFFECTS, ACUTE AND DELAYED:

THIS PRODUCT IS NOT HAZARDOUS AS DEFINED BY HAZARDOUS COMMUNICATION STANDARD. HOWEVER, AS WITH ALL CHEMICAL; HANDLE WITH CARE, AVOID EYE AND SKIN CONTACT, AVOID INHALATION OF DUSTS OR VAPORS. WASH THOROUGHLY AFTER HANDLING. KEEP CONTAINERS CLOSED.

SECTION 5. FIRE-FIGHTING MEASURES

EXTINGUISHING MEDIA:

WATER, DRY CHEMICAL, CARBON DIOXIDE, FOAM.

SPECIAL HAZARDS ARISING FROM SUBSTANCE OR MEDIA:

FIREFIGHTERS SHOULD BE EQUIPPED WITH SELF-CONTAINED BREATHING APPARATUS TO GUARD AGAINST POTENTIALLY TOXIC AND IRRITATING FUMES. AVOID DUSTING. DUST CAN FORM EXPLOSIVE MIXTURES WITH AIR.

PROTECTION/ADVICE FOR FIREFIGHTER(S):

BE EQUIPPED WITH SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING.

SECTION 6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS:

REMOVE PERSONS FROM DANGER AREA.

ENVIRONMENTAL PRECAUTIONS:

AVOID ANY UNCONTROLLED RELEASE OF MATERIAL. DO NOT EMPTY INTO DRAINS OR THE AQUATIC ENVIRONMENT.

EMERGENCY PROCEDURES:

NO ADDITIONAL INFORMATION

METHODS AND MATERIALS FOR CONTAMINANT AND CLEANING UP:

WHERE SPILLS ARE POSSIBLE, A COMPREHENSIVE SPILL RESPONSE PLAN SHOULD BE DEVELOPED AND IMPLEMENTED. AVOID ANY UNCONTROLLED RELEASE OF MATERIAL.

UTILIZE RECOMMENDED PROTECTIVE CLOTHING AND EQUIPMENT (SEE SECTION 8). SPILLS SHOULD BE SWEEPED UP USING AN ABSORBENT DUST CONTROL PRODUCT AND PLACED IN CONTAINERS. SPILL AREA CAN BE WASHED WITH WATER. COLLECT WATER FOR APPROVED DISPOSAL. IN THE EVENT OF UNCONTROLLED RELEASE OF THIS MATERIAL, THE USER SHOULD DETERMINE IF THE RELEASE IS REPORTABLE UNDER APPLICABLE LAWS AND REGULATIONS.

SECTION 7. HANDLING AND STORAGE

PRECAUTIONS FOR SAFE HANDLING:

HANDLE WITH CARE. AVOID OVER EXPOSURE. USE NIOSH/OSHA APPROVED RESPIRATOR, WORK GLOVES, AND CLOTHING. WASH AFTER HANDLING. SENSITIVE INDIVIDUALS MAY EXPERIENCE RESPIRATORY ALLERGIES. MAY CAUSE SKIN IRRITATION. USE WITH LOCAL VENTILATION.

CONDITIONS FOR SAFE STORAGE, INCLUDING ANY INCOMPATIBILITIES:

USE PROCESS ENCLOSURES, LOCAL EXHAUST VENTILATION OR OTHER ENGINEERING CONTROLS TO KEEP AIRBORNE LEVELS BELOW RECOMMENDED EXPOSURE LIMITS.

KEEP AWAY FROM HEAT. KEEP AWAY FROM SOURCES OF IGNITION.

KEEP AWAY FROM STRONG OXIDIZING AND REDUCING AGENTS.

SPECIFIC END USES:

FELT TIP, MARKER INKS, WATER BASED COATINGS AND LEAK DETECTION

SECTION 8. EXPOSURE CONTROLS /PERSONAL PROTECTION

CONTROL PARAMETERS:

INGREDIENTS WITH LIMIT VALUES THAT REQUIRE MONITORING AT THE WORKPLACE - NOT REQUIRED

EXPOSURE CONTROLS:

APPROPRIATE ENGINEERING CONTROLS - THE USUAL PRECAUTIONARY MEASURES ARE TO BE ADHERED TO WHEN HANDLING CHEMICALS.

PERSONAL PROTECTIVE EQUIPMENT:



HAND PROTECTION

EYE PROTECTION

SKIN AND BODY

WEAR IMPERMEABLE RUBBER OR PLASTIC GLOVES

TIGHTLY SEALED SAFETY GOGGLES OR FULL FACE SIDE SHIELDS.

APRON, COVERALLS AND NON-LEATHER SOLED WORK SHOES.

WASH DYE CONTAMINATED CLOTHES AND SKIN WITH MILD SOAP AND DETERGENTS.

RESPIRATORY

HYGIENE MEASURES

WEAR OSHA/NIOSH APPROVED DUST MASK/RESPIRATOR

HANDLE IN ACCORDANCE WITH GOOD INDUSTRIAL HYGIENE AND SAFETY PRACTICES. WASH HANDS AFTER HANDLING MATERIAL.

OTHER PROTECTION

DELUGE SAFETY SHOWER AND EYE WASH STATION SHOULD BE LOCATED NEAR WORK AREA.

SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES

INFORMATION ON BASIC PHYSICAL AND CHEMICAL PROPERTIES :

APPEARANCE, COLOR, ODOR	YELLOW POWDER, NO ODOR
pH	8.0 - 9.0
MELTING POINT/FREEZING POINT	ND
INITIAL BOILING POINT/BOILING RANGE	0.00
FLASHPOINT	NORMALLY STABLE, NOT COMBUSTIBLE NOR FLAMMABLE
EVAPORATION RATE	NO DATA
FLAMMABILITY (SOLID,GAS)	NORMALLY STABLE, NOT COMBUSTIBLE NOR FLAMMABLE
UPPER EXPLOSIVE LIMITS	NA
LOWER EXPLOSIVE LIMITS	NA
VAPOR PRESSURE	NA
VAPOR DENSITY	NA
RELATIVE DENSITY	NA
SOLUBILITY IN WATER	SOLUBLE
PARTITION COEFFICIENT N-OCTANOL/WATER	NO DATA

AUTO-IGNITION TEMPERATURE	NO DATA
DECOMPOSITION TEMPERATURE	NO DATA
VISCOSITY, DYNAMIC	NO DATA
VISCOSITY, CINEMATIC	NO DATA
EXPLOSIVE PROPERTIES	N/A
OXIDIZING PROPERTIES	NA
OTHER INFORMATION	NA

SECTION 10. STABILITY AND REACTIVITY

CHEMICAL STABILITY	STABLE UNDER NORMAL STORAGE AND HANDLING CONDITIONS.
CONDITIONS TO AVOID	OXIDIZING & REDUCING AGENTS MAY DESTROY COLOR.
INCOMPATIBLE MATERIALS	OXIDIZING & REDUCING AGENTS MAY DESTROY COLOR.
HAZARDOUS DECOMPOSITION PRODUCTS	CO, CO ₂ , OXIDES OF NITROGEN AND OTHER POTENTIALLY TOXIC FUMES.

SECTION 11. TOXICOLOGICAL INFORMATION

TOXICOLOGICAL EFFECTS :

ORAL (ANIMAL)	GREATER THAN 7,000 MG/KG - RAT
DERMAL (ANIMAL)	NA
EFFECTS TO EYES (ANIMAL)	EYES - RABBIT, NOT IRRITATING
SKIN IRRITATION (ANIMAL)	SKIN - RABBIT, SLIGHT IRRITANT
SKIN CORROSION/IRRITATION	NOT CLASSIFIED
SERIOUS EYE DAMAGE/IRRITATION	CAUSES EYE IRRITATION
RESPIRATORY OR SKIN SENSITIZATION	NOT CLASSIFIED
GERM CELL MUTAGENICITY	NOT CLASSIFIED
CARCINOGENICITY	NOT CLASSIFIED
REPRODUCTIVE TOXICITY	NOT CLASSIFIED
SPECIFIC TARGET ORGAN TOXICITY (SINGLE EXPOSURE)	MAY CAUSE DROWSINESS OR DIZZINESS.
ASPIRATION HAZARD	NOT CLASSIFIED
INHALATION	MAY CAUSE DROWSINESS OR DIZZINESS.
EYE CONTACT	CAUSES SERIOUS EYE IRRITATION.
INGESTION	INGESTION MAY CAUSE NAUSEA, VOMITING AND DIARRHEA

SECTION 12. ECOLOGICAL INFORMATION

TOXICITY	NA
PERSISTENCE AND DEGRADABILITY	NA
BIOACCUMULATIVE POTENTIAL	NA
MOBILITY IN SOIL	LC-50 (LETHAL CONCENTRATION) UG = MICROGRAMS/LITER CHANNEL CATFISH - 2,267,000 UG/LITER RAINBOW TROUT - 1,372,000 UG/LITER BLUEGILL - 3,433,000 UG/LITER
OTHER ADVERSE EFFECTS	NA

SECTION 13. DISPOSAL CONSIDERATION

TSCA STATUS IN COMPLIANCE
E C CLASSIFICATION (67/548/EEC - 88/379/EEC) N/A
EINECS NUMBER
REACH CLASSIFICATION
R PHRASES
ADDITIONAL REGULATORY INFORMATION

SECTION 16. OTHER INFORMATION

INDICATION OF CHANGES:

NA

OTHER INFORMATION:

NA

GHS FULL TEXT PHRASES:

MAY BE HARMFUL IF INHALED	H333
CAUSES EYE IRRITATION	H320
CASUES MILD SKIN IRRITATION	H316

	HEALTH	FLAMMABILITY	REACTIVITY	PERSONAL PROT
H. M. I. S. CLASSIFICATION:	1	0	0	D
HMIS CODE: 4 - SEVERE HAZARD, 3 - SERIOUS HAZARD, 2 - MODERATE HAZARD, 1 - SLIGHT HAZARD, 0 - MINIMAL HAZARD				

SAFETY DATA SHEET (SDS)
REVISION DATE: 03/03/2016

ALL INFORMATION AND DATA APPEARING ON THIS SDS ARE BELIEVED TO BE RELIABLE AND ACCURATE. HOWEVER, IT IS THE USER' S RESPONSIBILITY TO DETERMINE THE SAFETY, TOXICITY, AND SUITABILITY FOR USE OF THE PRODUCT DESCRIBED. SINCE THE ACTUAL USE BY OTHERS IS BEYOND OUR CONTROL, NO GUARANTEE, EXPRESSED OR IMPLIED, IS MADE BY HUE CORPORATION. USER ASSUMES ALL RISK AND RESPONSIBILITY.

ATTACHMENT 3

SOPs Geoprobe® Screen Point 16 and Screen Point 22 Groundwater Samplers

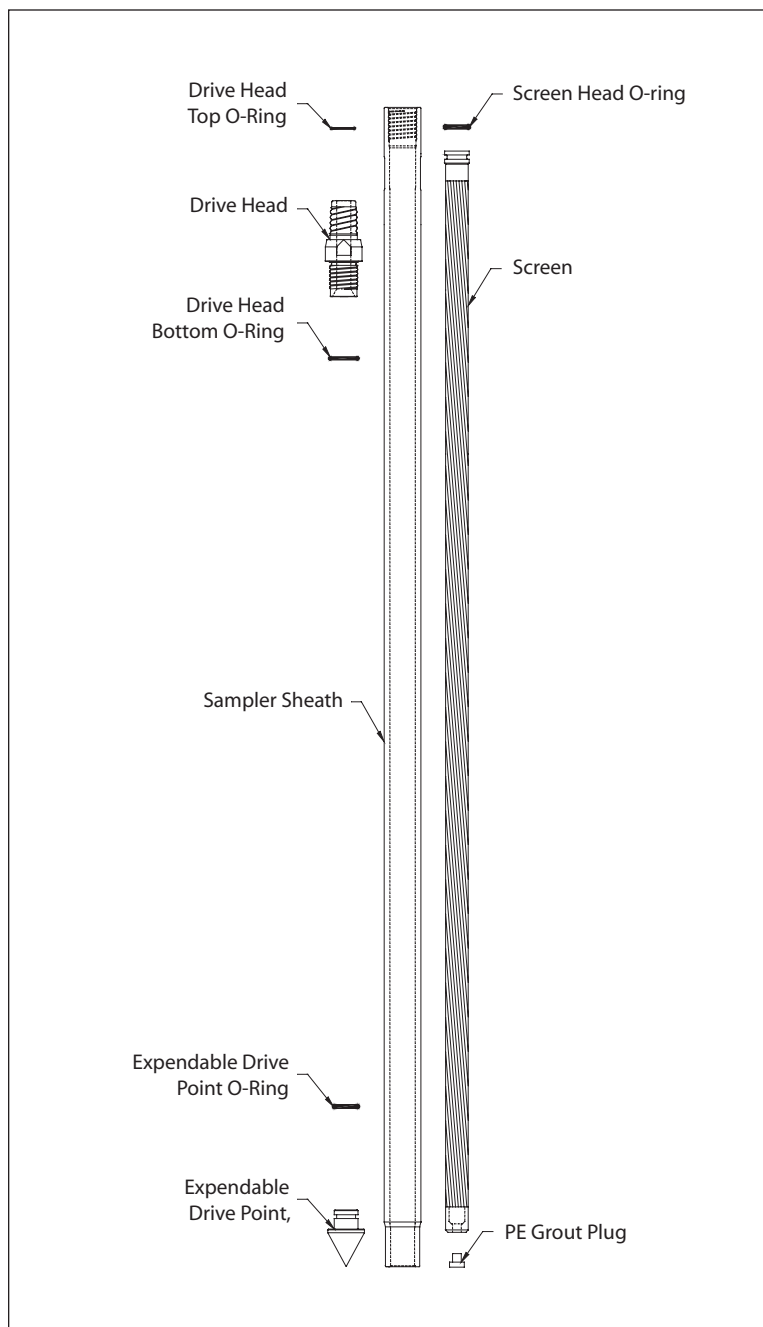


GEOPROBE® SCREEN POINT 16 GROUNDWATER SAMPLER

STANDARD OPERATING PROCEDURE

Technical Bulletin No. MK3142

PREPARED: November, 2006



GEOPROBE® SCREEN POINT 16 GROUNDWATER SAMPLER PARTS



**Geoprobe® and Geoprobe Systems®, Macro-Core® and Direct Image® are
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**Screen Point 16 Groundwater Sampler is manufactured
under U.S. Patent 5,612,498**

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1.0 OBJECTIVE

The objective of this procedure is to drive a sealed stainless steel or PVC screen to depth, deploy the screen, obtain a representative water sample from the screen interval, and grout the probe hole during abandonment. The Screen Point 16 Groundwater Sampler enables the operator to conduct abandonment grouting that meets American Society for Testing and Materials (ASTM) Method D 5299 requirements for decommissioning wells and borings for environmental activities (ASTM 1993).

2.0 BACKGROUND

2.1 Definitions

Geoprobe®: A brand name of high quality, hydraulically powered machines that utilize both static force and percussion to advance sampling and logging tools into the subsurface. The Geoprobe® brand name refers to both machines and tools manufactured by Geoprobe Systems®, Salina, Kansas. Geoprobe® tools are used to perform soil core and soil gas sampling, groundwater sampling and monitoring, soil conductivity and contaminant logging, grouting, and materials injection.

Screen Point 16 (SP16) Groundwater Sampler: A direct push device consisting of a PVC or stainless steel screen that is driven to depth within a sealed, steel sheath and then deployed for the collection of representative groundwater samples. The assembled SP16 Sampler is approximately 51.5 inches (1308 mm) long with an OD of 1.625 inches (41 mm). Upon deployment, up to 41 inches (1041 mm) of screen can be exposed to the formation. The Screen Point 16 Groundwater Sampler is designed for use with 1.5-inch probe rods and machines equipped with the more powerful GH60 Hydraulic Hammer. Operators with GH40 Series hammers may chose to use this sampler in soils where driving is difficult.

Rod Grip Pull System: An attachment mounted on the hydraulic hammer of a direct push machine which makes it possible to retract the tool string with extension rods or flexible tubing protruding from the top of the probe rods. The Rod Grip Pull System includes a pull block with rod grip jaws that are bolted directly to the machine. A removable handle assembly straddles the tool string while hooking onto the pull block to effectively grip the probe rods as the hammer is raised. A separate handle assembly is required for each probe rod diameter.

2.2 Discussion

In this procedure, the assembled Screen Point 16 Groundwater Sampler (Fig. 2.1A) is threaded onto the leading end of a Geoprobe® probe rod and advanced into the subsurface with a Geoprobe® direct push machine. Additional probe rods are added incrementally and advanced until the desired sampling interval is reached. While the sampler is advanced to depth, O-ring seals at each rod joint, the drive head, and the expendable drive point provide a watertight system. This system eliminates the threat of formation fluids entering the screen before deployment and assures sample integrity.

Once at the desired sampling interval, extension rods are sent downhole until the leading rod contacts the bottom of the sampler screen. The tool string is then retracted approximately 44 inches (1118 mm) while the screen is held in place with the extension rods (Fig. 2.1B). As the tool string is retracted, the expendable point is released from the sampler sheath. The tool string and sheath may be retracted the full length of the screen or as little as a few inches if a small sampling interval is desired.

There are three types of screens that can be used in the Screen Point 16 Groundwater Sampler. Two of the these, a stainless steel screen with a standard slot size of 0.004 inches (0.10 mm) and a PVC screen with a standard slot size of 0.010 inches (0.25 mm), are recovered with the tool string after sampling. The third screen is also manufactured from PVC with a standard slot size of 0.010 inches (0.25 mm), but is designed to be left downhole when sampling is complete. This disposable screen has an exposed screen length of approximately 43 inches (1092 mm). The two screens that are recovered with the sampler both have an exposed screen length of approximately 41 inches (1041 mm).

(continued on following page)

An O-ring on the head of the stainless steel screens maintains a seal at the top of the screen. As a result, any liquid entering the sampler during screen deployment must first pass through the screen. PVC screens do not require an O-ring because the tolerance between the screen head and sampler sheath is near that of the screen slot size.

The screens are constructed such that flexible tubing, a mini-bailer, or a small-diameter bladder pump can be inserted into the screen cavity. This makes direct sampling possible from anywhere within the saturated zone. A removable plug in the lower end of the screens allows the user to grout as the sampler is extracted for further use.

Groundwater samples can be obtained in a number of ways. A common method utilizes polyethylene (TB25L) or Teflon® (TB25T) tubing and a Check Valve Assembly (GW4210). The check valve (with check ball) is attached to one end of the tubing and inserted down the casing until it is immersed in groundwater. Water is pumped through the tubing and to the ground surface by oscillating the tubing up and down.

An alternative means of collecting groundwater samples is to attach a peristaltic or vacuum pump to the tubing. This method is limited in that water can be pumped to the surface from a maximum depth of approximately 26 feet (8 m). Another technique for groundwater sampling is to use a stainless steel Mini-Bailer Assembly (GW41). The mini-bailer is lowered down the inside of the casing below the water level where it fills with water and is then retrieved from the casing.

The latest option for collecting groundwater from the SP16 sampler is to utilize a Geoprobe® MB470 Series Mechanical Bladder Pump (MBP)*. The MBP may be used to meet requirements of the low-flow sampling protocol (Puls and Barcelona 1996, ASTM 2003). Through participation in a U.S. EPA Environmental Technology Verification study, it was confirmed that the MB470 can provide representative samples (EPA 2003).

**The Mechanical Bladder Pump is manufactured under U.S. Patent No. 6,877,965 issued April 12, 2005.*

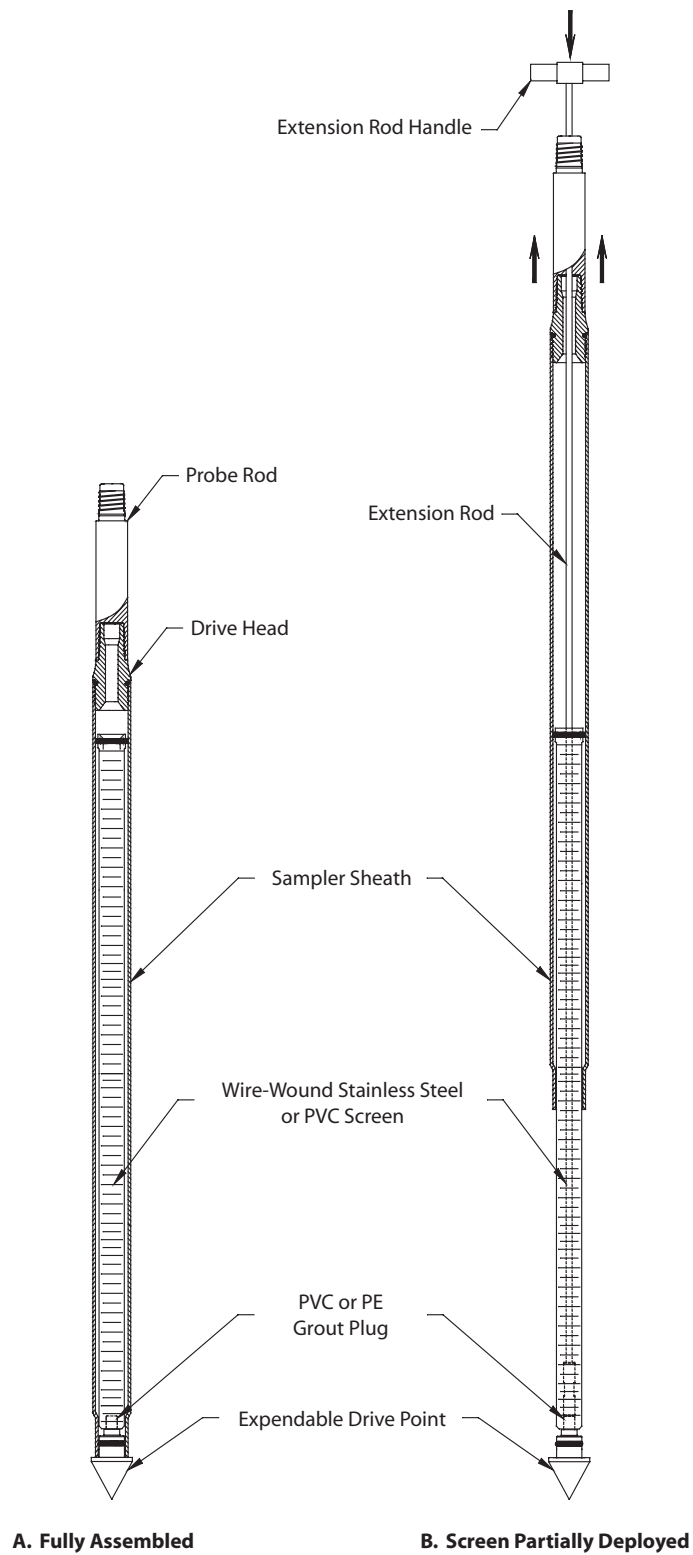


FIGURE 2.1
Screen Point 16 Groundwater Sampler

3.0 TOOLS AND EQUIPMENT

The following tools and equipment can be used to successfully recover representative groundwater samples with the Geoprobe® Screen Point 16 Groundwater Sampler. Refer to Figures 3.1 and 3.2 for identification of the specified parts. Tools are listed below for the most common SP16 / 1.5-inch probe rod configurations. Additional parts for optional rod sizes and accessories are listed in Appendix A.

SP16 Sampler Parts	Part Number
SP16 Sampler Sheath.....	15187
SP16 Drive Head, 0.5-inch bore, 1.5-inch rods*	18307
SP16 O-ring Service Kit, 1.5-inch rods (<i>includes 4 each of the O-ring packets below</i>)	15844
<i>O-rings for Top of SP16 Drive Head, 1.5-inch rods only (Pkt. of 25)</i>	15389
<i>O-rings for Bottom of SP16 Drive Head (Pkt. of 25)</i>	13196
<i>O-rings for GW1520 Screen Head (Pkt. of 25)</i>	GW1520R
<i>O-rings for SP16 Expendable Drive Point (Pkt. of 25)</i>	GW1555R
Screen, Wire-Wound Stainless Steel, 4-Slot*	GW1520
Grout Plugs, PE (Pkg. of 25)	GW1552K
Expendable Drive Points, steel, 1.625-inch OD (Pkg. of 25)*	GW1555K
Screen Point 16 Groundwater Sampler Kit, 1.5-inch Probe Rods (<i>includes 1 each of:</i> 15187, 18307, 15844, GW1520, GW1535, GW1540, GW1555K, and GW1552K)	15770

Probe Rods and Probe Rod Accessories	Part Number
Drive Cap, 1.5-inch probe rods, threadless, (for GH60 Hammer)	12787
Pull Cap, 1.5-inch probe rods	15090
Probe Rod, 1.5-inch x 60-inch*	11121

Extension Rods and Extension Rod Accessories	Part Number
Screen Push Adapter.....	GW1535
Grout Plug Push Adapter.....	GW1540
Extension Rod, 60-inch*	10073
Extension Rod Coupler.....	AT68
Extension Rod Handle	AT69
Extension Rod Jig.....	AT690
Extension Rod Quick Link Coupler, pin.....	AT695
Extension Rod Quick Link Coupler, box.....	AT696

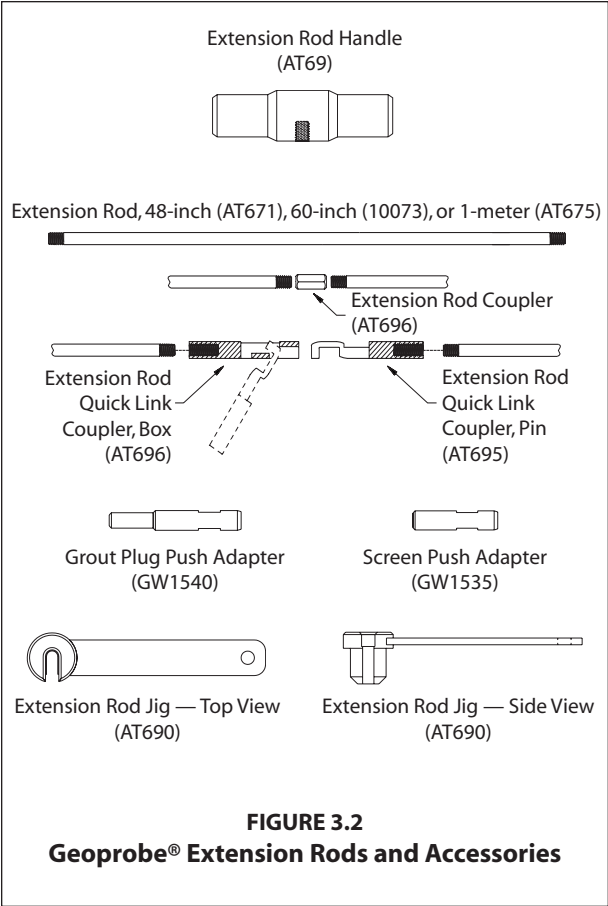
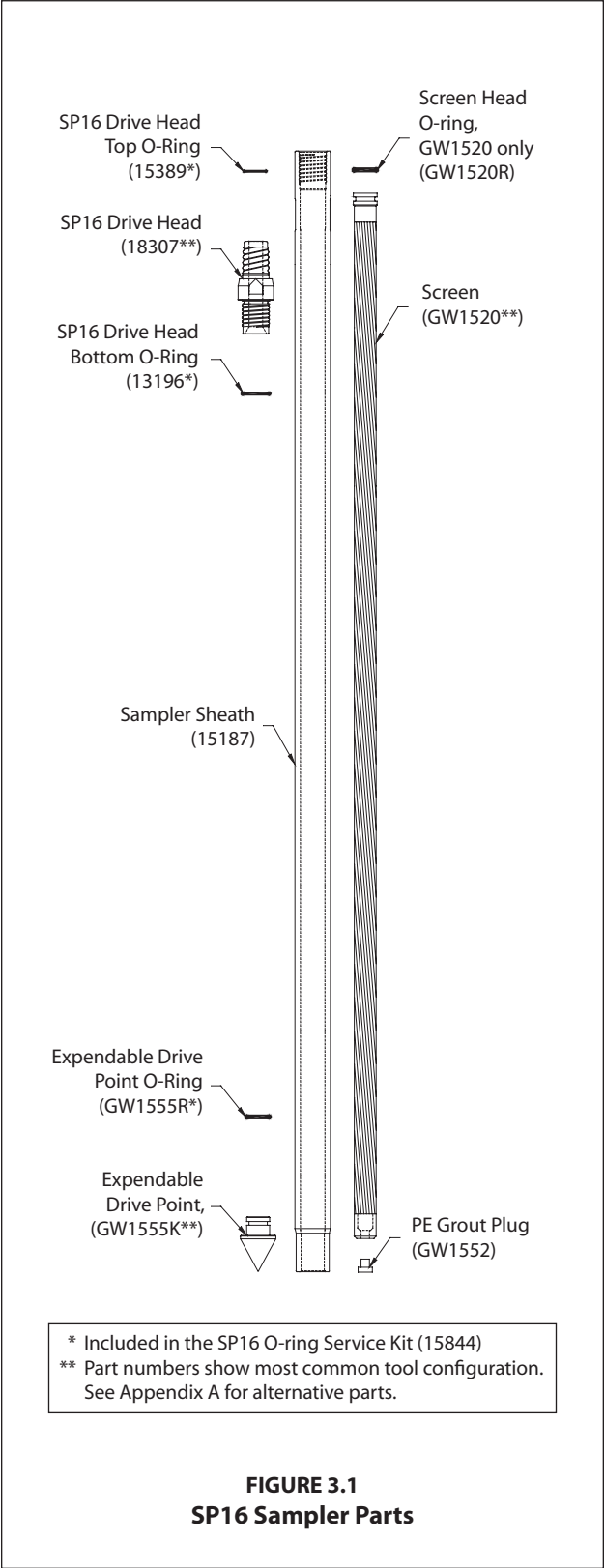
Grout Accessories	Part Number
Grout Nozzle, for 0.375-inch OD tubing	GW1545
High-Pressure Nylon Tubing, 0.375-inch OD / 0.25-inch ID, 100-ft. (30 m).....	11633
Grout Machine, self-contained*	GS1000
Grout System Accessories Package, 1.5-inch rods	GS1015

Groundwater Purging and Sampling Accessories	Part Number
Polyethylene Tubing, 0.375-inch OD, 500 ft. *	TB25L
Check Valve Assembly, 0.375-inch OD Tubing*	GW4210
Water Level Meter, 0.438-inch OD Probe, 100 ft. cable*	GW2000
Mechanical Bladder Pump**	MB470
Mini Bailer Assembly, stainless steel.....	GW41

Additional Tools	Part Number
Adjustable Wrench, 6.0-inch	FA200
Adjustable Wrench, 10.0-inch	FA201
Pipe Wrenches	NA

* See Appendix A for additional tooling options.

** Refer to the Standard Operating Procedure (SOP) for the Mechanical Bladder Pump (Technical Bulletin No. MK3013) for additional tooling needs.



4.0 OPERATION

4.1 Basic Operation

The SP16 sampler utilizes a stainless steel or PVC screen which is encased in an alloy steel sampler sheath. An expendable drive point is placed in the lower end of the sheath while a drive head is attached to the top. O-rings on the drive head and expendable point provide a watertight sheath which keeps contaminants out of the system as the sampler is driven to depth.

Once the sampling interval is reached, extension rods equipped with a screen push adapter are inserted down the ID of the probe rods. The tool string is then retracted up to 44 inches (1118 mm) while the screen is held in place with the extension rods. The system is now ready for groundwater sampling. When sampling is complete, a removable plug in the bottom of the screen allows for grouting below the sampler as the tool string is retrieved.

4.2 Sampler Options

The Screen Point 15 and Screen Point 16 Groundwater Samplers are nearly identical. Subtle differences in the design of the SP16 sampler make it more durable than the earlier SP15 system. Operators of GH60-equipped machines should always utilize SP16 tooling. Operators of machines equipped with GH40 Series hammers may also choose SP16 tooling when sampling in difficult probing conditions.

A 1.75-inch OD Expendable Drive Point (17066K) and Disposable PVC Screen (16089) provide two useful options for the SP16 sampler. The 1.75-inch drive point may be used when soil conditions make it difficult to remove the sampler after driving to depth. The disposable PVC screen may be left downhole after sampling (when regulations permit) to eliminate the time required for screen decontamination.

4.3 Decontamination

In order to collect representative groundwater samples, all sampler parts must be thoroughly cleaned before and after each use. Scrub all metal parts using a stiff brush and a nonphosphate soap solution. Steam cleaning may be substituted for hand-washing if available. Rinse with distilled water and allow to air-dry before assembly.

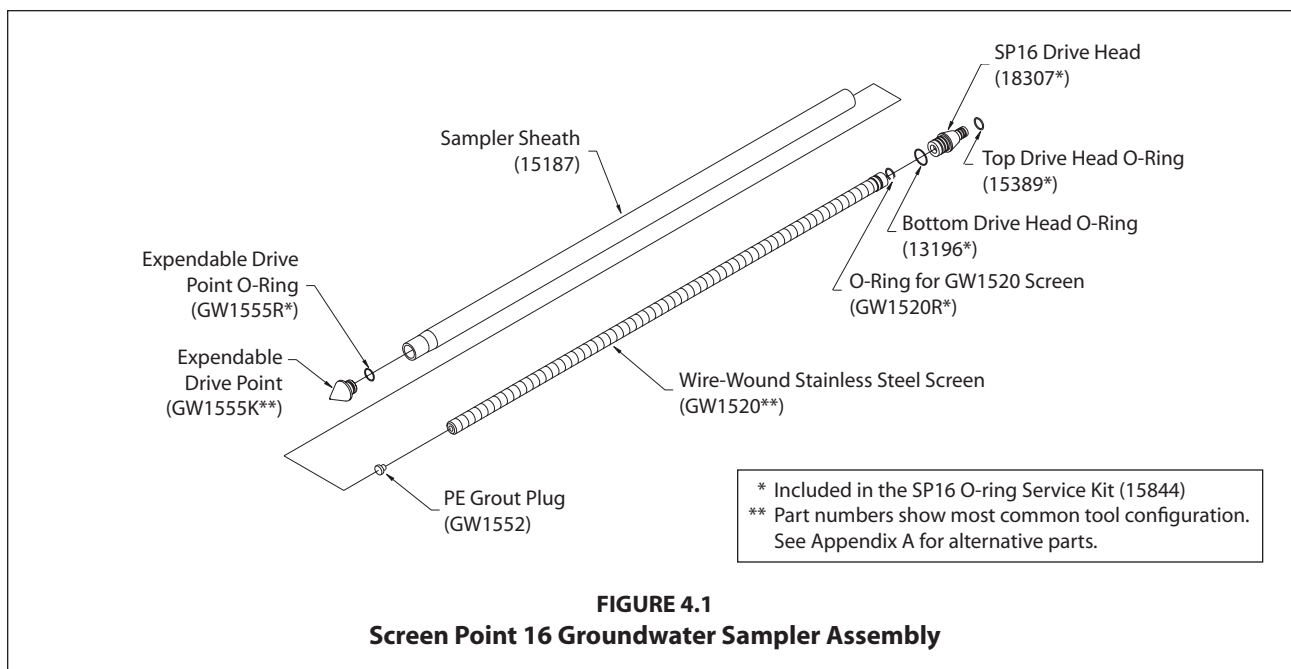
4.4 SP16 Sampler Assembly (Figure 4.1)

Part numbers are listed for a standard SP16 sampler using 1.5-inch probe rods. Refer to Page 6 for screen and drive head alternatives.

1. Place an O-ring on a steel expendable drive point (GW1555K). Firmly seat the expendable point in the necked end of a sampler sheath (15187).
2. Install a PE Grout Plug (GW1552) in the bottom end of a Wire-wound Stainless Steel Screen (GW1520). Place a GW1520R O-ring in the groove on the top end of the screen.
3. Slide the screen inside of the sampler sheath with the grout plug toward the bottom of the sampler. Ensure that the expendable point was not displaced by the screen.
4. Install a bottom O-ring (13196) on a Drive Head (18307 or 15188). Thread the drive head into the sampler sheath using an adjustable wrench if necessary to ensure complete engagement of the threads. Attach a Drive Cap (12787 or 15590) to the top of the drive head.

NOTE: The 18307 drive head should be used whenever possible as the smaller 0.5-inch ID provides a greater material cross-section for increased durability.

Sampler assembly is complete.

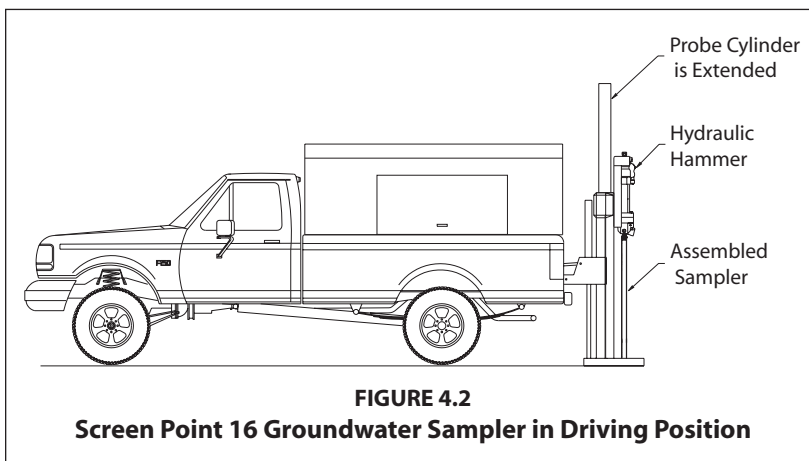


4.5 Advancing the SP16 Sampler

To provide adequate room for screen deployment with the Rod Grip Pull System, the probe derrick should be extended a little over halfway out of the carrier vehicle when positioning for operation.

1. Begin by placing the assembled sampler (Fig. 2.1.A) in the driving position beneath the hydraulic hammer of the direct push machine as shown in Figure 4.2.
2. Advance the sampler with the throttle control at slow speed for the first few feet to ensure that the sampler is aligned properly. Switch to fast speed for the remainder of the probe stroke.
3. Completely raise the hammer assembly. Remove the drive cap and place an O-ring in the top groove of the drive head. Distilled water may be used to lubricate the O-ring if needed.

Add a probe rod (length to be determined by operator) and reattach the drive cap to the rod string. Drive the sampler the entire length of the new rod with the throttle control at fast speed.



4. Repeat Step 3 until the desired sampling interval is reached. Approximately 12 inches (305 mm) of the last probe rod must extend above the ground surface to allow attachment of the puller assembly. A 12-inch (305 mm) rod may be added if the tool string is over-driven.
5. Remove the drive cap and retract the probe derrick away from the tool string.

4.6 Screen Deployment

1. Thread a screen push adapter (GW1535) on an extension rod of suitable length (AT671, 10073, or AT675). Attach a threaded coupler (AT68) to the other end of the extension rod. Lower the extension rod inside of the probe rod taking care not to drop it down the tool string. An extension rod jig (AT690) may be used to hold the rods.
2. Add extension rods until the adapter contacts the bottom of the screen. To speed up this step, it is recommended that Extension Rod Quick Links (AT695 and AT696) are used at every other rod joint.
3. Ensure that at least 48 inches (1219 mm) of extension rod protrudes from the probe rod. Thread an extension rod handle (AT69) on the top extension rod.
4. Maneuver the probe assembly into position for pulling.
5. Raise (pull) the tool string while physically holding the screen in place with the extension rods (Fig. 4.3.B). A slight knock with the extension rod string will help to dislodge the expendable point and start the screen moving inside the sheath.

Raise the hammer and tool string about 44 inches (1118 cm) if using a GW1520 or GW1530 screen. At this point the screen head will contact the necked portion of the sampler sheath (Fig. 4.3.C.) and the extension rods will rise with the probe rods. Use care when deploying a PVC screen so as not to break the screen when it contacts the bottom of the sampler sheath.

The Disposable Screen (16089) will extend completely out of the sheath if the tool string is raised more than 45 inches (1143 mm). Measure and mark this distance on the top extension rod to avoid losing the screen during deployment.

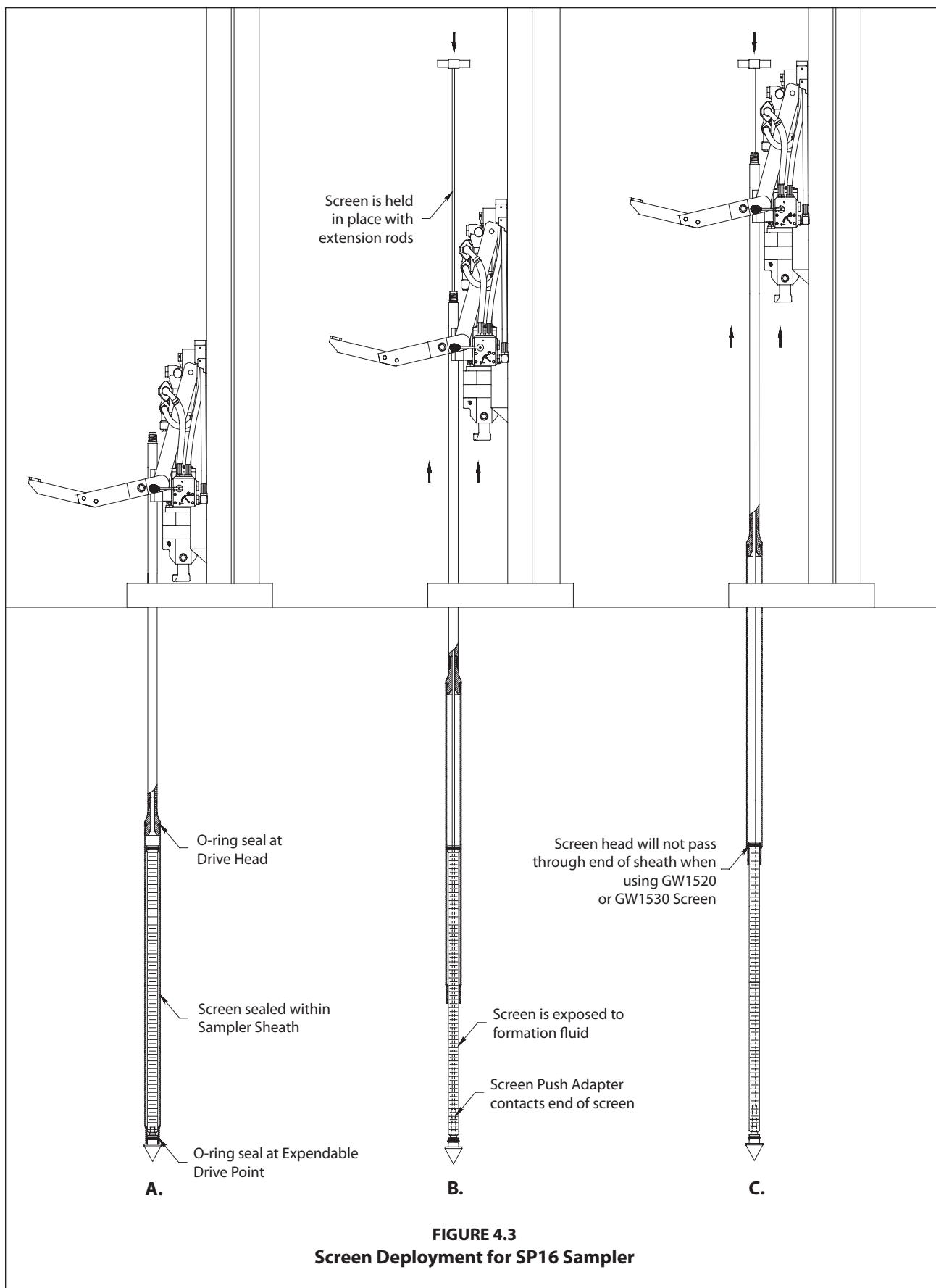
6. Remove the rod grip handle, lower the hammer assembly, and retract the probe derrick. Remove the top extension rod (with handle) and top probe rod. Finally, extract all extension rods.
7. Groundwater samples can now be collected with a mini-bailer, peristaltic or vacuum pump, tubing bottom check valve assembly, bladder pump, or other acceptable small diameter sampling device.

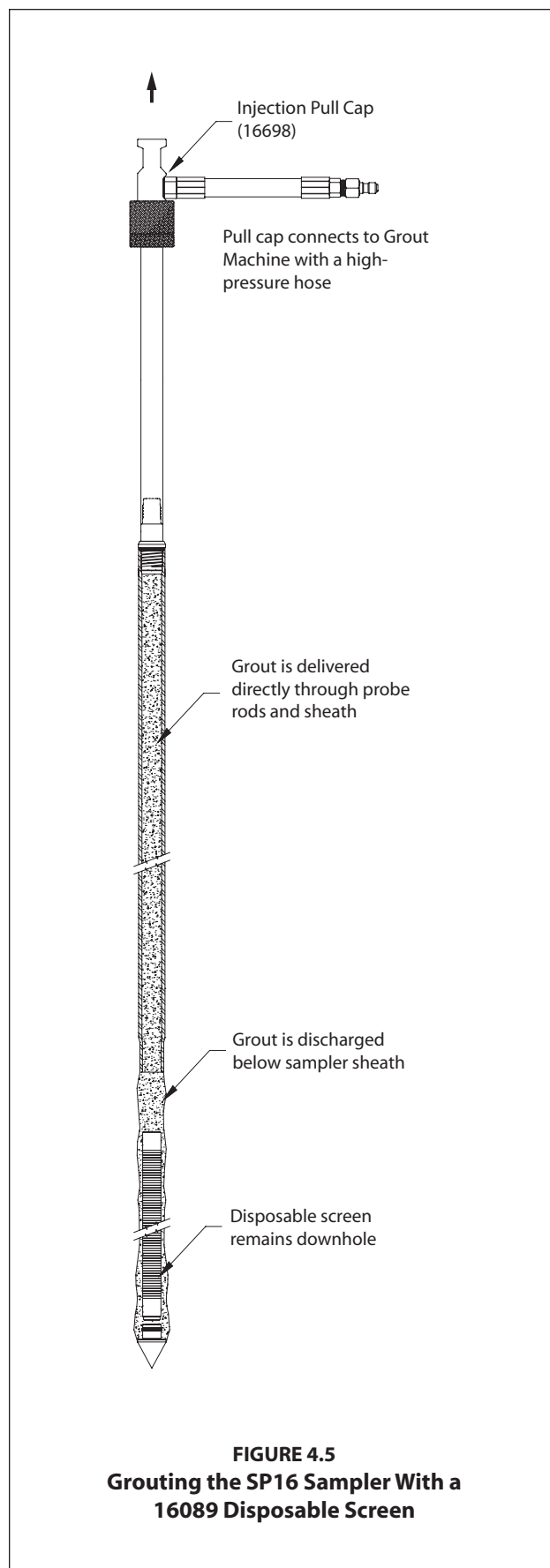
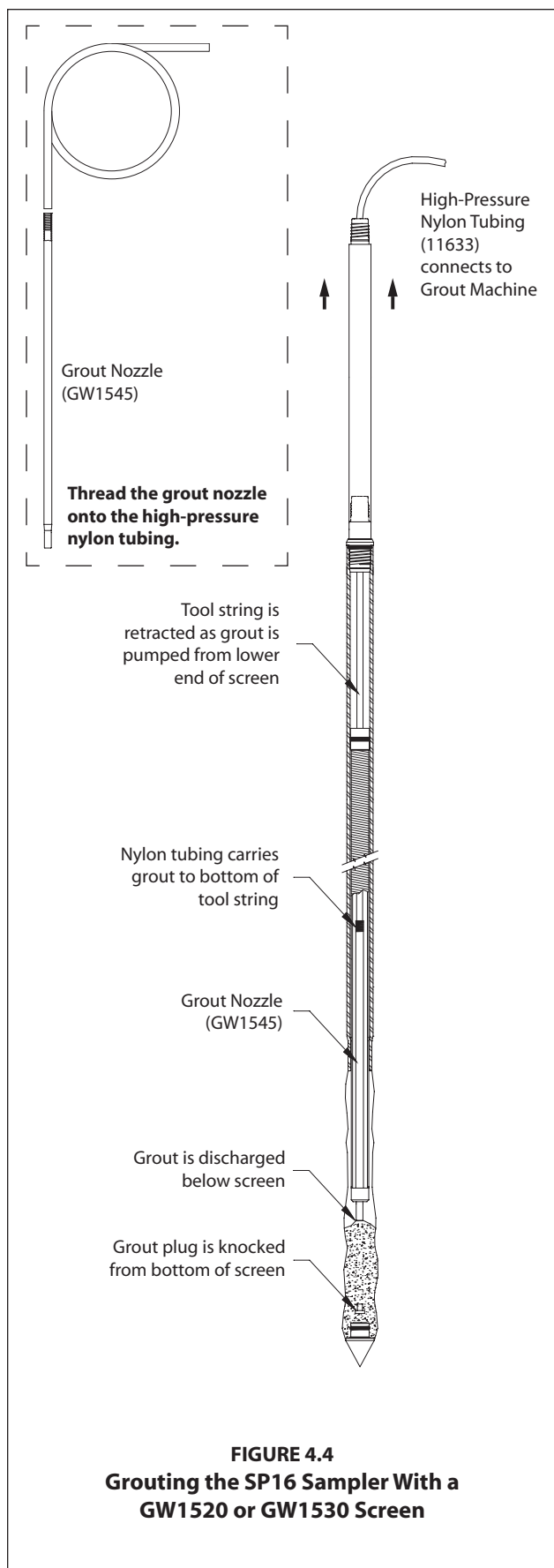
When inserting tubing or a bladder pump down the rod string, ensure that it enters the screen interval. The leading end of the tubing or bladder pump will sometimes catch at the screen head giving the illusion that the bottom of the screen has been reached. An up-and-down motion combined with rotation helps move the tubing or bladder pump past the lip and into the screen.

4.7 Abandonment Grouting for GW1520 and GW1530 Screens

The SP16 Sampler can meet ASTM D 5299 requirements for abandoning environmental wells or borings when grouting is conducted properly. A removable grout plug makes it possible to deploy tubing through the bottom of GW1520 and GW1530 screens. A GS500 or GS1000 Grout Machine is then used to pump grout into the open probe hole as the sampler is withdrawn. The following procedure is presented as an example only and should be modified to satisfy local abandonment grouting regulations.

1. Maneuver the probe assembly into position for pulling. Attach the rod grip puller to the top probe rod. Raise the tool string approximately 4 to 6 inches (102 to 152 cm) to allow removal of the grout plug.
2. Thread the Grout Plug Push Adapter (GW1540) onto an extension rod. Insert the adapter and extension rod inside the probe rod string. Add extension rods until the adapter contacts the grout plug at the bottom of the screen. Attach the handle to the top extension rod. When the extension rods are slightly raised and lowered, a relatively soft rebound should be felt as the adapter contacts the grout plug. This is especially true when using a PVC screen.





3. Place a mark on the extension rod even with the top of the probe rod. Apply downward pressure on the extension rods and push the grout plug out of the screen. The mark placed on the extension rod should now be below the top of the probe rod. Remove all extension rods.

Note: When working with a stainless steel screen, it may be necessary to raise and quickly lower the extension rods to jar the grout plug free. When the plug is successfully removed, a metal-on-metal sensation may be noted as the extension rods are gently "bounced" within the probe rods.

4. A Grout Nozzle (GW1545) is now connected to High-Pressure Nylon Tubing (11633) and inserted down through the probe rods to the bottom of the screen (Fig. 4.4). It may be necessary to pump a small amount of clean water through the tubing during deployment to jet out sediments that settled in the bottom of the screen. Resistance will sometimes be felt as the grout nozzle passes through the drive head. Rotate the tubing while moving it up-and-down to ensure that the nozzle has reached the bottom of the screen and is not hung up on the drive head.

Note: All probe rods remain strung on the tubing as the tool string is pulled. Provide extra tubing length to allow sufficient room to lay the rods on the ground as they are removed. An additional 20 feet is generally enough.

5. Operate the grout pump while pulling the first rod with the rod grip pull system. Coordinate pumping and pulling rates so that grout fills the void left by the sampler. After pulling the first rod, release the rod grip handle, fully lower the hammer, and regrip the tool string. Unthread the top probe and slide it over the tubing placing it on the ground near the end of the tubing.
6. Repeat Step 5 until the sampler is retrieved. Do not bend or kink the tubing when pulling and laying out the probe rods. Sharp bends create weak spots in the tubing which may burst when pumping grout. Remember to operate the grout pump only when pulling the rod string. The probe hole is thus filled with grout from the bottom up as the rods are extracted.
7. Promptly clean all probe rods and sampler parts before the grout sets up and clogs the equipment.

4.8 Abandonment Grouting for the 16089 Disposable Screen

ASTM D 5299 requirements can also be met for the SP16 samplers when using the 16089 disposable screen. Because the screen remains downhole after sampling, the operator may choose either to deliver grout to the bottom of the tool string with nylon tubing or pump grout directly through the probe rods using an Injection Pull Cap (16698). A GS500 or GS1000 Grout Machine is needed to pump grout into the open probe hole as the sampler is withdrawn. The following procedure is presented as an example only and should be modified to satisfy local abandonment grouting regulations.

1. Maneuver the probe assembly into position for pulling with the rod grip puller.
2. Thread the screen push adapter onto an extension rod. Insert the adapter and extension rod inside the probe rod string. Add extension rods until the adapter contacts the bottom of the screen. Attach the handle to the top extension rod.
3. The disposable screen must be extended at least 46 inches (1168 mm) to clear the bottom of the sampler sheath. Considering the length of screen deployed in Section 4.7, determine the remaining distance required to fully extend the screen from the sheath. Mark this distance on the top extension rod.
4. Pull the tool string up to the mark on the top extension rod while holding the disposable screen in place.

The screen is now fully deployed and the sampler is ready for abandonment grouting. Apply grout to the bottom of the tool string during retrieval using either flexible tubing (as described in Section 4.7) or an injection pull cap (Fig. 4.5). This section continues with a description of grouting with a pull cap.

5. Remove the rod grip handle and maneuver the probe assembly directly over the tool string. Thread an Injection Pull Cap (16698) onto the top probe rod and close the hammer pull latch over the top of the pull cap.
6. Connect the pull cap to a Geoprobe® grout machine using a high-pressure grout hose.
7. Operate the pump to fill the entire tool string with grout. When a sufficient volume has been pumped to fill the tool string, begin pulling the rods and sampler while continuing to operate the grout pump. Considering the known pump volume and sampler cross-section, time tooling withdrawal to slightly "overpump" grout into the subsurface. This will ensure that all voids are filled during sampler retrieval.

The grouting process can lubricate the probe hole sufficiently to cause the tool string to slide back downhole when disconnected from the pull cap. Prevent this by withdrawing the tool string with the rod grip puller while maintaining a connection to the grout machine with the pull cap.

4.9 Retrieving the Screen Point 16 Sampler

If grouting is not required, the Screen Point 16 Sampler can be retrieved by pulling the probe rods as with most other Geoprobe® applications. The Rod Grip Pull System should be used for this process as it allows the operator to remove rods without completely releasing the tool string. This avoids having the probe rods fall back downhole when released during the pulling procedure. A standard Pull Cap (15164) may still be used if preferred. Refer to the Owner's Manual for your Geoprobe® direct push machine for specific instructions on pulling the tool string.

5.0 REFERENCES

- American Society of Testing and Materials (ASTM), 2003. D6771-02 Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations. ASTM, West Conshohocken, PA. (www.astm.org)
- American Society of Testing and Materials (ASTM), 1993. ASTM 5299 *Standard Guide for Decommissioning of Groundwater Wells, Vadose Zone Monitoring Devices, Boreholes, and Other Devices for Environmental Activities*. ASTM West Conshohocken, PA. (www.astm.org)
- Geoprobe Systems®, 2003, *Tools Catalog, V.6*.
- Geoprobe Systems®, 2006, *Model MB470 Mechanical Bladder Pump Standard Operating Procedure (SOP), Technical Bulletin No. MK3013*.
- Puls, Robert W., and Michael J. Barcelona, 1996. Ground Water Issue: Low-Flow (Minimal Drawdown) Ground Water Sampling Procedures. EPA/540/S-95/504. April.
- U.S. Environmental Protection Agency (EPA), 2003. Environmental Technology Verification Report: Geoprobe Inc., Mechanical Bladder Pump Model MB470. Office of Research and Development, Washington, D.C. EPA/600R-03/086. August.

Appendix A ALTERNATIVE PARTS

The following parts are available to meet unique soil conditions. See section 3.0 for a complete listing of the common tool configurations for the Geoprobe® Screen Point 16 Groundwater Sampler.

SP16 Sampler Parts and Accessories.....	Part Number
SP16 Drive Head, 0.625-inch bore, 1.5-inch rods.....	15188
Expendable Drive Points, aluminum, 1.625-inch OD (Pkg. of 25).....	GW1555ALK
Expendable Drive Points, steel, 1.75-inch OD (Pkg. of 25).....	17066K
Screen, PVC, 10-Slot	GW1530
Screen, Disposable, PVC, 10-Slot	16089

Groundwater Purging and Sampling Accessories	Part Number
Polyethylene Tubing, 0.25-inch OD, 500 ft.....	TB17L
Polyethylene Tubing, 0.5-inch OD, 500 ft.....	TB37L
Polyethylene Tubing, 0.625-inch OD, 50 ft.....	TB50L
Check Valve Assembly, 0.25-inch OD Tubing.....	GW4240
Check Valve Assembly, 0.5-inch OD Tubing	GW4220
Check Valve Assembly, 0.625-inch OD Tubing	GW4230
Water Level Meter, 0.375-inch OD Probe, 100-ft. cable	GW2001
Water Level Meter, 0.438-inch OD Probe, 200-ft. cable	GW2002
Water Level Meter, 0.375-inch OD Probe, 200-ft. cable	GW2003
Water Level Meter, 0.438-inch OD Probe, 30-m cable	GW2005
Water Level Meter, 0.438-inch OD Probe, 60-m cable	GW2007
Water Level Meter, 0.375-inch OD Probe, 60-m cable	GE2008

Grouting Accessories.....	Part Number
Grout Machine, auxiliary-powered	GS500

Probe Rods, Extension Rods, and Accessories	Part Number
Probe Rod, 1.5-inch x 1-meter	17899
Probe Rod, 1.5-inch x 48-inch.....	13359
Drive Cap, 1.5-inch rods (for GH40 Series Hammer)	15590
Rod Grip Pull Handle, 1.5-inch Probe Rods (for GH40 Series Hammer)	GH1555
Extension Rod, 48-inch.....	AT671
Extension Rod, 1-meter	AT675

Equipment and tool specifications, including weights, dimensions, materials, and operating specifications included in this brochure are subject to change without notice. Where specifications are critical to your application, please consult Geoprobe Systems®.



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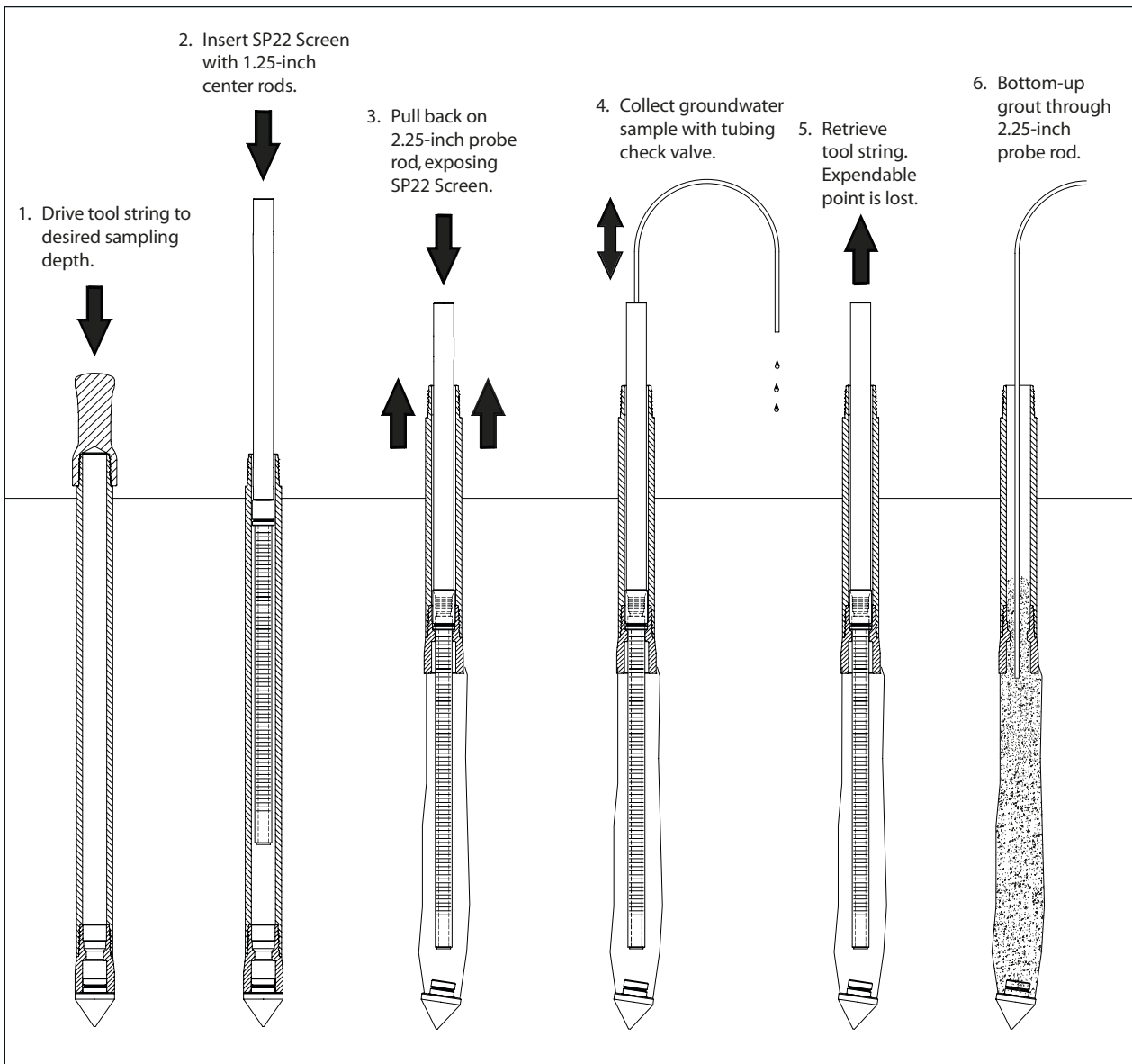
601 N. Broadway • Salina, Kansas 67401
1-800-GEOPROBE (1-800-436-7762) • Fax (785) 825-2097
www.geoprobe.com

GEOPROBE® SCREEN POINT 22 GROUNDWATER SAMPLER

STANDARD OPERATING PROCEDURE

Technical Bulletin No. MK3173

PREPARED: April 2010



OPERATION OF THE GEOPROBE® SCREEN POINT 22 GROUNDWATER SAMPLER



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**Screen Point 22 Groundwater Sampler is manufactured
under U.S. Patent 5,612,498**

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1.0 OBJECTIVE

The objective of this procedure is to deploy a stainless steel or PVC screen at depth, obtain a representative water sample from the screen interval, and grout the probe hole during abandonment. The Screen Point 22 Groundwater Sampler enables the operator to conduct abandonment grouting that meets American Society for Testing and Materials (ASTM) Method D 5299 requirements for decommissioning wells and borings for environmental activities (ASTM 1993).

2.0 BACKGROUND

2.1 Definitions

Geoprobe®: A brand name of high quality, hydraulically powered machines that utilize static force and percussion or rotation to advance sampling and logging tools into the subsurface. The Geoprobe® brand name refers to both machines and tools manufactured by Geoprobe Systems®, Salina, Kansas. Geoprobe® tools are used to perform activities such as soil core and soil gas sampling, groundwater sampling and monitoring, soil conductivity and contaminant logging, grouting, and materials injection.

Screen Point 22 (SP22) Groundwater Sampler: A direct push device consisting of a PVC or stainless steel screen that is lowered (post-run) to depth within a sealed string of steel probe rods and then deployed for the collection of representative groundwater samples. Upon deployment, up to 48 inches (1219 mm) of screen can be exposed to the formation. There is also an optional 12-inch screen that can be used. The Screen Point 22 Groundwater Sampler is designed for use with 2.25-inch probe rods and machines equipped with the more powerful GH60 and GH80 series hydraulic hammers. Operators with GH40 series hammers may choose to use this sampler in soils where driving is easier.

Rod Grip Pull System: An attachment mounted on the hydraulic hammer of a direct push machine which makes it possible to retract the tool string with probe rods or flexible tubing protruding from the top of the probe rods. The Rod Grip Pull System includes a pull block with rod grip jaws that are bolted directly to the machine. A removable handle assembly straddles the tool string while hooking onto the pull block to effectively grip the probe rods as the hammer is raised. A separate handle assembly is required for each probe rod diameter.

2.2 Discussion (Fig. 2.1)

In this procedure, 2.25-inch probe rods are advanced into the subsurface with a Geoprobe® subsurface machine (Fig. 2.1, Step 1). While the tool string is advanced to depth, O-ring seals at each rod joint, the expendable point holder, and the expendable drive point provide a watertight system. This eliminates the threat of formation fluids entering the screen before deployment and assures sample integrity.

Once the leading end of the 2.25-inch probe rods reaches the desired sampling interval, an SP22 screen is lowered to the bottom of the rods using a string of either 1.25-inch outside diameter (OD) light-weight center rods, 1.25-inch probe rods, or 0.75-inch schedule 40 flush-thread PVC riser (Fig. 2.1, Step 2). The 2.25-inch rods are then retracted while the SP22 screen is held in place with the 1.25-inch rods or PVC riser (Fig. 2.1, Step 3). As the 2.25-inch tool string is retracted, the expendable point is released from the expendable point holder. The tool string and expendable point holder may be retracted the full length of the screen or as little as a few inches if a small sampling interval is desired.

The SP22 Sampler can also be used with the Geoprobe® DT22 system. (Fig. 2.2)

(continued on following page)

Expendable Drive Points

The SP22 system utilizes an SP22 Expendable Point Holder (33764) and standard 2.45-inch (62-mm) OD steel Expendable Drive Points for 2.25-inch probe rods (AT2015K). Extended Shank Expendable Drive Points (19442) are available for soft soil conditions where standard points may be advanced out of the point holder during percussion. A third option is to use a part number 43128 SP22 Expendable Point Holder along with 1.625-inch (41-mm) steel Expendable Drive Points (GW1555K). These smaller drive points are more economical to purchase and ship, but must not be used with GH80 Series Hydraulic Hammers as they may not stay seated during percussion.

Screens

Two types of screens have been developed for use in the Screen Point 22 Groundwater Sampler - a stainless steel screen with a standard slot size of 0.004 inches (0.10 mm) and a PVC screen with a standard slot size of 0.010 inches (0.25 mm). These screens are available in nominal 48- and 12-inch lengths. Effective screen lengths for the 48- and 12-inch PVC screens are 48 inches (1219 mm) and 12 inches (305 mm), while 48- and 12-inch stainless steel screens have effective screen lengths of 43 inches (1092 mm) and 14 inches (356 mm) respectively. Both types of screens are recovered with the tool string after sampling.

The SP22 PVC Screen Head Adapter (37871) provides yet another screen option for the SP22 sampler. Using this adapter, a section of slotted 0.75-inch Schedule 40 PVC pipe may be lowered through the 2.25-inch probe rods using a string of flush-threaded 0.75-inch Schedule 40 PVC Riser. An SP22 PVC Screen Plug (38968) is installed in the leading end of the slotted pipe prior to use. The slotted pipe may be cut and the screen plug installed to provide custom screen lengths.

An O-ring is located at the top of each stainless screen and on the screen adapters. When a screen is deployed, this O-ring maintains a seal between the top of the screen and the inner wall of the probe rods or expendable point holder as indicated in Figure 2.1. As a result, any liquid entering the tool string must first pass through the screen.

Screens are constructed such that equipment can be inserted into the screen cavity for sample collection as noted in the following section and illustrated in Figure 2.1, Step 4. This makes direct sampling possible from anywhere within the saturated zone.

The inner rod string and screen are generally removed prior to grouting through the 2.25-inch rod string as shown in Figure 2.1, Steps 5-6. However, a removable plug in the lower end of the screens allows for grouting through flexible tubing extending out the bottom of the screen as with the Geoprobe® SP15/16 Groundwater Samplers if desired.

Sample Collection

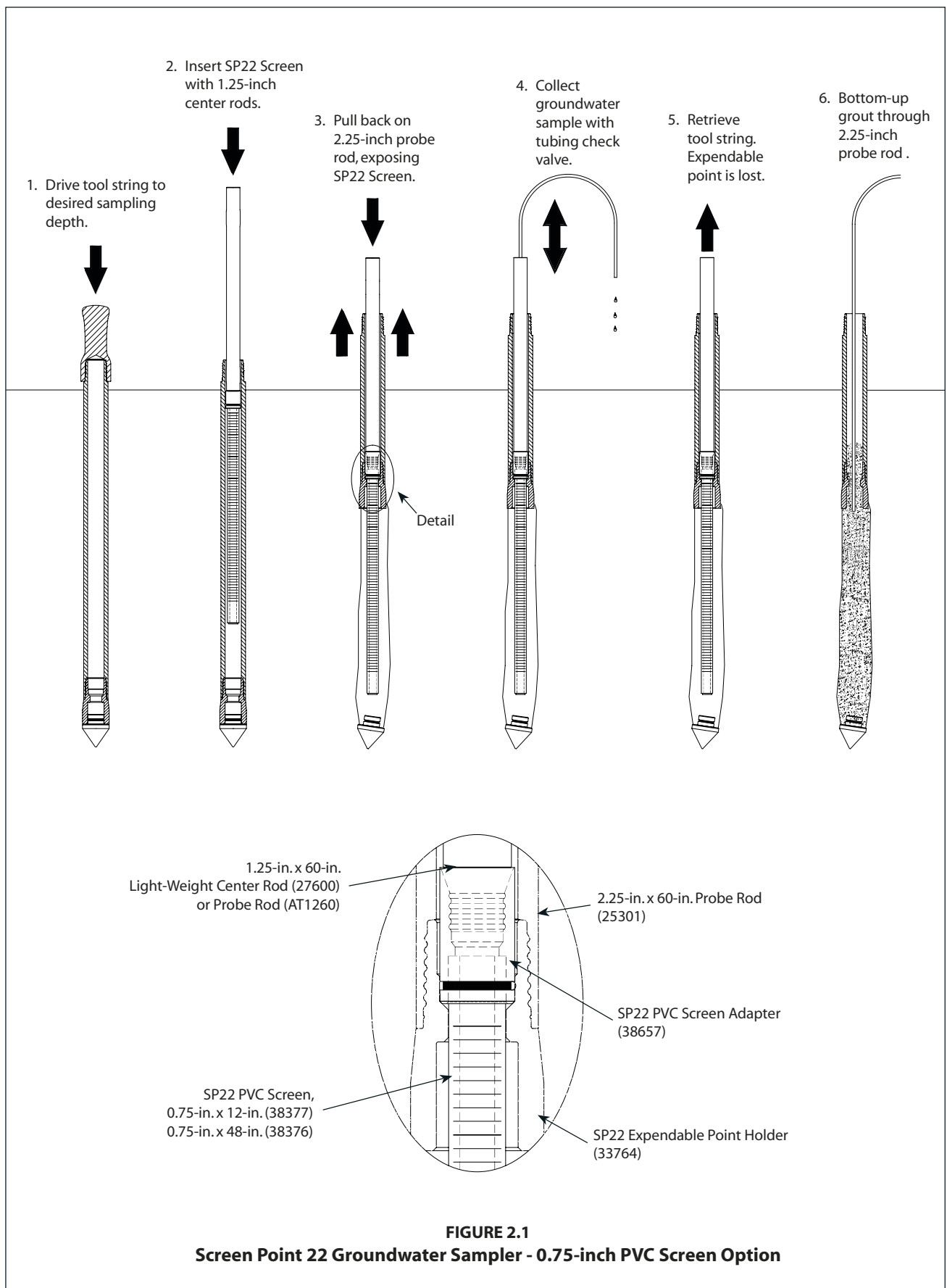
Groundwater samples can be obtained from the SP22 screen in a number of ways. A common method utilizes 0.375-inch OD polyethylene (TB25L) or Tefion® (TB25T) tubing and a check valve assembly. The check valve (with check ball) is attached to one end of the tubing and inserted down the casing until it is immersed in groundwater. Water is then pumped through the tubing and to the ground surface by oscillating the tubing up and down.

An SP22 Check Valve Assembly (37893) is recommended if sampling through 1.25-inch light-weight center rods. The SP22 Check Valve Assembly is approximately 20 inches long to enable it to pass through the stepped diameters at each rod joint that may cause problems for other, shorter check valves.

An alternative means of collecting groundwater samples is to attach a peristaltic or vacuum pump to tubing that is inserted through the inner rods to within the SP22 screen. This method is limited in that water can be pumped to the surface from a maximum depth of approximately 26 feet (8 m). Another technique for groundwater sampling is to use a stainless steel Mini-Bailer Assembly (GW41). The mini-bailer is lowered down the inside of the casing below the water level where it fills with water and is then retrieved from the casing.

The latest option for collecting groundwater from the SP22 Sampler is to utilize a Geoprobe® MB470 Series Mechanical Bladder Pump (MBP)*. The MBP may be used to meet requirements of the low-flow sampling protocol (Puls and Barcelona 1996, ASTM 2003). Through participation in a U.S. EPA Environmental Technology Verification study, it was confirmed that the MB470 can provide representative samples (EPA 2003).

**The Mechanical Bladder Pump is manufactured under U.S. Patent No. 6,877,965 issued April 12, 2005.*



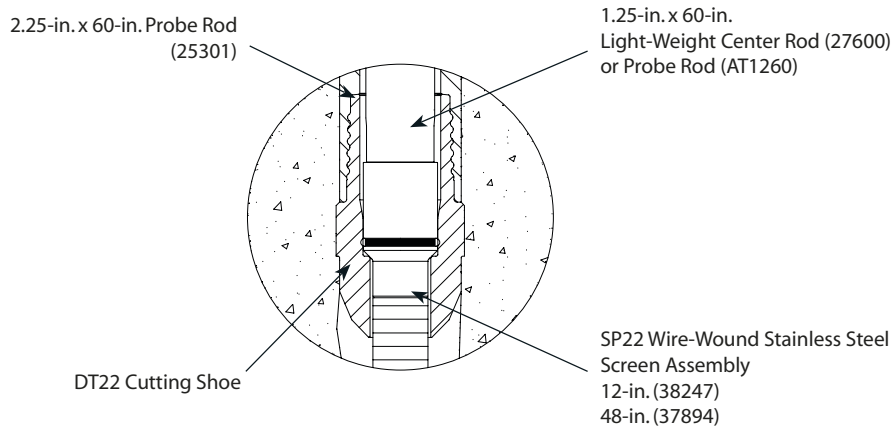
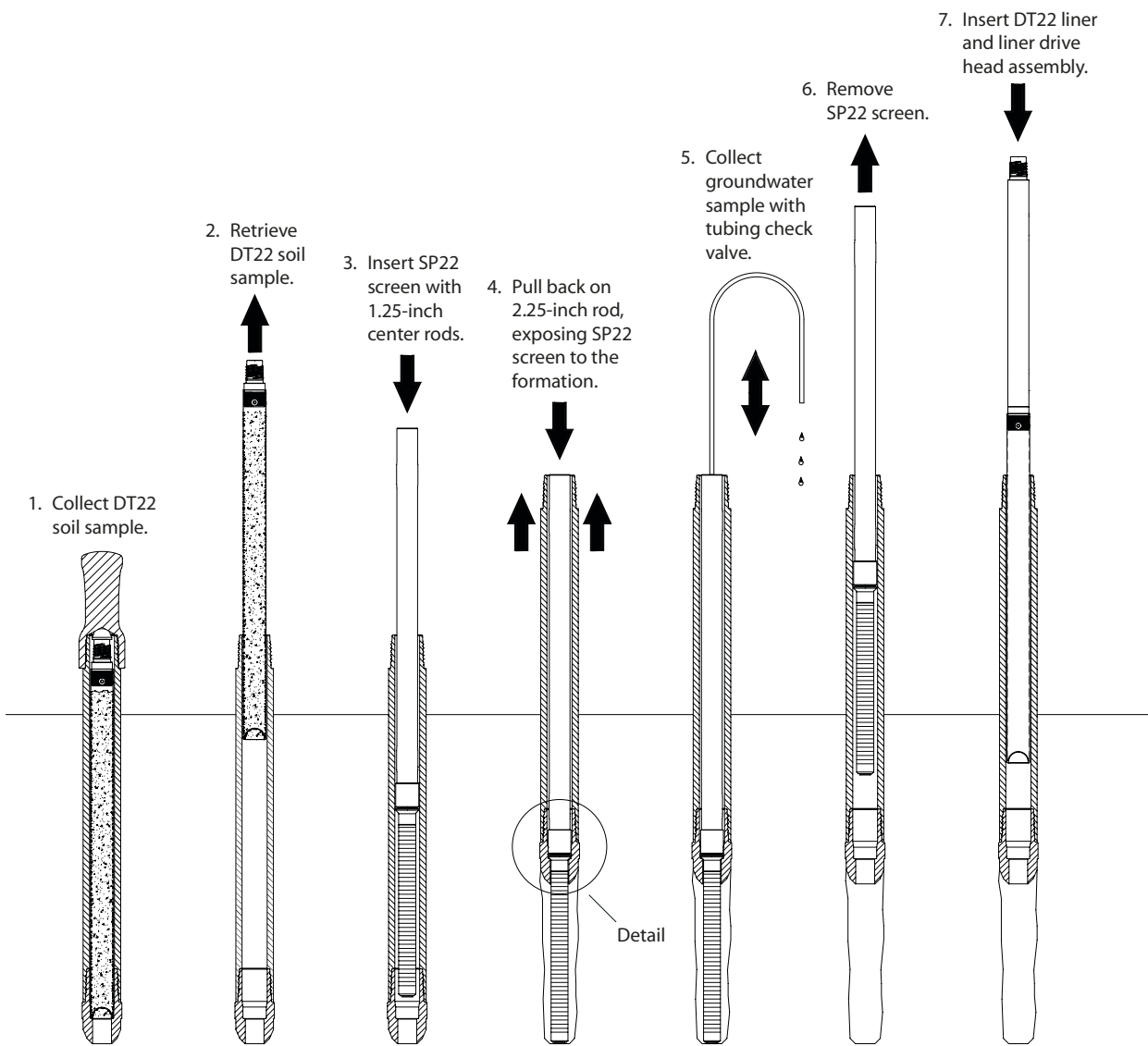


FIGURE 2.2
Screen Point 22 Groundwater Sampler Operation with DT22 Sampling System

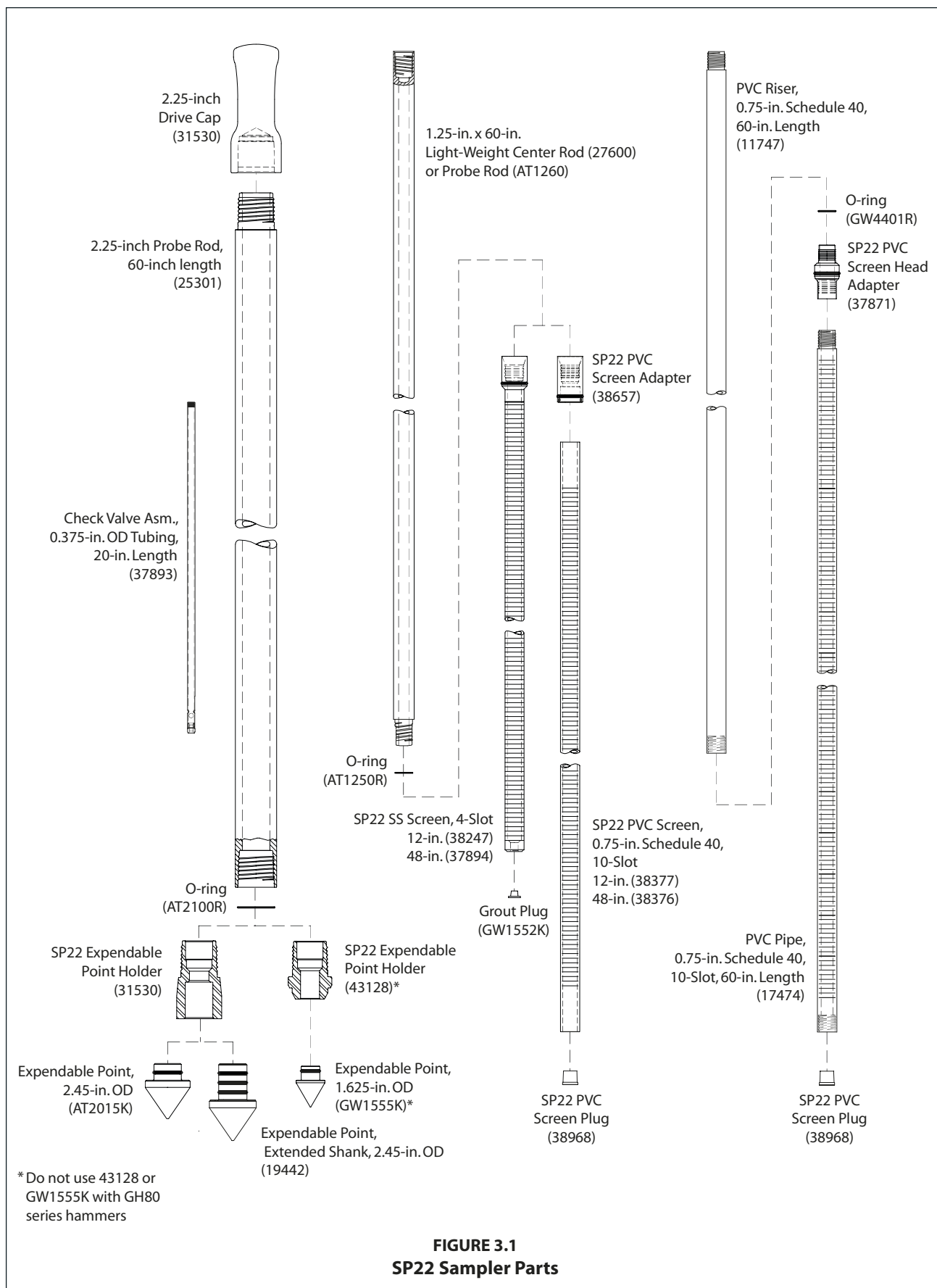
3.0 TOOLS AND EQUIPMENT

The following tools and equipment can be used to successfully recover representative groundwater samples with the Geoprobe® Screen Point 22 Groundwater Sampler. Refer to Figures 3.1 and 3.2 for identification of the specified parts. Tools are listed below for the most common SP22 / 2.25-inch probe rod configurations. Additional rod sizes and accessories are available. Contact Geoprobe Systems® for information regarding tools and equipment options.

SP22 Sampler Parts	Part Number
SP22 Screen, Wire-Wound Stainless Steel, 4-Slot (48-in.)	37894
SP22 Screen, Wire-Wound Stainless Steel, 4-Slot (12-in.)	38247
Grout Plugs, PE (Pkg. of 25)	GW1552K
SP22 Screen, PVC, 10-Slot, 0.75-in. x 48-in.	38376
<i>SP22 Screen, PVC, 10-Slot, 0.75-in. x 48-inch, Kit (includes 2 each of 38376 and 38429)</i>	<i>38664</i>
SP22 Screen, PVC, 10-Slot, 0.75-in. x 12-in.	38377
<i>SP22 Screen, PVC, 10-Slot 0.75-in. x 12-in., Kit (includes 2 each of 38377 and 38429)</i>	<i>38667</i>
SP22 PVC Screen Plug.....	38968
<i>SP22 PVC Screen Plug Kit (includes 10 of 38968)</i>	<i>38530</i>
SP22 PVC Screen Adapter, 0.75-in. PVC x 1.25-in. Probe Rod Box	38657
SP22 PVC Screen Head Adapter, 0.75-in. (for flush-threaded 0.75-in. Schedule 40 PVC)	37871
SP22 O-ring Kit (Pkg. of 10 O-rings for SP22 PVC screen adapters and stainless steel screens) ...	37853
O-rings, 0.75-in. PVC Riser (Pkg. of 25)	GW4401R
SP22 Expendable Point Holder, 2.25-in. Probe Rods, AT2045K and 19442 Points	33764
SP22 Expendable Point Holder, 2.25-in. Probe Rods, GW1555 Points*	43128
 Outer Casing (2.125-inch Probe Rods) and Inner Rod String	 Part Number
Probe Rod, 2.25-in. x 60-in.	25301
Expendable Drive Points, Steel, 2.45-in. OD (Pkg. of 25)	AT2015K
Expendable Drive Points, Steel, 2.45-in. OD, extended shank.....	19442
Expendable Points, steel, 1.625-in. OD (Pkg. of 25)*	GW1555K
Drive Cap, 2.25-in. Probe Rods, Threadless, (for GH60 and GH80 Series Hammers)	31530
O-Rings, 2.25-in. Probe Rods (Pkg. of 25)	AT2100R
Rod Grip Handle, 2.25-in. Probe Rods, (for GH60 and GH80 Series Hammers)	29385
Light-Weight Center Rod, 1.25-in. x 60-in.	27600
Probe Rod, 1.25-in. x 60-in.	AT1260
O-ring, 1.25-in. rods (Pkg. of 25)	AT1250R
Rod Grip Handle, 1.25/1.5-in. Rods, (for GH60 and GH80 Series Hammers)	15554
PVC Riser, 0.75-in. Schedule 40 x 60-inch	11747
PVC Pipe, 0.75-in. Schedule 40 x 60-inch, 10-Slot	17474
 Grout Accessories	 Part Number
High-Pressure Nylon Tubing, 0.375-in. OD / 0.25-in. ID, 100-ft. (30 m)	11633
Grout Machine, Auxiliary-Powered	GS2200
Grout System Accessories Package, 2.25-in. rods	GS1015
 Groundwater Purging and Sampling Accessories	 Part Number
Polyethylene Tubing, 0.375-in. OD, 500 ft.	TB25L
Check Valve Assembly, 0.375-in. OD Tubing x 20 in. Long	37893
Water Level Meter, 0.438-in. OD Probe, 100 ft. cable	GW2000
Mechanical Bladder Pump**	MB470
Mini Bailer Assembly, Stainless Steel	GW41

* Not for use with GH80 Series Hydraulic Hammers

** Refer to the Standard Operating Procedure (SOP) for the Mechanical Bladder Pump (Technical Bulletin No. MK3013) for additional tooling needs.



4.0 OPERATION

4.1 Basic Operation

The SP22 Sampler utilizes a stainless steel or PVC screen which is lowered (post-run) through an alloy steel 2.25-inch OD probe rod tool string. An expendable drive point is placed in an expendable point holder on the leading 2.25-inch probe rod prior to advancement (Fig. 4.1). This expendable point is removed and stays in the subsurface as the rods are pulled back to exposes the SP22 screen. O-rings on the probe rods, the expendable point holder, and the expendable drive point provide a watertight tool string which keeps contaminants out of the system as the 2.25-inch rods are driven to depth in preparation for installation of the SP22 screen.

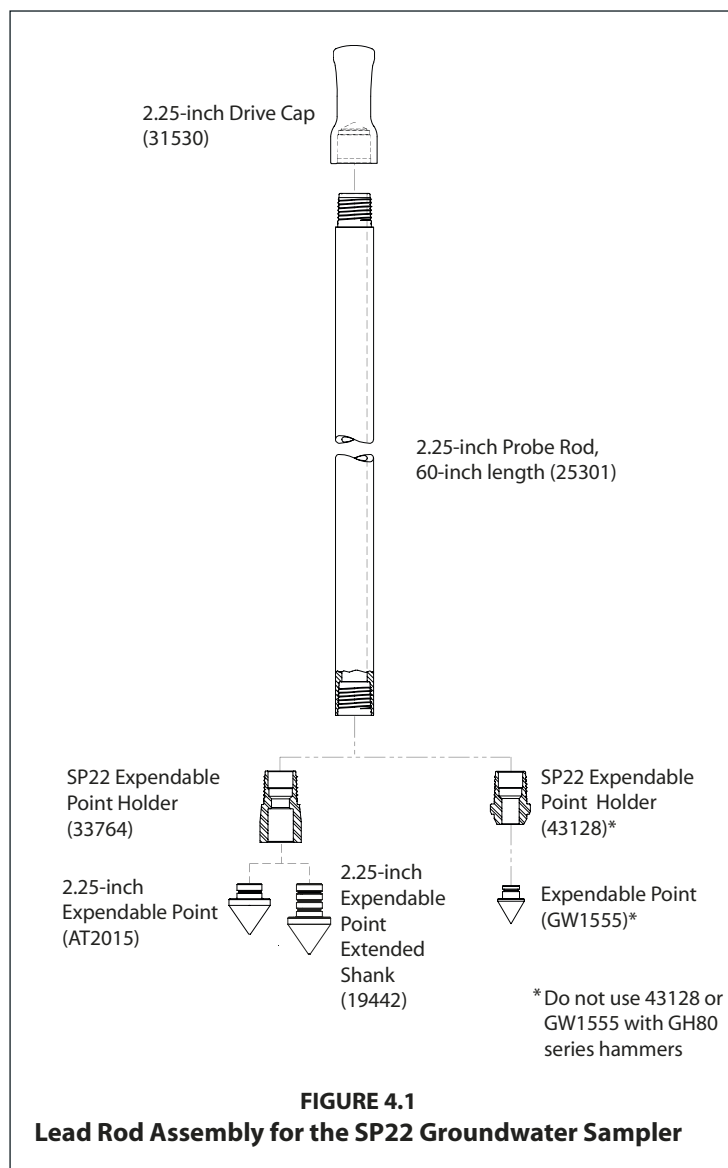
Once the sampling interval is reached with the 2.25-inch probe rods, the stainless steel or PVC screen is lowered through the rods using 1.25-inch probe rods, 1.25-inch light-weight center rods, or 0.75-inch PVC riser pipe. The 2.25-inch tool string is then retracted while the screen is held in place with the inner rods or riser. The system is now ready for groundwater sampling. When sampling is complete, the inner rods and screen are removed for grouting during retrieval or the 2.25-inch rods. Alternatively, a removable plug is located in the bottom of the screens to allow grouting directly through the inner tool string with high-pressure tubing during retrieval.

4.2 Decontamination

In order to collect representative groundwater samples, all sampler parts must be thoroughly cleaned before and after each use. Scrub all metal parts using a stiff brush and a nonphosphate soap solution. Steam cleaning may be substituted for hand-washing if available. Rinse with distilled water and allow to air-dry before assembly.

4.3 Lead Rod Assembly (Fig. 4.1)

1. Place an O-ring on the expendable point holder.
2. Thread expendable point holder into the 2.25-inch probe rod.
3. Place an O-ring on a steel expendable drive point.
4. Firmly seat the expendable point in the expendable point holder.
5. Place 2.25-inch Drive Cap (31530) on the top of the 2.25-inch probe rod. The lead rod assembly is now ready to be driven to depth.



4.4 Advancing the Tool String (Fig. 4.2, step 1)

To provide adequate room for screen deployment with the Rod Grip Pull System, the probe derrick should be extended a little over halfway out of the carrier vehicle when positioning for operation.

1. Drive first 2.25-inch probe rod (as assembled in section 4.3).
2. Advance the tool string at a slow speed for the first few feet to ensure that the string is aligned properly.
3. Completely raise the hammer assembly. Remove the drive cap and place an O-ring in the top groove of the driven probe rod. Distilled water may be used to lubricate the O-ring if needed.

Add a probe rod (length to be determined by operator) and reattach the drive cap to the rod string. Drive the tool string the entire length of the new rod.

4. Repeat Step 3 until the desired sampling interval is reached. Approximately 12 inches (305 mm) of the last probe rod must extend above the ground surface to allow attachment of the puller assembly. A 12-inch (305 mm) rod may be added if the tool string is over-driven.
5. Remove the drive cap and retract the probe derrick away from the tool string.

4.5 Screen Deployment (Fig 4.2, step 2 - 4)

1. Attach an SP22 stainless steel or PVC screen to a 1.25-inch probe rod, 1.25-inch light-weight center rod, or 0.75-inch flush-thread PVC riser using an SP22 PVC Screen Adapter (38657) or SP22 PVC Screen Head Adapter (37871) as shown in Figure 3.1. Note that the 38657 screen adapter is connected to the SP22 PVC screen using the setscrews provided with the adapter.

and lower it into the driven casing.

2. Lower the screen into the 2.25-inch probe rod casing and add rods or riser until the screen head contacts the bottom of the tool string.
3. Ensure that at least 48 inches (1219 mm) of rods or riser protrudes from the top 2.25-inch probe rod.
4. Maneuver the probe assembly into position for pulling.
5. Raise (pull) the outer 2.25-inch tool string while physically holding the screen in place with the inner 1.25-inch rods or 0.75-inch riser. A slight knock with the inner tool string will help to dislodge the expendable point and start the screen moving inside the probe rod.

Raise the hammer and outer tool string to expose the desired length of screen. The inner rods will begin raising with the outer rods when the screen adapter contacts the necked portion of the expendable point holder or DT22 Cutting Shoe. Use care when deploying a PVC screen so as not to break the screen when it contacts the expendable point.

6. Remove the rod grip handle, lower the hammer assembly, and retract the probe derrick. Remove the top 2.25-inch probe rod.
7. Groundwater samples can now be collected with a mini-bailer, peristaltic or vacuum pump, tubing bottom check valve assembly, bladder pump, or other acceptable small diameter sampling device.

When inserting tubing or a bladder pump down the rod string, ensure that it enters the screen interval. The leading end of the tubing or bladder pump will sometimes catch at the screen head giving the illusion that the bottom of the screen has been reached. An up-and-down motion combined with rotation helps move the tubing or bladder pump past the lip and into the screen.

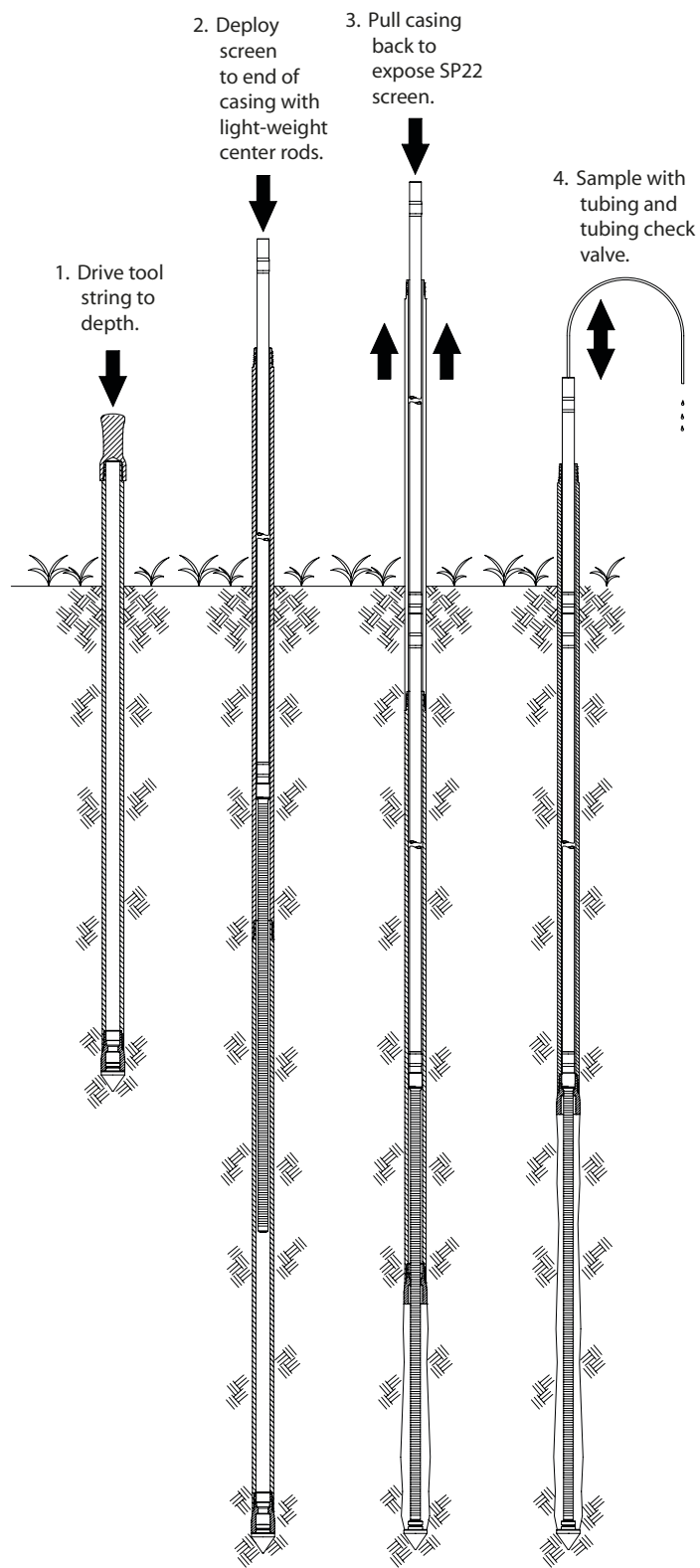


FIGURE 4.2
Screen Deployment for SP22 Sampler

4.6 Abandonment Grouting for SP22 Screens

The SP22 Sampler can meet ASTM D 5299 requirements for abandoning environmental wells or borings when grouting is conducted properly. A removable grout plug makes it possible to deploy tubing through the bottom of the SP22 screens, but the easiest method is to remove the inner string of rods; including the SP22 screen. A Grout Machine is then used to pump grout into the open probe hole as the outer casing is withdrawn. The following procedure is presented as an example only and should be modified to satisfy local abandonment grouting regulations. (Figure 4.3)

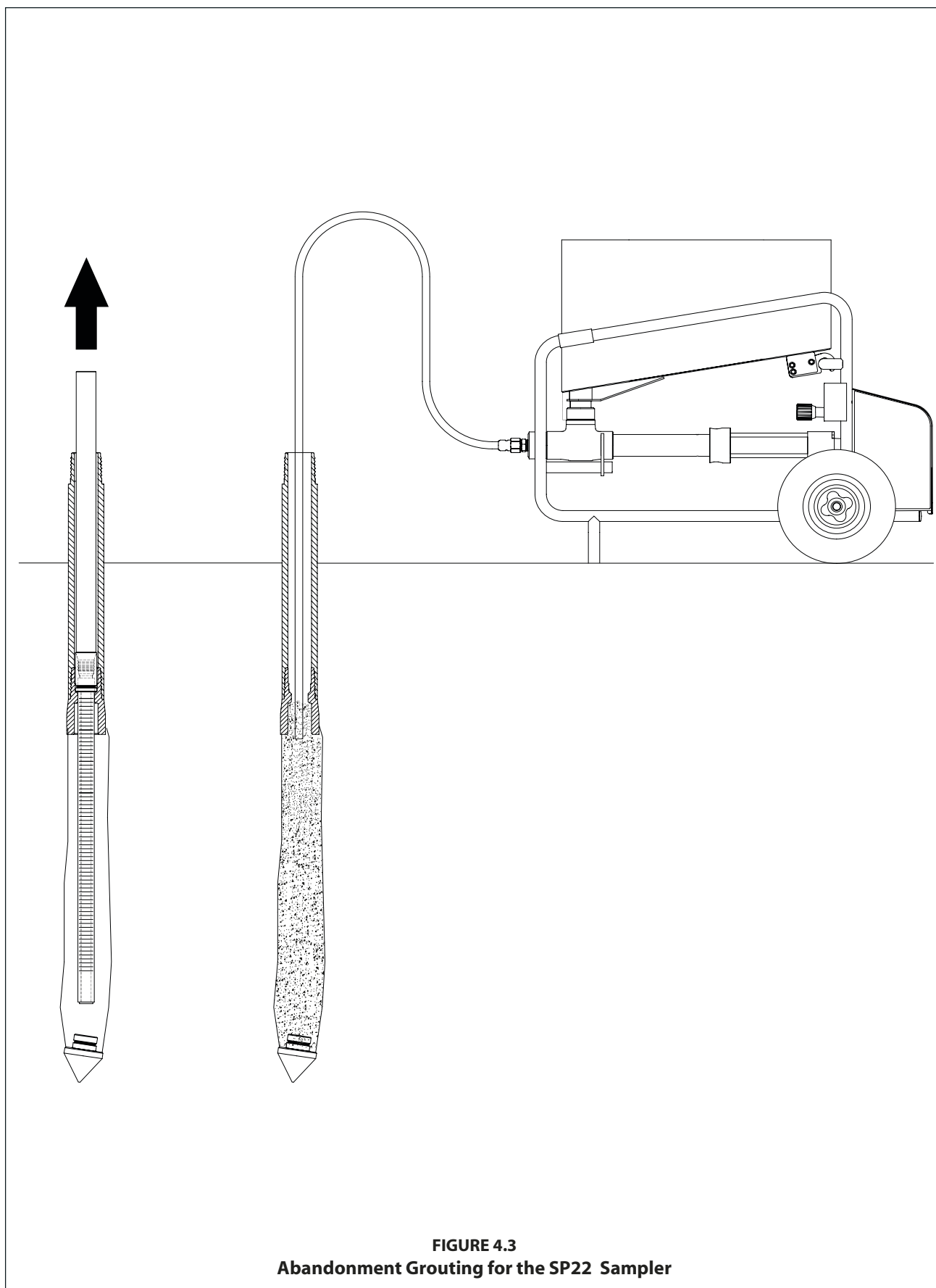
1. Maneuver the probe assembly into position for pulling.
2. High-Pressure Nylon Tubing (11633) is inserted down through the probe rods through the bottom of the expendable point holder (Fig. 4.3).

Note: All probe rods remain strung on the tubing as the tool string is pulled. Provide extra tubing length to allow sufficient room to lay the rods on the ground as they are removed. An additional 20 feet is generally enough.

3. Operate the grout pump while pulling the first rod with the rod grip pull system. Coordinate pumping and pulling rates so that grout fills the void left by the sampler. After pulling the first rod, release the rod grip handle, fully lower the hammer, and regrip the tool string. Unthread the top probe and slide it over the tubing placing it on the ground near the end of the tubing.
4. Repeat Step 5 until the tool string is retrieved. Do not bend or kink the tubing when pulling and laying out the probe rods. Sharp bends create weak spots in the tubing which may burst when pumping grout. Remember to operate the grout pump only when pulling the rod string. The probe hole is thus filled with grout from the bottom up as the rods are extracted.
5. Promptly clean all probe rods and sampler parts before the grout sets up and clogs the equipment.

4.7 Retrieving the Screen Point 22 Sampler

If grouting is not required, the Screen Point 22 Sampler can be retrieved by pulling the probe rods as with most other Geoprobe® applications. The Rod Grip Pull System should be used for this process as it allows the operator to remove rods without completely releasing the tool string. This avoids having the probe rods fall back downhole when released during the pulling procedure. A standard Pull Cap (33622) may still be used if preferred. Refer to the Owner's Manual for your Geoprobe® direct push machine for specific instructions on pulling the tool string.



5.0 REFERENCES

- American Society of Testing and Materials (ASTM), 2003. D6771-02 Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations. ASTM, West Conshocken, PA. (www.astm.org)
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- Geoprobe Systems®, 2003, *Tools Catalog, V.6*.
- Geoprobe Systems®, 2006, *Model MB470 Mechanical Bladder Pump Standard Operating Procedure (SOP), Technical Bulletin No. MK3013*.
- Puls, Robert W., and Michael J. Barcelona, 1996. Ground Water Issue: Low-Flow (Minimal Drawdown) Ground Water Sampling Procedures. EPA/540/S-95/504. April.
- U.S. Environmental Protection Agency (EPA), 2003. Environmental Technology Verification Report: Geoprobe Inc., Mechanical Bladder Pump Model MB470. Office of Research and Development, Washington, D.C. EPA/600R-03/086. August.

Equipment and tool specifications, including weights, dimensions, materials, and operating specifications included in this brochure are subject to change without notice. Where specifications are critical to your application, please consult Geoprobe Systems®.



A DIVISION OF KEJR, INC.

Corporate Headquarters

1835 Wall Street • Salina, Kansas 67401
1-800-GEOPROBE (1-800-436-7762) • Fax (785) 825-2097
www.geoprobe.com



Arcadis U.S., Inc.
630 Plaza Drive, Suite 200
Highlands Ranch
Colorado 80129
Phone: 720 344 3500
Fax: 720 344 3535
www.arcadis.com