October 11, 2019 Reference No. 058502

Mr. Zachary Sasnow
Corrective Action Project Manager
U.S. EPA, Region 5
77 West Jackson Boulevard DW-8J
Chicago, Illinois
U.S.A. 60604 3590

Dear Mr. Sasnow:

Re: Scope of Work to Complete Slag Area Incremental Soil Sampling
EPA ID #MID 041 793 340
RACER Nodular Facility - Saginaw, Michigan

This letter presents the Scope of Work (Scope) to complete Incremental Sampling Methodology (ISM) soil sampling of two slag areas present at Revitalizing Auto Communities Environmental Response Trust's (RACER) Former Nodular Industrial Lands (Site) in Saginaw, Michigan. This Scope was developed in accordance with the recommendations presented in the May 29, 2019 memo from GHD to the United States Environmental Protection Agency (U.S. EPA) entitled “response to U.S. EPA Comments from April 4, 2019 Site Meeting”.

The following figures, tables and Attachments were prepared in support of the Scope:

Figure 1	Proposed Slag Area ISM Sampling Locations
Table 3.1	Summary of Analytical Methods
Table 3.2	Soil Sample Parameter List
Table 3.3	Laboratory Precision and Accuracy Limits
Table 3.4	Summary of Sampling and Analysis Program
Table 3.5	Container, Preservation, Shipping, and Packaging Requirements
Attachment A	EGLE Incremental Sampling Methodology and Applications
Attachment B	Laboratory Standard Operating Procedures
Attachment C	Scope of Work Approval Form

1. Background

During the April 4, 2019 Site orientation with U.S. EPA, the parcels at the south end of IU-I (IU-I South) were inaccessible. As requested by U.S. EPA, GHD completed a Site inspection on April 11, 2019 and found the parcel to be heavily vegetated with miscellaneous trash and debris located throughout the

parcel. GHD also identified two areas with visible surficial slag; Area 1 (5,700 square feet [ft^2]; 0.13 acres) and Area 2 (16,000 ft^2; 0.37 acres), as presented on Figure 1.

2. Proposed Soil Sampling Activities

In order to evaluate the potential impacts due to the presence of slag, ISM will be implemented to characterize the surficial (0-6 inch) soil layer, consistent with *Interstate Technology Regulatory Council Incremental (ITRC) Technical and Regulatory Guidance Document on Incremental Sampling Methodology, 2012* and Michigan Department of Environment, Great Lakes and Energy (EGLE) *Incremental Sampling Methodology and Applications* (provided in Appendix A). Surficial soils samples will be collected to evaluate the likely worst case scenario which is contact with soil in direct contact with the weathered slag. Soil samples will be submitted under chain of custody procedures for laboratory analysis of Target Analyte List (TAL) Metals, Mercury and pH. GHD will treat each slag area presented in Figure 1 as a distinct Decision Unit (DU). Each DU will be divided into approximately 30 increments from which three replicate samples will be collected from each DU (6 total samples). Individual soil aliquots will be collected from the top 6 inches of soil and composited into three soil samples per DU.

2.1 Sample Collection Procedure

GHD will begin by establishing a grid over the two DUs, grid specifications are presented on Figure 1. Grid spacing has be evaluated to provide reasonable coverage of each DU. GHD will plan collect a minimum of 1 kilogram (2.2 pounds) of soil per sample to be submitted for laboratory sub-sampling and analysis.

Individual soil aliquots will be collected using a 0.75 inch diameter by 6 inch length hand coring device. Samples will be collected from the surficial 6 inches of soil at the locations presented in Figure 1. Core size has been determine to collect an approximate volume of 43.4 milliliters (ml) or approximately 42 g of dry soil per aliquot. Soil aliquots will be composited in the field.

Due to the course nature of slag, if individual sample locations are unable to produce sufficient soil recovery the individual sample location will be adjusted to a location where full recovery is possible (within 1 foot of the original location). If no such location is available in the vicinity of the proposed location, sufficient volume of material will be collected and screened using a #10 sieve (<2 mm particle size) to produce the required 43.4 ml of soil for that aliquot.

Replicate samples will be collected using the same approach.

3. Analytical Methods and Quality Control Samples

Eurofins TestAmerica will be the laboratory company supporting the environmental sample analysis for this project utilizing their facilities in North Canton, Ohio (Metals and pH).

3.1 Laboratory Analytical Methods

Soil samples will be analyzed for specified chemical constituents by the project laboratory. The methods that will be used for sample analyses are presented in Table 3.1. Specific analytes and targeted quantitation limits for chemical constituents are presented in Table 3.2. The precision and accuracy criteria for laboratory analyses are provided in Table 3.3.

3.2 Quality Assurance/Quality Control Procedures

3.2.1 Field Quality Assurance/Quality Controls

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, and field replicate sample to assess the overall precision of the sampling and analysis events. The specific QA/QC samples and collection frequency are summarized in Table 3.4. Equipment blank samples will be collected at a frequency of one per day, following sampling equipment decontamination procedures. Equipment blank 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. Equipment/Field blank samples will not be required for samples collected using pre-cleaned or pre-cleaned, disposable sampling equipment.

Two field replicate samples will be collected per DU. In addition, one laboratory duplicate will be collected from one of the field replicate samples during the laboratory sub-sample process to assess precision of laboratory soil processing. Field replicate 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 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 container, preservation, shipping, and packaging requirements presented in Table 3.5.

3.2.2 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 B. The acceptance criteria for these QC checks will be consistent with the analytical methods provided in Table 3.1 and applicable laboratory SOP.

3.2.3 Laboratory Report Deliverables

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

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

3.3 Data Review and Validation

Upon receipt of the final data packages from the project laboratory the data will be reviewed and validated. 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 evaluating the QA/QC data based on the applicable review criteria specified in "National Functional Guidelines for Inorganic Superfund Methods Data Review", EPA 540-R-2017-001, January 2017. 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.

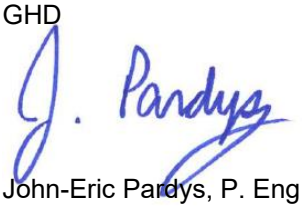
4. Reporting

Following the completion of the soil sampling, a report will be prepared summarizing the completed field program and the analytical results. The report will be submitted to U.S. EPA and will include recommendations on next steps, if required. In accordance with GHD's ISO 9001:2008 accreditation, all records will be stored in GHD's controlled filing system for a minimum 10-years including a backup and retention program.

Should you have any questions, please do not hesitate to call.

Yours truly,

GHD



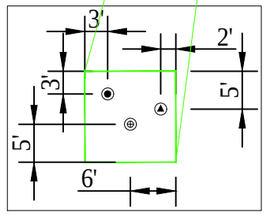
John-Eric Pardys, P. Eng.

JEP/kf/5-rev.1

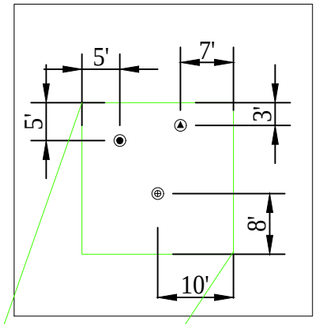
Encl.

cc: Dave Favero, RACER
Michael Tomka, GHD

AREA 1 - SLAG AREA
SCALE: 1"=20 AREA: APPROX. 5762 sq.ft



AREA 1 - SLAG AREA
GRID SAMPLE LOCATIONS (12ft.GRID)



AREA 2 - SLAG AREA
GRID SAMPLE LOCATIONS (20ft.GRID)

AREA 2 - SLAG AREA
SCALE: 1"=30' AREA: APPROX. 15840 sq.ft

0 251 502 ft

LEGEND

- A — INVESTIGATIVE UNIT BOUNDARY AND IDENTIFIER
- APPROXIMATE FORMER PROPERTY BOUNDARY
- SLAG AREA
- APPROXIMATE LIMITS OF RACER PROPERTY
- PROPOSED ISM SAMPLING LOCATIONS

NOTE: TOPO - SANBORN, 1996

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

RACER
SAGINAW NODULAR INDUSTRIAL LAND

SAGINAW, MICHIGAN

PROPOSED ISM SAMPLE LOCATIONS
SLAG AREA SOIL SAMPLING

GHD

Source Reference:
MICHIGAN STATE PLANE SOUTH, NAD 83 USING INTERNATIONAL FEET, NGVD 88
AERIAL SOURCE: IMAGE ©2015 GOOGLE (IMAGERY DATE 6/17/2016)

Project Manager:	Reviewed By:	Date:	
I.R.	M.T.	October 2019	
Scale: 1" = 500'	Project N°: 58502-A03	Report N°: SASN005	Drawing N°: figure 1

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Table 3.1

Summary of Analytical Methods
Work Plan to Complete Slag Area Soil Sampling
RACER Nodular Facility
Saginaw, Michigan

Parameter	Preparation Method[1]	Analytical Method[1]
Soil Samples		
TAL Metals	SW 3050/7471	SW 6020B/7471
pH	-	SW 9045C

Notes:

[1] Preperation and Analytical Method References:
- SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986. Actual method versions employed will include the latest promulgated version of the method adopted by the lab.

TAL -Target Analyte List

Table 3.2

Sediment Sample Parameter List
Work Plan to Complete Slag Area Soil Sampling
RACER Nodular Facility
Saginaw, Michigan

Compound	Estimated Quantitation Limits (EQL)[1] Soil (mg/kg)	Method Detection Limits (MDL)[2] Soil (mg/kg)
Metals		
Silver	0.200	0.0220
Aluminum	10.0	3.02
Arsenic	1.00	0.0600
Beryllium	0.200	0.0470
Cadmium	0.200	0.0430
Cobalt	0.200	0.0520
Chromium	0.400	0.250
Copper	0.400	0.229
Iron	20.0	8.04
Manganese	1.00	0.402
Nickel	0.400	0.244
Lead	0.200	0.0623
Antimony	0.400	0.125
Selenium	1.00	0.120
Thallium	0.200	0.0480
Vanadium	1.00	0.229
Zinc	4.00	1.64
Barium	1.00	0.289
Calcium	200	50.8
Potassium	200	55.6
Magnesium	200	48.7
Sodium	200	51.1
Mercury	0.100	0.0180
General Chemistry		
pH	0.100 Standard unit	--

Notes:

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

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

Table 3.3

Laboratory Precision and Accuracy Limits
Work Plan to Complete Slag Area Soil Sampling
RACER Nodular Facility
Saginaw, Michigan

Analysis	Analyte Description	LCS Limits	MS/MSD Limits
Metals	Silver	80-120 (20)	75-125 (20)
	Aluminum	80-120 (20)	75-125 (20)
	Arsenic	80-120 (20)	75-125 (20)
	Beryllium	80-120 (20)	75-125 (20)
	Cadmium	80-120 (20)	75-125 (20)
	Cobalt	80-120 (20)	75-125 (20)
	Chromium	80-120 (20)	75-125 (20)
	Copper	80-120 (20)	75-125 (20)
	Iron	80-120 (20)	75-125 (20)
	Manganese	80-120 (20)	75-125 (20)
	Nickel	80-120 (20)	75-125 (20)
	Lead	80-120 (20)	75-125 (20)
	Antimony	80-120 (20)	75-125 (20)
	Selenium	80-120 (20)	75-125 (20)
	Thallium	80-120 (20)	75-125 (20)
	Vanadium	80-120 (20)	75-125 (20)
	Zinc	80-120 (20)	75-125 (20)
	Barium	80-120 (20)	75-125 (20)
	Calcium	80-120 (20)	75-125 (20)
	Potassium	80-120 (20)	75-125 (20)
	Magnesium	80-120 (20)	75-125 (20)
	Sodium	80-120 (20)	75-125 (20)
	Mercury	80-120 (20)	80-120 (20)
General Chemistry	pH	97-103 (20)	--

Notes:

LCS - Laboratory Control Sample
MS/MSD - Matrix Spike/Matrix Spike Duplicte Sample

Table 3.4

Summary of Sampling and Analysis Program
Work Plan to Complete Slag Area Soil Sampling
RACER Nodular Facility
Saginaw, Michigan

Investigation Activity	Sample Matrix	Field Parameters	Laboratory Parameters	Quality Control Samples					
				Investigative Samples	Equipment Blanks	Replicate Samples	Laboratory Duplicate	MS/MSD (1)	Total
Slag Area Soil Sampling (0-0.5 ft)	Soil	None	TAL Metals, pH	2	1	4	1	1	9

Notes:

(1) - Matrix Spike/Matrix Spike duplicate (MS/MSD) analyses are required for samples submitted for metals analyses are to be analyzed at a frequency of one per group of ten (10) or fewer investigative samples for the activities detailed above. The MS/MSD is a pair a of two samples--spike and spike duplicate.

TAL -Target Analyte List

Table 3.5

Container, Preservation, Shipping and Packaging Requirments
Work Plan to Complete Slag Area Soil Sampling
RACER Nodular Facility
Saginaw, Michigan

Analyses	Sample Containers[1]	Preservation	Maximum Holding Time from Sample Collection[2]	Volume of Sample	Shipping	Normal Packaging
SOLID (Soil)						
Metals	Two 32-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for analysis	Min. of 30 cores (Min of 1.2 kg)	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
pH	Two 32-ounce glass jar	Iced, 4 ± 2° C	Analyze immediately	Min. of 30 cores (Min of 1.2 kg)	Overnight or Hand Deliver	Foam Liner or Bubble-wrap

Notes:

[1] - Multiple parameters (Metals and pH) on a single sample may be combined into two 32 ounce glass jar.

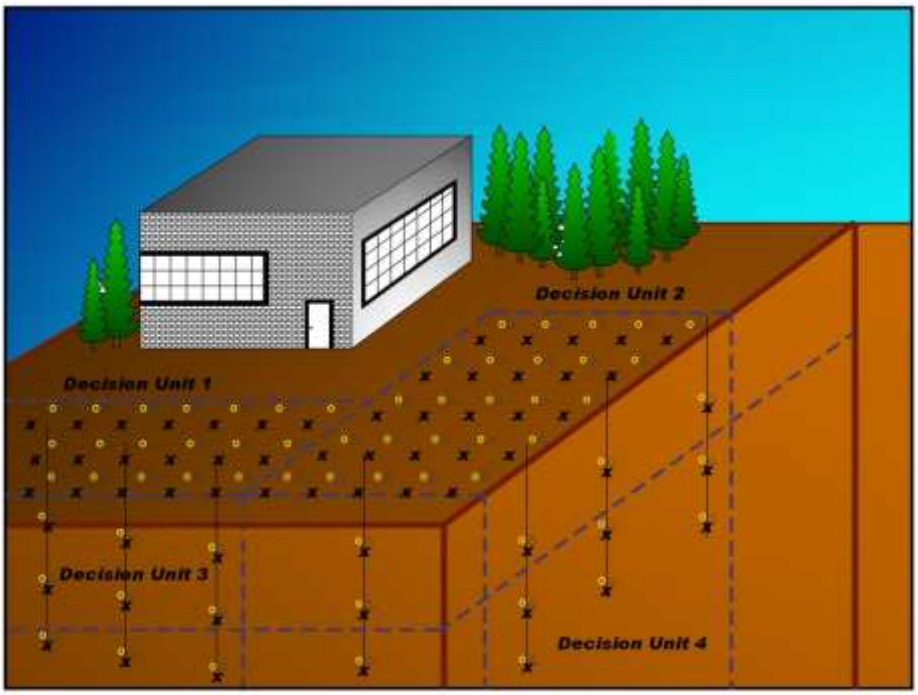
[2] - These are technical holding times, i.e., are based on time elapsed from time of sample collection.

[3] - Sample containers provided are not to be filled but instead provide sufficient capacity to hold the minimum of 30 cores, which are each approximately 42 grams

Attachment A
EGLE Incremental Sampling Methodology and Applications

INCREMENTAL SAMPLING METHODOLOGY AND APPLICATIONS

REMEDIATION AND REDEVELOPMENT DIVISION RESOURCE MATERIALS



Prepared by:
Michigan Department of Environmental Quality
Remediation and Redevelopment Division
525 West Allegan Street
Lansing, Michigan 48933

RRD-RESOURCE MATERIALS
January 2018

In order to promote a consistent and informed approach for Michigan Department of Environmental Quality (MDEQ) staff, this document was developed to provide information to MDEQ staff and contractors on methodology and applications for using incremental sampling techniques.

This document is available as a technical reference to assist any party interested in using incremental sampling techniques to evaluate contaminated media and make risk management decisions.

This document is explanatory and does not contain any regulatory requirements. It does not establish or affect the legal rights or obligations for incremental sampling. It does not have the force or effect of law and is not legally binding on the public or the regulated community. Any regulatory decisions made by the MDEQ regarding incremental sampling methodology and applications will be made by applying the governing statutes and Administrative Rules to relevant facts.

Approved: Kathleen Shirey, Acting Director
Remediation and Redevelopment Division
January 2, 2018

Note:
For the purpose of this technical resource document, the term “facility” is being used as a general reference to a property with environmental contamination and is not intended to be applied as it is statutorily defined in the Natural Resources and Environmental Protection Act (NREPA), PA 451 of 1994, as amended.

TABLE OF CONTENTS

SUMMARY

This document is provided as a resource for environmental professionals interested in applying Incremental Sampling (*IS*) methodology. *IS* is a structured sampling and analytical method designed to obtain a sample that is representative of the entire volume of environmental media targeted for sampling, while providing reproducible results for improved decision making. *IS* may be used at sites of environmental contamination alone or in combination with other sampling protocols. For purposes of these resource materials, *IS* applies to the evaluation of average contaminant concentrations in solid materials including soils, fill, and sediments within a horizontally and vertically defined area determined by utilizing the data quality objectives (DQO) process. The DEQ has successfully applied *IS* methodology to the investigation of organic and inorganic contaminants in these solid media.

This document is not intended to comprehensively describe all details and applications of *IS*. This document expands on information that may be difficult to obtain from other resources, and is brief in regard to subjects that are discussed at great length in available resources (see Appendix A for additional resources). *IS* is also referred to as "Multi-Incremental Sampling (MIS©)", "Incremental Composite Sampling (ICS)", or "Incremental Sampling Methodology (ISM)" in the literature. The Interstate Technology and Regulatory Council (ITRC) document titled "Incremental Sampling Methodology" represents the most comprehensive *IS* reference available at this time and is recommended as a useful *IS* resource (ITRC 2012).

1.0 INTRODUCTION

Incremental Sampling (*IS*) is a combined field sampling and laboratory sample processing protocol designed to provide an unbiased, statistically valid estimate of the mean contaminant concentration (within a pre-defined volume of media). *IS* reduces the data variability commonly associated with traditional discrete field sampling practices and laboratory methods.

IS produces an unbiased and reproducible data set when properly implemented. The *IS* methodology produces data that is typically more representative of soil, fill material and/or sediment contaminant concentrations in a specified volume/area than that achieved by using traditional discrete sampling practices.

The purpose of this document is to describe, in general terms:

- *Incremental Sampling Concepts*
- *Systematic Planning and Data Quality Objectives (DQOs)*
- *Decision Unit (DU) Designation and Sampling Design*
- *Field Implementation*
- *Laboratory Processing and Analysis*

It is not the intent of this document to provide a detailed discussion of all *IS* concepts or strategies. A list of selected references, which provide a more thorough discussion of the concepts presented in this document, is presented in Appendix A.

2.0 SAMPLING CONCEPTS

2.1 *IS* and Theory of Sampling®

The understanding of the Theory of Sampling and what makes a representative sample is critical for sample collection. Knowledge of this theory is important for management, planners, sampling staff, laboratory analysts, and data users. The Theory of Sampling, its principles and practices, are applicable to any sampling situation and all media.

The Theory of Sampling describes and evaluates all errors in the sampling of materials as well as methods for minimizing error. Primary sources of errors in sampling include material heterogeneity and non-representative sampling. Material heterogeneity is comprised of: (1) the makeup of the material (compositional) and (2) the nonrandom spatial or temporal distribution (distributional heterogeneity) of elements within the material.

Compositional error is minimized by collecting more mass. Distributional error is minimized by increasing the number of samples from the population (i.e., predetermined area and volume). To control bias, correct sampling methods employ the following two principles:

1. Every element within the population has an equal chance of being in the sample
2. The integrity of the sample is preserved during the entire sampling process.

Therefore, a representative sample is one where both error and bias are controlled to an acceptable level.

2.2 *IS* Concepts

IS is a detailed sampling method that adheres to the Theory of Sampling to obtain a representative sample from a predetermined area and volume (i.e., DU). *IS* includes the collection of an appropriate mass, number of increments (i.e., portions of a DU sample), and a defined sampling protocol that includes quality control and procedures for maintaining sample integrity and minimizing error.

The high variability of data that is often observed between samples that are collected from a site using discrete field sampling methods can primarily be attributed to the particulate nature of the soils, fill material and sediment media (i.e., compositional heterogeneity) and variability in the spatial distribution of contaminants throughout a site (i.e., distributional heterogeneity). Compositional heterogeneity describes the variability of contaminant concentrations between the particles that make up the sample population and introduces what is called "fundamental error". *IS* minimizes this source of error by ensuring that adequate sample mass be collected in the field and subsequently subsampled and analyzed by the laboratory in a manner that maintains representativeness.

Distributional heterogeneity is a function of spatial and temporal variability because contaminant particles are not randomly distributed across the sampled population. Distributional heterogeneity introduces "grouping and segregation error" when the sample consists of too few, or spatially and/or temporally biased, increments to adequately represent the variability of the population. *IS* addresses this source of error through the collection of multiple, systematically random sample increments. There are three fundamental elements necessary to properly conduct site characterization using *IS*. These are (1) systematic planning, (2) proper field sample collection, and (3) proper laboratory processing, subsampling, and analysis. A critical component of the systematic planning process is defining the volume of interest (i.e., the DU) that will be sampled using *IS*. The DU is site-specific and typically represents the smallest volume of environmental media about which a decision will be made. The *IS* method produces a single sample that will ideally have the same composition as the DU. To obtain an *IS* sample, 30 to 100 systematically random, equal volume and shape increments are collected from throughout the DU and combined to make a single (1 to 5 Kilogram [kg]) sample. In the laboratory, the *IS* sample is processed following *IS* protocol for subsampling to produce a representative aliquot for laboratory analysis. A minimum of three replicate *IS* samples are required to evaluate sampling precision. Replicate samples may be collected at any point in the sampling process (field sample, mass reduction, laboratory etc.).

3.0 ***IS VS. COMPOSITE SAMPLING***

Composite sampling is a technique that physically combines a number of spatially discrete samples from a body of material into a single sample for analysis. *IS* samples are a type of composite sample. However, traditional composite samples as collected in the environmental industry, typically consist of too few increments, too small a sample mass (both field and analytical), and an insufficient laboratory subsampling to address the problems of variability inherent in contaminated soils, fill material and sediments.

IS addresses the issues problematic to traditional composite sampling, thereby becoming a different sampling method that provides significantly improved results. A reoccurring problem with traditional composite sampling is that it does not adequately address the issue of common contaminant heterogeneity, at the site, or in the lab. The *IS* process addresses heterogeneity by considering the number of increments, the mass of the sample, the size and shape of the specific volume of interest

(DU), and a project-specific laboratory protocol for processing. As such, *IS* represents a more rigorous form of sampling designed to produce results that are representative, reproducible, and defensible. Sampling methods that include "some of the elements of IS" have been proposed and used in the State of Michigan. These alternative sampling methods have provided mixed results. A major benefit of using *IS* is the confidence provided to site management (and other decision makers) by obtaining a representative, reproducible and defensible site characterization. The benefits of *IS* should not be expected unless the fundamental elements of IS are used, as described in this document. For example, collecting fewer than the recommended number of increments has been shown to result in significantly decreased data quality. Alternative sampling methods that do not incorporate the minimum expectations of *IS* (as described in this document) should not be referred to as *IS*.

IS is a proven method which provides substantial improvement in data quality representative of a site-specific area/volume when compared to traditional discrete or composite sampling. Additionally, because *IS* requires fewer analyses and less sample handling compared to effective discrete sampling schemes utilizing many samples, *IS* is often more cost effective.

4.0 SYSTEMATIC PLANNING AND DATA QUALITY OBJECTIVES

4.1 Systematic Planning

Systematic planning is a planning process that is based on the scientific method and includes concepts such as objectivity of approach and acceptability of results. Systematic planning is based on a common sense, graded approach to ensure that the level of detail in planning is commensurate with the importance and intended use of the work and the available resources. Systematic planning is at the core of the *IS* methodology.

4.2 Data Quality Objectives (DQO) Process

The United States Environmental Protection Agency (USEPA) seven-step data quality objectives (DQO) process is the recommended systematic planning tool for developing effective sampling and analysis plans. The DQO process should involve all stakeholders including the regulatory agency, owners, consultants and concerned parties. Use of the DQO process is often overlooked or abbreviated. Use of the DQO process is intended to reduce the need for additional sampling events, collecting more samples than necessary and/or disagreements about data interpretation.

A summary of the multi-step DQO process is presented below.

1. State the problem.

The first step includes describing the problem in a clear, uncomplicated manner within its regulatory context. It involves discussions and developments of the Conceptual Site Model (CSM), the identification of team members and decision-makers, as well as, defining the budget and schedule constraints.

2. Identify the decision.

This step identifies the principal study question(s) and defines alternative actions that might be taken depending on the results of the study. The output of this step is a decision statement or set of statements that link the principal study question to potential actions that will resolve the problem.

3. Identify inputs to the decision.
This step uses the decision statement(s) to identify the data needed to make the decision. The type and source of information are discussed. Establishing threshold criteria to be used for choosing alternative courses of action may also be identified. Identification of the appropriate sampling and analysis methods for meeting data requirements may also be identified.

4. Define the study boundaries.
This step includes defining and determining the population(s) of interest, the spatial boundaries within which data will be collected, the time frame for data collection, practical constraints on collecting data, and the smallest subpopulation, area, volume, and/or time for which separate decisions must be made. This step is where DUs are identified.

5. Develop a decision rule.
This step converts the decision statement (from step 2) into a decision rule. The Decision Rule includes the statistical parameter of interest (e.g., Upper Confidence Limit [UCL] of the mean), the action level(s), and integrates previous DQO outputs into "if-then" statements that will be used to guide decision making in regard to various alternative actions.

6. Specify tolerable limits on decision errors.
One challenge in developing sampling designs is to balance the potential for decision errors against the practical constraints of site investigations. All environmental data (as well as the decisions based on that data) include uncertainty. The purpose of this step is to determine how much uncertainty can be tolerated while still making sound and defendable decisions (i.e., the tolerable limit on decision errors).

Questions often explored in the process of completing this step include:

- How much confidence in the decision is required?
- What are the consequences of making an incorrect decision?
- What range of DU compositional and distributional heterogeneity can be expected?
- How close is the actual DU mean to the decision criteria?
- Are the populations adequately defined?

7. Optimize the design for obtaining data.
The final step of the DQO process uses the results of the first six steps to select and design a specific sampling program to achieve the desired goals at the lowest cost. This includes choosing final DU dimensions, the number of increments per DU, where replicate samples will be collected, and determining specific field and laboratory analytical methods.

5.0 DECISION UNIT DESIGNATION AND SAMPLING DESIGN

5.1 Introduction

IS is a method for estimating the mean concentration of contaminants in specified area/volumes called DUs. The DU represents each area/volume for which a decision will be made. Each DU is characterized by systematically collecting a predetermined number of increments which are combined to form the incremental sample. For additional information on DUs and Sampling Design refer to the ITRC "Incremental Sampling Methodology" document (ITRC 2012).
An effective sampling design (including DU development and number of increments) is dependent on a successful DQO process and a well-developed CSM. The CSM presents the current understanding of

the site, evaluates migration and exposure pathways, identifies potential data gaps, and assists in coordinating sampling strategies for achieving investigation objectives. Some investigation objectives may include:

- Characterization of source areas/releases.
- Delineation of the extent of contamination.
- Characterization of waste/fill material
- Determination of exposure concentrations.
- Confirmation sampling.
- Establishing background concentrations.

5.2 Decision Unit (DU)

Determining the size, shape, location, and number of DUs is one of the most critical components of the *IS* planning process. All involved parties should agree on the size, configuration and location of DUs. When considering the size of any DU, it must be understood that the entire DU will pass or fail based on the DU sample results (as established by the DQO process). The DU should represent the smallest area/volume for which a decision is to be made as established by the DQO process.

DUs may be based on the known or suspected locations and dimensions of source areas, or on the size of exposure areas used in risk scenarios. The shape and size of DUs should consider:

- Areas that establish exposure areas
- Contaminant transport and exposure pathways
- Spatial distribution of contaminants
- Geologic and other physical characteristics (e.g., formation and soil type boundaries)

A DU source area is a distinct area/volume containing elevated or potentially elevated concentrations of contaminant(s) in soils, solids and sediments as indicated by site history and the CSM. These may include areas where:

- Stained soils or contaminated soils are thought or known to exist
- Releases are thought or known to have occurred.
- Contaminants or contaminated material were suspected to be stored, handled, and/or disposed.
- Sampling data has identified elevated concentrations over a specific volume/area.

A DU exposure area is often defined as an area where receptors could come into contact with contaminants. DUs based on exposure areas are an invaluable tool in risk-based decision making. Exposure areas may include:

- Residential yards
- Schools, playgrounds, and parks
- Gardens and agricultural fields
- Non-residential lots
- Receptor home ranges

The primary use of *IS* data from an exposure area is to estimate the average exposure and, subsequently, chronic risk to human health or impact on the environment. Therefore, the exposure area DU should be based upon the area where exposure is or potentially could occur. The size and placement of exposure areas also depend on current use and/or proposed future use of the site. Site-

specific information and the CSM should be used in designating exposure. In situations where future land use is uncertain, the location of future residences and areas of known and/or suspected contamination may need to be addressed with appropriate sized DUs to account for potential future exposure and risk.

Particular sampling challenges exist for the following situations:

- Exposure areas with acute toxicity risks: The individual DUs within the exposure area may be so small that a large number of DUs will have to be sampled to make decisions about the exposure area that it may not be practical
- Risks from vapor sources: The individual DUs within the exposure area may be so small that sampling would not be practical. In addition, the vapor intrusion pathway considers vapor sources from multiple media; therefore, evaluation of the vapor intrusion pathway using concentrations of contaminants found solely in soils (or other solid media) is not appropriate.
- Contaminant conditions that change significantly over time (high variability): The variability of the contaminant should be considered and potentially addressed in the sampling protocol

To ensure sample correctness, consistent with the Theory of Sampling, every DU within the exposure area has to be assessable. Sampling is not recommended if the CSM establishes DUs that cannot be correctly sampled, regardless of the method, because the errors in the sampling process are unavoidable.

5.3 Residential and Non-Residential Exposure Area DUs

Exposure areas for residential use can vary in size (e.g., ¼ acre lot to 1 acre lot); however, if there are smaller areas within the exposure area that receive higher use in an exposure area, that area should be considered for evaluation as a separate DU. Swing sets and sandboxes in residential yards are examples of such exposure areas.

Exposure areas for non-residential properties are site-specific. Designation of these exposure areas should be determined during the DQO process. It may be useful to designate DUs and evaluate properties for future land use (e.g., residential land use). This may help avoid unnecessary land use restrictions and/or the need for reinvestigation should future development plans call for a more sensitive land use.

5.4 DU Sampling Design

Once the DUs are determined, the sampling design should be developed consistent with the DQO requirements. DU sampling design, and in particular the number of increments appropriate for sampling, takes into account the objectives of the site investigation including the type and quality of information needed to make the decision. A minimum of 30 to 50 increments per DU is recommended to obtain a representative and reproducible estimate of the mean concentration in a DU that is characteristic of moderate heterogeneity. Depending on the degree of uncertainty that can be tolerated within the project-specific DQOs, fewer increments may result in unacceptable uncertainty and decision errors. A larger number of increments (e.g., 60 to 100) and/or a larger sample mass may be necessary where higher levels of heterogeneity are expected. Sampling design concepts are provided in the next section.

6.0 FIELD IMPLEMENTATION

6.1 Introduction

This section addresses *IS* field practices. To help ensure data quality, it is recommended that all field sampling and field processing activities be performed or supervised by personnel trained in *IS*.

6.2 Sample Planning

The first step in successfully implementing *IS* is to complete the DQO process as described in Section 4.2. Once the specific objectives have been set, the proper sampling plan can be prepared. The sampling plan will take into consideration the mass of the sample needed, the number of increments, increment spacing, the depth of the increments, and the sample tool(s) to be used. Proper planning of the *IS* sampling procedures will ensure that a representative sample will be collected and that the physical sampling process will be conducted efficiently and without complication.

The total mass of an *IS* sample and the number of increments are dependent (in part) on the heterogeneity of the DU. Between 1 and 2 kg (for the total sample) and a minimum of 30 to 50 increments per DU is recommended for a DU that is characteristic of moderate heterogeneity. A sample mass of 2 kg or more and up to 100 increments may be needed for highly heterogeneous DUs.

6.3 Sampling Tools

The sample mass, number of increments, and increment depth can be determined through the DQO process, and the appropriate sampling tool can be determined based on the mass per increment and soil type expected to be encountered. The following tables (Table 1 and 2) can help in determining how to incorporate these factors to plan an appropriate *IS* sampling approach. Table 1 shows an estimate of the increment mass needed to provide initial sample masses of 1 to 2 kg based on the number of increments collected. Table 2 shows the mass obtained by using typical soil coring tools.

Table 1
Estimated Mass/Increment (grams [g])

		Sample Mass	
		1 kg	2 kg
# of Increments	30	~35 g	~70 g
	40	~25 g	~50 g
	50	~20 g	~40 g
	60	~17 g	~35 g
	80	~13 g	~25 g
	100	~10 g	~20 g

Table 2
Coring tool average mass per inch of core*

Core tool diameter	0.75 inch	1.0 inch	1.5 inch	2.0 inch
Mass/inch of core	~7 g	~12 g	~28 g	~50 g

*The mass identified in Table 2 applies to unsaturated fine to medium textured soils. Very moist to wet soil may require more mass to account for the additional water content.

As an example, if the DQOs require a minimum 1 kg sample and 50 increments at a 2 inch sampling depth, at least 20 g per increment would be required. Using a 1.0 inch diameter sample corer at a depth of 2 inches would provide approximately 24 g of soil per increment. This would produce the desired initial sample with an approximate 1.2 kg sample mass.

The cohesiveness and composition of the soil substrate should also be considered in choosing an appropriate sampling tool. The sampling tool should obtain cylindrical increments of a constant depth throughout the vertical increment, and should equally retain all particle sizes. The diameter of the sampling tool should be a minimum of three times the diameter of the largest particle present. In general, sampling tools should have a minimum diameter of at least 16 millimeters (mm). For less cohesive soils, such as dry sands, retainers may be needed so that the entire, complete core increment is retained.

For *IS* sampling projects where cylindrical coring samplers are not appropriate (i.e., non-cohesive soils, wet sediments, etc.), scoops or other devices can be used. However, care should be taken to obtain a "core-shaped" increment over the entire depth of interest. Depending on site familiarity, one or several sampling tools should be readily accessible during all sampling activities.

There are a variety of soil coring sampling tools that are available for nonvolatile *IS* sample collection. Many of these are commercially available and custom made tools can be designed for specific sampling needs. *IS* sample collection of volatile organic compounds (VOCs) can be accomplished using the same coring device used for the regular collection of methanol preserved VOC samples.

6.4 Field Collection

The field collection process can be made effective and efficient with appropriate planning. This is achieved after the DQO process and a determination of DUs, sample mass, depth, number of increments, and types of sampling tools are considered.

6.4.1 Surficial IS Samples

Surficial *IS* samples are generally the easiest type of *IS* sample to collect. Surficial *IS* samples should be collected in a random systematic approach throughout the DU. The positioning of the first *IS* point can be randomly selected (typically toward a corner of the DU) then the remaining *IS* points are dictated by a sampling grid based off this first point. With this random systematic sampling approach, a grid is laid out across the DU and all soil increments are collected from grid nodes (see Figure 1).

Figure 1
Random Systematic Sampling Approach

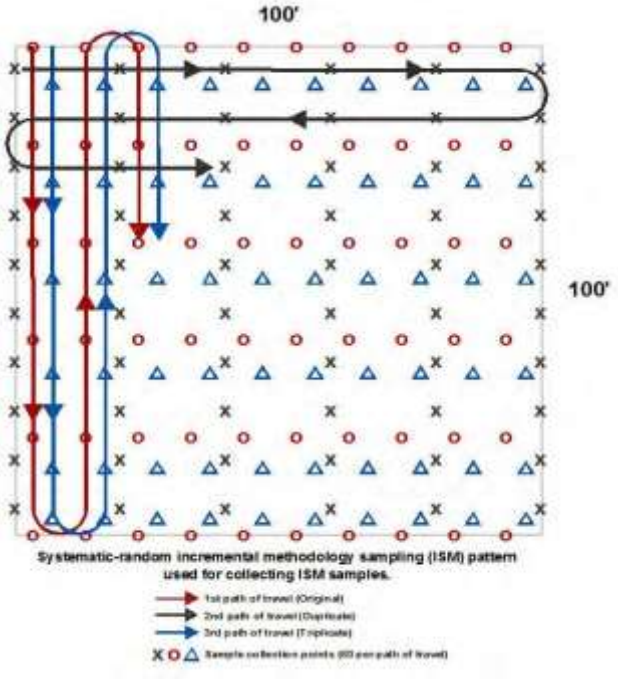


*Figure from ITRC 2012

The grid pattern for any individual DU can be roughly determined based on the area of the DU and the number of increments required. A simple equation can be used to determine the grid pattern as follows:

Grid spacing (feet) = square root of the area (feet^2)/square root of the number of increments

Table 3 shows several grid spacing distances based on specific increment requirements and DU sizes.

Table 3
Typical Grid Spacing (feet)

		Area of DU (Acres)							
		0.10	0.20	0.25	0.5	1.0	2.0	2.5	5.0
# of Increments	30	12	17	19	27	38	54	60	85
	40	10	15	16	23	33	47	52	74
	50	9	13	15	21	30	42	47	66
	60	8	12	13	19	27	38	43	60
	80	7	10	12	16	23	33	37	52
	100	6	9	10	15	21	30	33	47

It should be noted that while a specific number of increments may be specified, collecting a few more or a few less increments is acceptable as long as the appropriate mass is collected and the DU is systematically sampled over its entirety. For example, if 30 increments are specified and the grid pattern over the DU works out to be a 6 by 6 grid, a total of 36 increments will be collected. Additionally, if 50 increments are specified and a 7 by 7 grid is used, a total of 49 increments will be collected.

An *IS* sample is initially prepared by collecting multiple increments from a specified DU and physically combining these increments into a single sample. For *IS* samples collected for analyses, other than VOCs or phthalates, the sample is usually collected in a 1 or 2 gallon sealable plastic "Ziploc" -type bag. Carrying this bag in a 5-gallon bucket will aid in the ease of collection. VOC samples should be collected in a 0.5 or 1 Liter small mouthed amber glass bottle containing adequate methanol (see below). More detail regarding samples for VOC analysis is provided below.

Surficial samples are typically collected using a "step probe" where the probe is set to collect an increment from a specific depth. The probe is pushed into the soil to the specified depth and the sample increment is extracted from the ground. This increment is then removed from the probe and placed directly into the sample bag. The process is continued throughout the DU along the grid pattern until all increments are collected. If replicate samples are required, the same grid pattern is used but it is based on a new randomly selected starting point. Note that replicate samples can be collected on the same "pass" across the DU; each replicate is simply placed in a separate sample bag. Also note that the exact location within the grid where the increment is collected is not particularly important, however, collecting each increment in the same general vicinity within each grid may improve the overall coverage of the DU.

Since all increments collected for a specified DU are combined into one sample for analysis, there is no need to decontaminate the sampling tool between increments. Sampling tools should be decontaminated between DUs or when collecting replicate samples.

Grid patterns for regularly shaped DUs (square or rectangular) are relatively easy to lie out. Depending upon the size of the DU and terrain features or other obstructions, pin flags, or other markers can be placed along the edges of the sampling grid to assist with the visual delineation of the increment sampling point. The sampler can then use these markers to either pace out or otherwise measure the specified distance between *IS* points. The use of marked string between the edges of the sampling grid is sometimes used to demarcate the sampling grid. Larger DUs may require markers at each *IS* point or the use of a global positioning system to locate each point. For odd shaped DUs, a trial run with no sample collection can be conducted to quickly establish whether the proposed sampling grid will produce the proper number of increments and, in turn, the proper mass.

While *IS* sample collection can be performed by a single individual sampler, a two-person team is often the most efficient method. A two-person team permits one person to collect the increments while the second holds the sample container (plastic bag in bucket, amber bottle for VOCs, etc.) and keeps track of the number of increments collected. Replicate samples can be collected by the team at the same time as the original sample (using an additional sampling tool) or collected after the initial sample using a tool that has been decontaminated.

6.4.2 Subsurface IS Samples

All DUs are three dimensional and the *IS* DU characterization is designed to be representative of a specified volume or mass of soil/sediment. While obtaining good spatial coverage for subsurface soils is more challenging than surficial soils, it can still be accomplished. The objectives are the same as for surface soil in that a reliable and reproducible mean estimate of contaminants present in the DU is desired.

6.4.2.1 Subsurface IS Sampling from Borings

Subsurface DUs may include pre-determined depth intervals or lithology units as determined by the DQO process. Subsurface *IS* sampling can be accomplished using a variety of boring tools that collect subsurface soil cores. These include hand tools (push probes, soil corers, etc.), as well as, powered boring/coring machines (direct push and drill rigs) that are capable of collecting soil cores at depth. Regardless of the tool used, subsurface *IS* sampling is conducted in the same manner as surficial *IS* sampling.

Cores from multiple borings within each DU are collected. Each core from the specified subsurface DU is an increment and is combined with the other increments for the *IS* sample. The individual core may be subsampled to reduce the mass of the increment. Common techniques to subsample the cores include core wedge and plug. The core wedge technique entails vertically splitting the core in half, or in quarters, along the axis of the core. The plug technique involves collecting multiple plugs from specified intervals throughout the core. The collection of field replicates in the subsurface will follow the same IS methodology used to produce the initial sample (see Section 6.5). Refer to the ITRC *Incremental Sampling Methodology*, February 2012 document for detailed information.

6.4.2.2 Subsurface Excavation Sidewall and Bottom Sampling

While *IS* soil samples collected from excavations are subsurface samples, excavation side walls and bottoms are accessible, which allows for the use of methods similar to *IS* surface soil sampling. The difference in the accessibility of these excavated faces may dictate the proper tool needed for collecting an appropriate *IS* sample. When conditions are safe for the sampler to physically enter the excavation, *IS* sampling can be conducted in the exact same manner as surficial *IS* sampling utilizing the same tools. Sidewall sampling can be treated as if it were a horizontal sample with regard to laying out the proper grid for collecting the individual increments.

When it is not safe for the sampler to enter the excavation (i.e., too deep, steep sidewalls, etc.), *IS* samples can be collected from the edge of the excavation using a probe or scoop tool mounted on an extendable shaft. All appropriate precautions should be taken when sampling in this manner, as there are still potential dangers when working on the edges of excavations. Sidewall grids can be marked by placing flags along the top edge of the excavation or by lowering weighted strings with systematically random marked intervals down into the excavation at the proper grid spacing.

6.4.2.3 Potential Subsurface Limitations

The recommended number of increments to be collected from a subsurface DU is the same as that for a surface soil DU. In some cases, as with direct push or drill rig borings, collecting the recommended number (30 to 100) of increments may not be cost-effective or practical. Reducing the recommended number of increments may be an option if the project DQOs are satisfied. It is important to recognize that a reduced number of increments increases uncertainty and decision error resulting in a less precise and more biased estimate of the mean contaminant concentration.

6.4.3 Volatile Organic Chemicals (VOC) IS Samples

IS samples can be collected for VOCs contaminant analyses. *IS* VOC soil samples are collected using methanol as the field preservative. The mass and number of increments for each *IS* sample is determined through the DQO process, which specifies the total amount of methanol for the number and mass of increments. This is typically determined at a 1:1 ratio of volume of methanol (ml) to mass of

soil (g). This methanol is placed in an appropriately sized (usually a 500 or 1,000 milliliter [mL]) small-mouthed amber glass bottle. The increments are placed directly into the bottle as they are collected. Each increment mass should be as similar as possible however the individual increments typically do not need to be weighed in the field during collection.

The increments collected for a VOC *IS* sample in this manner can be collected in the same manner as when collecting samples for other analyses from surface and subsurface soils. The only real difference is in the mass of soil collected for each increment. Incremental mass for VOC increments is typically only 5 to 10 g.

As with all *IS* samples, collecting a larger mass of soil for an *IS* sample results in a sample that is more representative of the material sampled. However, the handling, shipping, and costs of large volumes of methanol usually present logistical issues that dictate that *IS* VOC samples be comprised of 30 to 50 increments and have a mass of 300 to 500 g.

Increments should be collected using tools that minimize the loss of VOCs during sample collection and allow the collection of the proper mass of soil. Sample increments should be quickly transferred from the tool to the bottle containing the methanol. Syringe-type devices similar to the ones used to collect discrete VOC samples are preferable.

For determining percent moisture (for reporting dry weight), a separate and unpreserved soil sample, representative of the increments must be collected. This sample should be collected in the same manner as the *IS* VOC sample. This is usually accomplished by collecting an additional increment at each *IS* increment location and combining these increments in an unpreserved container for submittal to the laboratory.

6.4.4 Waste Pile IS Samples

IS may be used to characterize waste piles and soil piles (e.g., disposal or treatment options). The DU may include one or more waste piles as determined by the DQO process. If equipment is being used to move the piles from an excavation source or the piles are moved to a staging area or roll-off box, the increments may be collected from the device transporting the material (e.g., shovel, pay loader, or track hoe bucket) using a systematic random approach. Typically, a small core device is used to collect the sample increment as the material is moved. If equipment is not available to move the piles, the process may include collecting increments from throughout the vertical and horizontal extent of the pile using appropriate coring tools. Collection of *IS* samples may require a team of two or more persons to accommodate safety concerns if heavy equipment is used.

6.5 Collection of Field Replicate IS Samples

Replicate *IS* samples should be taken whenever there is a reduction in mass (sample) to evaluate the precision of the sampling method. Replicates are used to evaluate precision of the sampling process in the field and in the laboratory. Three or more replicate *IS* samples are required to statistically evaluate the sampling precision of any particular DU. *IS* replicate samples are collected and analyzed in the same manner as the initial *IS* sample.

The relative standard deviation (RSD) between replicates is used to assess data precision and reproducibility (and, therefore, the confidence) in the data generated. The higher the RSD the less confidence there is that the mean contaminant concentration reported accurately represents the DU(s).

Although dependent on the site-specific level of uncertainty that can be tolerated, an RSD of less than 30 percent between replicates is generally considered precise enough to make decisions.

Depending on the degree of similarity between DUs of any particular investigation, the collection of triplicates from a minimum of 10 percent of the DUs is normally recommended for *IS*. The number of replicates per DU and the frequency of replicate sampling should be clearly addressed in the DQO process and needs to consider contaminant variability, the existence of separate populations, and the precision desired. If these qualities are considerably different between DUs, then replicate sampling should be performed for each different 'DU type'. For sites with multiple similar DUs and where otherwise appropriate, replicates from one DU may be used to provide an estimate of variability that can then be extrapolated to other similar DUs. For multiple similar DUs, the DU expected to have the highest variability should be selected for replicates.

6.6 IS Field Processing for Non-VOC Samples

IS sample processing techniques, such as sieving, grinding, and subsampling, are designed to ensure that the mass of sample analyzed by the laboratory is representative of the DU. These techniques are implemented, as appropriate, to reduce data variability as compared to conventional sample handling and processing techniques. However, these techniques can introduce sampling error, especially if conducted in the field. It is recommended that all *0* sample processing be performed in a controlled laboratory setting rather than in the field. On a specific case-by-case basis and depending on site logistics, the type of soil, the total number and/or mass of *IS* samples, etc., sample processing may be initiated in the field for some non-VOC contaminants with the appropriate precautions as noted below. Any field processing of *IS* samples should be discussed with the laboratory in advance to enable the laboratory to adjust their standard operating procedures (SOP's) to produce representative aliquots from *IS* field subsampling for laboratory analysis.

Moist samples may require air drying to facilitate sieving. If done in the field, it should be done in an appropriate dust-free location where temperatures and ultraviolet light are not expected to cause degradation of certain contaminants. Mostly sandy soil samples with little vegetation and very low moisture content can be sieved (typically using a #10 sieve, less than 2 mm particle size) in the field to remove pebbles and organic debris. Sands and smaller size particles are generally considered "soil," while larger particles are considered gravel, rocks, or other materials (e.g., sticks and roots). Field sieving might be an option when the originally collected *IS* sample has a large amount of these larger particles and a proper amount of "soil" is needed to meet the total mass required for the sample (i.e., by DQO requirements). Alternative sieve sizes may be of interest on a case-by-case basis and these should be determined through the DQO process. Unless field subsampling is to be performed, the entire sieved *IS* sample fraction should be submitted to the laboratory for appropriate additional processing and subsampling.

As noted above, laboratory subsampling is recommended in lieu of field subsampling, especially when contaminants have been deposited as solid particulates (e.g., energetics, metals at firing ranges, etc.). Field subsampling may be appropriate when the laboratory performing contaminant analysis does not have the ability to conduct the proper subsampling in the laboratory (e.g., with a mobile laboratory).

If field subsampling is to be performed, the entire *IS* sample may need to be air-dried and sieved. Field subsampling should be conducted in the same manner as it would be in the laboratory. After the needed processing, the *IS* sample should be spread out in a thin layer on an appropriate clean surface. The subsample is then obtained by collecting a minimum of 30 to 50 increments from systematic random locations in the same manner as when collecting surficial *IS* increments. The increments

collected to form the subsample should equally represent the vertical depth of the processed sample. This is best achieved by using a rectangular, flat-bottom sampling tool (scoop) with sides and a minimum of 16 mm width. Curved or spoon-shaped sampling tools should be avoided as they will introduce greater bias into the subsampling process. The mass of the subsample required will be dictated by the requirements for the analytical test(s) needed. Replicates of the field processed soil should be collected and submitted for analysis to evaluate the precision of the *IS* field processing procedure.

If it is determined in the field that the total mass of an *IS* sample is too great, simply dividing or splitting the sample into separate volumes for analysis is not an acceptable method of mass reduction. While extra mass can add to the cost of laboratory sample processing, field sample processing in this manner would add unnecessary error to the sample results. Therefore, it is important to correctly estimate the number and volume of increments to achieve the desired total sample mass.

7.0 *IS LABORATORY PROCESSING AND ANALYSIS*

7.1 Introduction

The procedures used in the laboratory to prepare and analyze samples are as important as how the samples are collected in the field. The laboratory should be involved with project planning and the DQO process. The laboratory's standard operating procedures should be sufficiently developed to obtain representative subsamples from the field generated *IS* sample mass. Improper laboratory processing and subsampling increases error, which may cause failure to meet the DQO. The reader is referred to the Laboratory Sample Processing and Analysis Section of the ITRC Guidance (ITRC 2012) for more detail on laboratory methods (including Quality Assurance/ Quality Control) and processing options.

7.2 Laboratory Sieving (Non-VOCs)

The entire incremental sample is normally submitted to the laboratory for processing and analysis. In the laboratory, the sample is typically air-dried and may be sieved (typically at 2 mm). The less than 2 mm sized soil particles are generally considered "soil" and are of most interest for contaminant analysis while larger particles are considered gravel, rocks or other materials (e.g., sticks and roots). Sieving the soil sample to the less than 2 mm size also establishes the maximum particle size of the sample, which may be necessary to determine the minimum aliquot mass necessary for extraction/analysis in the laboratory (see below). Although sieving to the less than 2 mm particle size is typical, there may be contaminant investigations or analyses where alternate particle sizes may be of interest (e.g., lead). In these cases, the rationale for sieving to other specific particle sizes (and associated changes to laboratory processing/analysis) should be addressed in the project DQOs and the sampling plan.

7.3 Laboratory Subsampling (Non-VOCs)

Proper subsampling in the laboratory provides a representative sample (aliquot) for analyses. In the laboratory, the sample is either subsampled by hand or mechanically using a sectorial splitter (also called a rotary riffle splitter). When subsampling by hand, the entire dried and sieved sample is spread out in a thin layer (slab cake). Using a systematic random sampling scheme, 30 to 50 increments are selected from the slab cake. The mass of the aliquot (subsample) needed for all of the analytical tests is used to determine the mass of each increment.

7.4 Aliquot Mass

The final subsample mass (i.e., the aliquot mass) must be used completely in the analytical preparation step. The ITRC and the USEPA SW-846 Method 8330B (USEPA a,b) guidance documents discuss the minimum aliquot mass required to reduce "Fundamental Error" of the laboratory analyses to a minimum (e.g., 15 percent or less). The appropriate aliquot mass is (in part) based on the maximum particle size in the soil sample, with both greater mass and/or reduced particle size acting to reduce the fundamental error. Although the ability to increase the aliquot mass must be balanced with DQO requirements, laboratory analytical methods that use an aliquot mass of 10 g or more are generally preferred. This may, however, be dependent on the analytical method used, the laboratory equipment available, and other factors. Laboratory methods may need to be modified to meet project DQOs as determined by advance consultation with the selected laboratory. The ITRC guidance document has several suggestions for increasing the sample aliquot mass.

7.5 Grinding and Milling

Grinding and milling are options to reduce fundamental error. Grinding is used to achieve a reduction in particle size. Milling is used to achieve particles of uniform small size. Grinding/milling samples also reduces the potential for segregation error. These are services that laboratories may offer. Thermal stability and volatility of the contaminant(s) should be considered; therefore, grinding/milling is not recommended for VOCs and certain SVOCs. Grinding/milling may not be appropriate for samples being analyzed for bioaccessibility/bioavailability.

7.6 Laboratory Processing for Volatile Hazardous Substances

IS soil samples are collected for volatile contaminant analyses per a modified version of SW-846 Method 5035A (EPA a,c) and analytical Method 8260B (USEPA a,d). Typically, *IS* soil samples collected for volatile contaminant analysis include 30-100 increment soil plugs inserted into a “1 ml/1 g” corresponding volume of methanol (e.g., 40 10 g plugs into 400 mL of methanol). Replicate samples would be collected and analyzed separately. Alternatively, individual increments can be preserved in 40 mL vials with 10 mL of methanol per 10 g of soil. This may facilitate commercial shipping because the individual container volume stays below 30 mL. The methanol is then composited at the lab to produce the methanol extract for the entire DU sample.

A separate, unpreserved soil sample for percent moisture determination should be collected if necessary to report the results on a dry weight basis. Typically, the unpreserved soil sample should be collected in the same manner as the *VOC* samples, with an additional increment collected at each *IS* increment location and placed in an unpreserved container of adequate size and submitted to the laboratory. The subsample to be used for percent moisture determination should be collected using the hand sampling (2D slabcake) process (described above) on the sample prior to air drying.

7.7 Laboratory Processing for Semi-Volatiles, Polychlorinated Biphenyls (PCBs), Pesticides, Herbicides, Energetics, and Other Hazardous Substances

Some contaminants (including SVOCs, PCBs, pesticides, herbicides, phenols, energetics, and certain metals (Arsenic, Mercury, and Lead)) may require special laboratory and *IS* field processing and subsampling methods to avoid sample contaminant loss and promote sample representativeness. The DQO process should evaluate field collection procedures and laboratory subsampling methods for all contaminants of concern. Advance consultation with the selected laboratory is essential for the DQO planning process.

7.8 Scheduling Laboratory Analysis

During the preparation of the DQOs there should be discussion with the laboratory personnel about laboratory methods, capacity, and sample scheduling. Currently, samples for DEQ investigations are handled by the Contract Laboratory procedure. The DEQ contract pricing for *IS* related services is available. Samples may be sent to the DEQ laboratory for shipment/transportation to a contracted laboratory.

8.0 RRD PROGRAM APPLICATIONS

8.1 Contaminated Site Remediation, Brownfields, Stockpiles and Sediments

IS has been used to advance progress at contaminated sites in Michigan (e.g., under Part 201 and Part 213). *IS* has been used successfully in the Brownfield Redevelopment Program to evaluate direct contact risks associated with arsenic and lead for defined areas and to identify areas where other contaminants of concern are located. *IS* has been used increasingly in Michigan where large scale developments are being designed for residential (and other) uses, while evaluating the necessary property restrictions and exposure controls. *IS* has also been used in Michigan for characterizing stockpiled soils and waste to determine suitability for re-use versus disposal. *IS* has been used to evaluate contaminant mass in sediments for streams and rivers.

8.2 Baseline Environmental Assessments (BEAs) and Due Care

IS is a sampling method that may be used for conducting a BEA for a property and for determining or demonstrating Due Care for some exposure pathways. The increased accuracy, precision, and reproducibility typical of *IS* (in comparison to discrete sampling) may make *IS* the preferred sampling method for meeting these objectives. *IS* sampling techniques can also be useful in determining where exposure risks may exist on smaller portions of the property, allowing for the implementation of protective measures that may be necessary.

9.0 Conclusion

If the *IS* process is followed, it can provide more representative and reproducible results than other traditional discrete sampling methods. This translates into better decision making within RRD programs to the benefit of all interested parties. While the RRD has employed *IS* methodology in a variety of program applications, additional *IS* applications continue to evolve. Please contact RRD staff for assistance in applying *IS* for meeting program objectives.

Acronym List – *IS*

Acronym	Definition
BEA	Baseline Environmental Assessment
CSM	Conceptual Site Model
DEQ	Department of Environmental Quality
DQO	Data Quality Objectives
DU	Decision Unit
EA	Exposure Area
EPA	Environmental Protection Agency
ESA	Environmental Site Assessment
g	Gram(s)
IS	*I*ncremental *S*ampling
ICS	Incremental Composite Sampling
ISM	Incremental Sampling Methodology
ITRC	Interstate Technology and Regulatory Council
Kg	Kilogram
MDEQ	Michigan Department of Environmental Quality
MIS	Multi-Incremental Sampling©
mL	milliliter
ml	methanol
mm	millimeter
PCBs	Polychlorinated Biphenyls
NREPA	Natural Resources and Environmental Protection Act, 1994 PA 451, as amended
Part 17	Michigan Environmental Protection Act, of the NREPA
Part 31	Water Resources Protection, of the NREPA
Part 201	Environmental Remediation, of the NREPA
Part 213	Leaking Underground Storage Tanks, of the NREPA
Part 615	Supervisor of Wells, of the NREPA
Part 625	Mineral Wells, of the NREPA
RRD	Remediation and Redevelopment Division
RSD	Relative Standard Deviation
SOP	Standard Operating Procedure
SVOC	Semi-Volatile Organic Compounds
UCL	Upper Confidence Level
USEPA	United States Environmental Protection Agency
VI	Vapor Sources (in text) or Vapor Intrusion
VOC	Volatile Organic Compounds

Appendix A: REFERENCES and ADDITIONAL RESOURCES

REFERENCES

Incremental Sampling Methodology

ITRC 2012. Incremental Sampling Methodology, February 2012
Hyperlink to ITRC Incremental Sampling Methodology
http://www.itrcweb.org/ism-1/

Data Quality Objectives

USEPA. 2000. Guidance for the Data Quality Objectives Process, EPA/600/R-96/055, August 2000
Hyperlink to USEPA Guidance for the Data Quality Objective Process
http://orau.org/ptp/PTP%20Library/library/EPA/QA/g4.pdf

USEPA. 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process, EPA/240/B-06/001, February 2006
Hyperlink to USEPA Guidance on Systematic Planning Using the Data Quality Objective Process
https://www.epa.gov/sites/production/files/documents/guidance_systematic_planning_dqo_process.pdf

Laboratory Processing and Analysis

USEPA. SW-846 - Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium
Hyperlink to USEPA SW-846 Hazardous Waste Test Methods
https://www.epa.gov/hazardous-waste-test-methods-sw-846

USEPA. 1996. SW-846 METHOD 5035 – CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES, December 1996
Hyperlink for USEPA SW-846 Method 5035 Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples
https://www.epa.gov/sites/production/files/2015-12/documents/5035.pdf

USEPA. 1996. SW-846 METHOD 8260B – VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS), December 1996
Hyperlink to USEPA SW-846 Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry
https://www.epa.gov/sites/production/files/2015-12/documents/8260b.pdf

USEPA. 2007. SW-846 Method 8330A: Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC), February 2007
Hyperlink for USEPA SW-846 Test Method 8330A: Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)
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MDEQ. 2012. Part 213 (Leaking Underground Storage Tanks) of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended, revised December 2012
Hyperlink to Part 213
http://www.legislature.mi.gov/(S(oaxbdazfvvnpcg451pln2w45))/documents/mcl/pdf/mcl-451-1994-ii-8-213.pdf

MDEQ. 2015. Part 201 (Environmental Remediation) of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended, revised March 2015
Hyperlink to Part 201
http://www.legislature.mi.gov/(S(yr0uyipwlvq33xcbd4lwonoa))/documents/mcl/pdf/mcl-451-1994-II-7-201.pdf

MDEQ-RRD. 2015. BEA Guide, Baseline Environmental Assessments (BEA), May 2015
Hyperlink to DEQ-RRD BEA Guide
http://www.michigan.gov/documents/deq/deq-rrd-BEA-BEACitizensGuide_357377_7.pdf

MDEQ-RRD. 2015. Due Care Guide, *Due Care Obligations*, May 2015
Hyperlink to DEQ-RRD Due Care Guide
http://www.michigan.gov/documents/deq/deq-rrd-duecare-citizenguide_253063_7.pdf

MDEQ-Office of Waste Management & Radiological Protection, Hazardous Waste Section, Permit & Corrective Action Unit. 2015. *Michigan Background Soil Survey 2005 (Updated 2015)*, MDEQ-MBSS 2005 (Updated 2015)
Hyperlink to DEQ Michigan Background Soil Survey 2005 (Updated 2015)
http://www.michigan.gov/documents/deq/deq-rrd-MichiganBackgroundSoilSurvey_495685_7.pdf

ADDITIONAL RESOURCES

Incremental Sampling Methodology

Hawai'i Department of Health. 2009. *Technical Guidance Manual for the Implementation of the Hawai'i State Contingency Plan*, Interim Final, November 12, 2009 (Sections 3, 4, and 5)
Hyperlink for Technical Guidance Manual for the Implementation of the Hawai'i State Contingency Plan
http://hawaiidoh.org/TGM.aspx?p=2500a.aspx&a=s367

Hawai'i Department of Health. 2011. Technical Guidance Manual Notes: Decision Unit and Multi-Increment™ Sample Investigations, HDOH 2011b, March 2011
Hyperlink to Hawai'i Department of Health Technical Guidance Manual Notes: Decision Unit and Multi-Increment(TM) Sample Investigations
http://hawaiidoh.org/references/HDOH%202011b.pdf

Data Quality Objectives

MDEQ. 2012. *Quality Management Plan (QMP)*, August 6, 2012
Hyperlink to DEQ Quality Management Plan
http://inside.michigan.gov/sites/deq/qmp/Quality%20Document/2012%20QMP/QMP%20August%206%202012%20%20PDF%20version.pdf

Ohio Division of Environmental Response and Revitalization. 2002. *Data Quality Objectives Process Summary*, DERR-00-DI-32, January 2002
Hyperlink to Ohio Division of Environmental Response and Revitalization Data Quality Objectives Process Summary
http://www.epa.ohio.gov/portals/30/rules/Data%20Quality%20Objectives%20Process%20Summary.pdf

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Hawai'i Department of Health. 2001. Guidance for the Evaluation of Imported and Exported Fill Material, Including Contaminant Characterization of Stockpiles, HDOH 2011e, October 2001
Hyperlink to Hawai'i Department of Health Guidance for the Evaluation of Imported and Exported Fill Material, Including Contaminant Characterization of Stockpiles
http://hawaiidoh.org/references/HDOH%202011e.pdf

Attachment B
Laboratory Standard Operating Procedures

Title: Soil Processing

[Method: ASTM D6323-12, ITRC Guidance Document, Soil Fractionation Method for Michigan]

Approvals (Signature/Date):

Technology Specialist	11/28/18 Date	Health & Safety Coordinator	10/23/18 Date
Quality Assurance Manager	11/30/18 Date	Technology Director	11/05/18 Date

This SOP was previously identified as NC-OP-044 Rev. 2, dated 5/31/17

1. SCOPE AND APPLICATION

1.1. These disaggregation, mixing and particle size reduction techniques are applicable to a wide range soil, sediment, tissue, water, and waste samples. Care must be taken to match the appropriate technique with the matrix, target analytes and quality objectives.

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

Note: If foreign or quarantined solids are received, refer to SOP NC-SM-019 Canton Foreign Soils, current revision, and contact your Environmental Health and Safety Coordinator for proper handling instructions

2. SUMMARY OF METHOD

2.1. Air-Dried Soil Processing: The sample is air dried at room temperature and disaggregated to break clumps into a fine powder to facilitate obtaining a representative sub-sample and improving analyte extraction efficiency.

2.2. Soil Fractionation for Lead: Applicable to lead impacted soil and designed to distinguish the lead in the fine soil fraction from the coarse soil fraction.

2.3. Incremental Sample Wet Mixing Process: Applicable to mixing incremental samples into a single composite. These samples are NOT air dried, but rather water is added to facilitate mixing in a heavy-duty mixer.

3. DEFINITIONS

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

3.2. Mix: To thoroughly blend the sample and reduce the analyte concentration differences between different parts of the overall sample. It is most effective when the particle size and density differences within the sample are small.

3.3. Incremental Sampling Methodology: A structured composite sampling and processing protocol that reduces data variability and provides a reasonably unbiased estimate of the mean contaminant concentrations in an area/volume of soil targeted for sampling. ISM provides representative samples of specific soil areas/volumes defined as decision units (DUs) by collecting numerous increments of soil (typically 30-100 increments) that are combined, processed, and subsampled according to specific protocols.

3.4. Grinding: A generic term for soil disaggregation or milling (ITRC Guidance Appendix E). The term grinding does not in itself represent any specific process.

3.5. Disaggregation: The act of breaking the soil clumps into individual small particles but keeping the small pebbles and hard crystalline particles intact (ITRC Guidance Appendix E).

3.6. Milling: Complete particle size reduction of all soil components including hard crystalline materials to a defined maximum particle size (e.g. <250 µm or <75 µm) (ITRC Guidance Appendix E).

3.7. Sample: For laboratory technicians, the sample is all the material delivered to the laboratory in a container collected by the field crew.

3.8. Subsample: The small representative amount removed from a field sample that selected for final analysis. Also referred to in some SOPs as “the aliquot”.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section of each analytical SOP. Specific selection of reagents may be required to avoid introduction of contaminants (i.e. samples being analyzed for VOCs should generally not come into contact with equipment that has been solvent-rinsed with acetone or methylene chloride).

4.2. Metallic components of particle size reduction equipment can contribute some metal content to the solid samples. Hence carbon steel components are usually preferable to stainless steel when necessary to minimize contamination from chromium, nickel and molybdenum. Some contamination from iron is common.

4.3. Particle size reduction equipment blanks should be generated before use. The type of blank generated may vary for each piece of equipment, and may be solid or aqueous in nature.

5. SAFETY

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

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled.

Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

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

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

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Overexposure may include headache, drowsiness and dizziness. Methanol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur: symptoms may be parallel to inhalation exposure. Irritant to the eyes.
Hydrochloric acid	Corrosive Poison	5ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Note: Always add acid to water to prevent violent reactions.			

1 – Exposure limit refers to the OSHA regulatory exposure limit.

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

5.6. When operating the electric chopper or grinder, be sure to keep all aqueous liquids clear to prevent the risk of electrical shock from any spills.

5.7. Avoid inhalation of sample dust. Work in a ventilation hood when necessary to avoid accidental dust inhalation. Wear a dust mask or respirator if the ventilation hood does not provide sufficient dust protection. The Environmental Health and Safety Coordinator must approve any and all use of dust masks and/or respirators.

5.8. If there is any malfunction in the equipment de-energize and tag out.

5.9. All noise levels are below OSHA limits.

5.10. Training: Only trained personnel are permitted to use the equipment mentioned in this document. A list of trained personnel will be maintained with EH&S and QA.

6. EQUIPMENT AND SUPPLIES

6.1. Drying tray, plastic or aluminum

6.1.1. Half cake sheet pan, Pactiv #614255, or equivalent

6.1.2. Quarter sheet cake pan, Pactiv #604245, or equivalent

6.2. Butcher Paper

6.3. Plastic wrap

6.4. Mortar and pestle

6.5. Automated mortar grinder

6.6. Food chopper, Black and Decker Handi chopper, or DeLonghi mini food processor, or equivalent

6.7. Coffee grinder, KitchenAid BCG100 or equivalent

6.8. Automated soil disaggregator

6.9. Wooden spatula: 6 in.

6.10. Stainless steel sieves: 1 mm, #10, #20, #60, #100, ¼ inch, other sizes by request with advanced notice

6.11. Electrolux Assistant 8 qt mixer, with dough hook or equivalent

6.12. Large cookie scoop with hand actuated ejector blade

6.13. Small cookie scoop with hand actuated ejector blade

6.14. Fluoropolymer scoop, not commercially available

6.14.1. Construct by fastening the bottom half of a fluorpolymer bottle to a wooden handle with stainless steel screws.

6.15. Stainless steel pot with cover, Bain-Marie 6 qt. or equivalent

6.16. Wooden spoon, 12” long

Picture of labware for multi-increment sample wet mixing process (Section 11.3.2.5): large scoop, small scoop, wooden spoon, fluoropolymer scoop, stainless steel pot/cover

6.17. Jaw crusher, Sepor Model 150 or equivalent

6.18. Freezer for sample storage.

6.19. 8 oz. Glass jars with lids

6.20. Top loading balance capable of weighing 100 g ±0.2 g.

6.21. Aluminum foil

7. REAGENTS AND STANDARDS

7.1. Deionized water: Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of preparation blanks.

7.2. Methanol: VOC grade

7.3. Acetone: Pesticide grade

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Not applicable to this procedure. Sample collection, preservation, and storage are dependent on the requested test method and analytes.

9. QUALITY CONTROL

9.1. Equipment processing blanks might be applicable for some particle size reduction or selection techniques. There is no single blank matrix that is suitable for all analytes, equipment or processes. The blank matrix should be chosen by the client/data user based on the advantages and limitations described below in Section 9. If no blank matrix is selected by the client, reagent water should be used as the default when possible as noted in Section 9.2.

9.2. Reagent water (or organic solvents) may be used to rinse the equipment surfaces. This liquid is then analyzed for the target analytes. This process is good at monitoring residue on equipment surfaces from previously processed samples. It does not evaluate the potential contribution of the equipment surface material to a solid sample. Sand may be run through processing equipment and then analyzed to monitor for both sample carryover residue and contamination from equipment surface erosion. This process is most applicable for organic analytes. Sand always contains metals. These metals concentrations might be too high for suitable blank demonstrations. Also, the sand material is frequently more abrasive than soil and can over-estimate sample contamination due to erosion of the equipment surfaces.

9.3. Teflon boiling chips can be suitable to monitor the cleanliness of processing equipment surfaces. This option is between reagent water and sand regarding abrasion of the equipment surfaces. This material is generally non-detect at parts per billion concentrations for most organic and inorganic analytes. The Teflon material does not mimic the behavior of soil in the subsequent sample extraction or digestion procedures.

9.4. As an alternative to or in addition to equipment blanks, half of a field sample may be reprocessed with the goal of evaluating differing analyte concentrations between the single and double processed sample aliquots. The occurrence of significantly elevated analyte concentrations in the double processed sample can be a good indication of carryover or contamination due to equipment surface erosion. This is most applicable for monitoring metals contamination in soil grinders.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable to this procedure.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

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

11.3. Sample Preparation

11.3.1. The following sections describe a variety of procedures. The client/data user must select the procedure that is most appropriate for the sample matrix, analytes, and quality objectives. The selection of the procedure(s) can be made by the client in consultation with the appropriate TestAmerica representatives during project planning. There is no single default procedure that can be used in the absence of client selection.

11.3.2. Solid Sample Mixing and Particle Size Reduction Procedures

11.3.2.1. In jar mixing

11.3.2.1.1. The flowable sample is thoroughly stirred in the sample jar using a wooden blade.

11.3.2.2. Horizontal surface mixing

11.3.2.2.1. The sample is transferred to an aluminum tray or onto a sheet of paper and mixed with a wood blade.

11.3.2.3. Mortar and pestle

11.3.2.3.1. A mortar and pestle can be used for samples in the 1 to 8 mm particle size. The final reduced size is between 5 um and 8 mm. This process can be used for wet or dry, organic or inorganic substances.

11.3.2.3.2. Fill the mortar about 1/3 with sample. Grind and mix the sample with the pestle. Transfer the processed sample to a separate container, and repeat the grind-and-mix step with additional sample aliquots as needed.

11.3.2.3.3. An automated mortar grinder may be appropriate for larger samples. Set the automated mortar grinder to the desired size and allow to run until the sample has been completely ground. If the grinder is not equipped with an automated scraper/agitator, the sample may be mixed by hand. Be sure that the grinder has stopped moving completely before opening the lid.

11.3.2.4. Dry mixing (incremental sampling methodology support)

11.3.2.4.1. Air dry, disaggregate, sieve, mix

11.3.2.4.1.1. Line a standard aluminum tray with a disposable aluminum tray ($^1/_2$ or $^1/_4$ sheet depending on sample size). If aluminum is a metal of interest line the tray with butcher paper. Do not use butcher paper when TOCs are of interest.

11.3.2.4.1.2. Remove large rocks and vegetation unless client indicates otherwise. Do not decant the free water. Mix the sample and spread the entire sample in a thin layer in the tray. If necessary to perform a pre-dried total solids analysis, remove approximately 10 g. If the samples require ISM processing, an appropriate subsampling procedure should be followed, as described in the subsampling SOP.

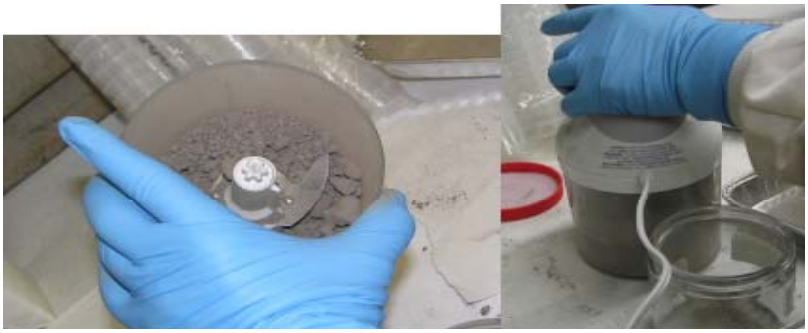
Note: it is not recommended to remove any portion of an ISM sample prior to drying and disaggregation. Any such removal from an ISM sample is considered a deviation and should be approved by the client.

11.3.2.4.1.3. Place the tray in the ventilated drying rack for up to five days at room temperature.

11.3.2.4.1.4. Periodically, stir the sample to expose moist sample to the air.

11.3.2.4.1.5. The dried sample must be crushable, and not prone to sticking together. Typically this means that sediment samples will be less than 30% moisture content and soil samples less than 15% moisture content. However, it is not necessary to do a percent moisture analysis.

11.3.2.4.1.6. Disaggregate the dried sample to break up the dried sample clumps with a bladed chopper or equivalent, but do not grind the small pebbles into powder.



11.3.2.4.1.7. If the volume capacity of the disaggregation equipment is large enough, transfer the whole sample to the disaggregator. If sample volume is too large, disaggregate the sample in sub-aliquots.

11.3.2.4.1.8. Pass the sample through a sieve to remove small pebbles and organic materials. Project specific guidelines will determine the sieve opening size. Typically, a #10 sieve is used for soils.

11.3.2.4.1.9. Combine all disaggregated sub-aliquots, and mix thoroughly by stirring, shaking or tumbling.

11.3.2.4.2. Air dry, disaggregate, mix

11.3.2.4.2.1. When the project objectives dictate that all small and medium sized materials be included in the final sample, use the procedure described in Section 11.3.2.4.1, but skip the sieving step in Section 11.3.2.4.1.8.

11.3.2.4.2.2. Collecting a representative subaliquot is more difficult when the sample has a variety of particle sizes. Refer to the subsampling SOP for recommended procedures. The one dimensional slabcake process is particularly applicable to dry, flowable samples with a wide range of particle sizes.

11.3.2.4.3. Other

11.3.2.4.3.1. Various permutations of soil disaggregation and sieving are possible depending on the needs of the project and can be accommodated but must be clearly defined in consultation with the client. These variations can include different sieve sizes and changing the order so that sieving is done prior to disaggregation. This would most likely be done to exclude a particular size of organic or rocky material.

11.3.2.5. Wet mixing (incremental sampling methodology support)

11.3.2.5.1. Weigh 100.0 +/- 0.2 g of each ¼ acre sub-sample. Stir the sample prior to and during the transfer from the original container to the weighing container. Record the weight to two decimal places.

11.3.2.5.1.1. If there are fewer than 40 sub-samples, increase the weight of sample proportionally. Calculate the new target weight as follows: target weight = 4000g/# sub-samples.

11.3.2.5.1.2. Exclude rocks, organic matter, and other debris from the weighed sub-sample by sieving through a ¼ inch sieve prior to weighing when such material is present.

11.3.2.5.1.3. The sieve may also be used to break up clay chunks. Sieving may be done either before or after weighing for this purpose. Use only when needed. Hard dry soil agglomerates should be broken up by hand crushing or chopping with a food chopper.

11.3.2.5.1.4. If a sub-sample is over ½ gravel, expand the maximum particle size from ¼ inch to 1.8 inches.

11.3.2.5.2. Transfer the weighed (and sieved as needed) sub-sample aliquot to a stainless steel pot used to collect all weighed

aliquots for that composite sample. The total mass of the composite sample will be at least 4 kg.

11.3.2.5.3. Repeat Section 11.3.2.5.1 until all sub-samples have been weighed and transferred to the compositing pot.

11.3.2.5.4. Assemble the heavy-duty mixer with mixing hook. The mixing hook must be inserted high in the mounting bracket to avoid dragging on the bottom of the bowl and allow small stones to pass under the hook. Transfer the entire composite sample from the covered stainless steel pot to the stainless mixing bowl.

11.3.2.5.5. Turn on mixer. Add reagent water to ensure complete mixing of the sample. The mixed sample will have uniformly distributed water, look visually homogeneous, and have the consistency of a thick paste. Do not add so much water as to form runny slurry. Use a wooden spoon to assist the mixing process by scraping mud from the sides and directing it to the center. The picture below shows the proper consistency. Mix for three minutes after the proper consistency has been achieved.

completely mixed composite sample.mpg

11.3.2.5.6. Record the volume of reagent water added and the total mixing time.

11.3.2.5.7. Scrape the mud from the wooden spoon and mixing hook.

11.3.2.5.8. Split the composite sample between 5-15 250 mL jars, depending on project requirements.

11.3.2.5.9. Use the large scoop to dispense the equal aliquots of the composite sample--one aliquot into each of 8 oz. jars. Repeat the process if there is sufficient sample for a complete set of large scoop aliquots (per Section 11.3.2.5.8).

11.3.2.5.10. Once the volume of wet composite sample in the bowl is less than the determined set of large scoops, switch to aliquoting with the small scoop. Dispense an equal amount of small scoops--one into each 8 oz. jar.

11.3.2.5.11. Use the fluoropolymer scoop to scrape inside the bowl, and dispense this part of the sample with the small scoop. If there is insufficient sample to use full scoops, the use of replicate partial scoops is acceptable.

11.3.2.5.12. When aliquoting is complete, the composite sample has been evenly distributed among the 8 oz. jars. Note: Multiple

jars are used for various analyses, quality control, and archive purposes.

11.3.2.5.13. Mix the contents of each 250 mL jar and remove about 10 g from each of the first three jars for three total solids (percent moisture) analyses. The relative percent difference (RPD) between the first two must not exceed 8%.

11.3.2.5.13.1. If the RPD exceeds 8%, repeat the total solids analysis on two fresh aliquots from the first two jars.

11.3.2.5.13.2. If the RPD still exceeds 8%, repeat the mixing process in Sections 11.3.2.5.1 to 11.3.2.5.12

11.3.2.5.14. Wipe the top of the jar to remove excess sample and install the cap. Transport all sample containers to Sample Receiving.

11.3.2.5.15. Discard the wooden spoon and spatulas. Wash the mixer bowl, hook and scoops using soap and water. Rinse with tap and reagent water.

11.3.2.6. Soil fractionation for lead analysis

11.3.2.6.1. Add sample ID label to outside of a disposable aluminum ($^1/_2$ or $^1/_4$ sheet depending on sample size). Line with butcher paper if aluminum is also an analyte of interest.

11.3.2.6.2. Transfer the soil sample to a tray. Remove large rocks and vegetation.. Spreading the sample in a thin layer speeds drying and reduces the formation of hard clay chunks.

11.3.2.6.3. Place the tray in the ventilated drying rack for up to five days.

11.3.2.6.4. Periodically, stir the sample if needed to expose moist sample to the air. The butcher paper may also be changed, if it has become damp.

11.3.2.6.5. Samples with high clay content tend to form large, hard clay aggregates. To reduce the formation of these hard "bricks", use the bottom of a clean disposable beaker to gently crush the semi-dried sample before drying is complete.

11.3.2.6.6. Allow the sample to dry until crumbly.

11.3.2.6.7. Assemble 8-inch sieve stack. The order from the bottom of the stack is collection pan, #60 sieve, and #10 sieve. Transfer sample ID label from drying pan to sieve stack.

Note: Project-specific sieve size requirements may vary from the reference method. These will be noted in TALS, both in the project and in the method or login notes. #100 (150um) sieves are commonly used in place of #60 sieves. The smallest sieve size should be the closest to the collection pan, with the next size up above it.

11.3.2.6.8. If significant amounts of clay are present, aggregates may be broken by pressing gently with a hand-operated mortar and pestle. Note that only this gentle crushing is permitted by the reference method. Samples that are being analyzed as soil fractions for lead should not be subjected to aggressive disaggregation such as the use of a soil disaggregator or coffee grinder.

11.3.2.6.9. Transfer dried soil to the #10 sieve at the top of the sieve stack. If fine particulates are present, use sufficient ventilation to prevent the analyst from inhaling the dust. Install sieve cover.

11.3.2.6.1. Place the sieve stack on the shaker table and secure. Run the shaker for one hour. Stop the shaker and remove the lid for each sample to check on the progress of sieving. Shake the samples by hand (in a different direction than the shaker table has traveled). If any sample passes through the sieve at this point, place the sieve stack(s) back on the shaker and shake for up to one additional hour.

11.3.2.6.2. Do not extend shaking beyond two hours without conferring with the client.

11.3.2.6.3. Record the weights of the three fractions--large (did not pass through the #10 sieve), coarse (passed through #10 sieve, but not the #60 sieve), and fine (passed through both #10 and #60 sieves). If different sieve sizes have been used, record the sizes on the bench sheet.

11.3.2.6.4. To weigh each fraction, place the corresponding sieve or pan on the balance, press “Tare”, transfer the fraction, and place sieve or pan back on the balance. The weight of the fraction will read as a negative value.

11.3.2.6.5. Discard the large fraction. Mix the fine fraction. Remove approximately 10g for total solids analysis. If required, perform splitting and/or subsampling in accordance with ISM procedures. See the subsampling SOP for further information.

11.3.2.6.6. If the coarse fraction is to be analyzed separately, mix the coarse fraction and remove approximately 10g for total solids analysis. The coarse fraction should be ground in a mortar

and pestle (Section 11.3.2.3) prior to removing the aliquot for metals digestion.

11.3.2.6.7. The combination of coarse and fine fractions is defined as the "total". If the "total" is to be measured, weigh 1/10 of the coarse fraction and 1/10 of the fine fraction. Combine, mix, and remove approximately 10g for total solids analysis.

11.3.2.6.8. Bottle coarse, fine, and "total"(if needed) fractions for metals analysis.

11.3.2.6.9. For Michigan samples, the "total" result is calculated from a weighted average of the results from the fine and coarse fractions.

Total Lead = [(A x Wf) + (B x Wc)] / (Wf + Wc)

Where:

A = Concentration of Lead (mg/Kg dry) in fine fraction

B = Concentration of Lead (mg/Kg dry) in coarse fraction

Wf = Total weight of fine fraction

Wc = Total weight of coarse fraction

11.3.2.6.10. Wash the sieves with soap, tap water, and deionized water. Dislodge objects from the screen with a green scratch pad, wooden tongue blade or small screwdriver, as necessary. Dry sieves in a low-heat oven or air-dry at ambient temperature over night, depending how soon they will be needed.

11.4. Sample Analysis

11.4.1. Not applicable to this procedure.

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable to this procedure.

13. METHOD PERFORMANCE

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

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. Used wood spatulas, aluminum sheets, butcher paper; discard in solid waste.

15.2.2. Dry ice is to be melted in the sink.

15.2.3. Acetone is to be disposed of in an appropriately labeled flammable waste barrel.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. U.S. EPA, 2000. TRW Recommendations for Sampling and Analysis of Soil at Lead (Pb) Sites. EPA-540-F-00-010. OSWER 9285.7-38. April. Available on-line at: http://www.epa.gov/superfund/programs/lead/products/sssiev.pdf

16.1.2. U.S. EPA, 2003. TRW Recommendations for Performing Human Health Risk Analysis on Small Arms Shooting Ranges. OSWER 9285.7-37. March. Available on-line at: http://www.epa.gov/superfund/programs/lead/products/firing.pdf

16.1.3. U.S. EPA, 2003. Superfund Lead-Contaminated Residential Sites handbook. OSWER 9285.7-50. August. Available on-line at: http://www.epa.gov/superfund/programs/lead/products/handbook.pdf

16.1.4. Michigan DEQ SOP #213 Revision #1, Nov. 9, 2004, Soil Fractions Preparation for Lead Analysis (Creating Total, Fine and Coarse Soil Samples).

16.1.5. ASTM D 6323-12, Laboratory Subsampling of Media Related to Waste Management Activities, 2012

16.1.6. ITRC Incremental Sampling Methodology, Available online at: http://www.itrcweb.org/ism-1/

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

16.1.8. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.9. Corporate Quality Management Plan (CQMP), current version

16.1.10 Revision History

Historical File:		Revision 0: 11/27/13		
		Revision 1: 01/23/15		
		Revision 2: 05/31/17		
		4/2/19: changed logo. No change		
		to revision # or date.		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. Not applicable to this procedure

17.2. Method deviations – None

Title: SUBSAMPLING

[Method: ASTM D6323-12]

Approvals (Signature/Date):

Technology Specialist	05/15/19 Date	Health & Safety Coordinator	05/16/19 Date
Quality Assurance Officer	06/18/19 Date	Technical Director	05/29/19 Date

This SOP was previously identified as SOP No. NC-OP-046, Rev 2, dated 5/31/17

Facility Distribution No. _____ **Distributed To:_____**

The controlled copies of this SOP are the PDF copy that is posted to the laboratory's SOP Directory and, where applicable, the copy that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies distributed outside of the facility are considered uncontrolled.

1. SCOPE AND APPLICATION

1.1. These mixing, subsampling, and splitting techniques are applicable to a wide range of soil, sediment, tissue, water, and waste samples. Care must be taken to match the appropriate technique with the matrix, target analytes and quality objectives.

1.2. The goal of all mixing, subsampling, and splitting techniques is to obtain representative splits or subsamples for preparation and analysis. Particle size reduction and processing can be beneficial in obtaining representative subsamples and specific processes for particle size reduction and processing can be found in the soil processing SOP (NC-OP-044) and non-soil processing SOP (NC-OP-045).

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

NOTE: If foreign or quarantined solids are received, refer to SOP NC-SM-019 Canton Foreign Soils, current revision, and contact your Environmental Health and Safety Coordinator for proper handling instructions.

2. SUMMARY OF METHOD

2.1. All samples should be mixed and subsampled appropriately for the test and analytes of interest.

2.2. Solid sample mixing procedures include in-jar mixing, horizontal surface mixing, and mortar and pestle.

2.3. Solid sample subsampling procedures include alternate scoop, one-dimensional slabcake, two-dimensional slabcake, and cone and quarter methods.

2.4. Liquid sample subsampling procedures include centrifuge, pipettes, coliwasa devices, and multiphase procedures.

3. DEFINITIONS

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

3.2. Mix: To thoroughly blend the sample and reduce the analyte concentration differences between different parts of the overall sample. It is most effective when the particle size and density differences within the sample are small.

3.3. Incremental Sampling Methodology: A structured composite sampling and processing protocol that reduces data variability and provides a reasonably unbiased estimate of the mean contaminant concentrations in an area/volume of soil targeted for sampling. ISM

provides representative samples of specific soil areas/volumes defined as decision units (DUs) by collecting numerous increments of soil (typically 30-100 increments) that are combined, processed, and subsampled according to specific protocols.

3.4. Grinding: A generic term for soil disaggregation or milling.

3.5. Disaggregation: The act of breaking the soil clumps into individual small particles but keeping the small pebbles and hard crystalline particles intact.

3.6. Milling: Complete particle size reduction of all soil components including hard crystalline materials to a defined maximum particle size (e.g. <250 µm or <75 µm).

3.7. Sample: For laboratory technicians, the sample is all the material delivered to the laboratory in a container collected by the field crew.

3.8. Subsample: The small representative amount removed from a field sample selected for final analysis. This is also referred to in some SOPs as the aliquot.

3.9. Representative subsample: A subsample taken in such a way that each particle had an equal chance of being selected. The most representative subsample is one that most closely resembles the true value of the material sampled or contains the least amount of error.

4. INTERFERENCES

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

4.2. Metallic components of particle size reduction equipment can contribute some metal content to the solid samples. Hence carbon steel components are usually preferable to stainless steel when necessary to minimize contamination from chromium, nickel and molybdenum. Some contamination from iron is common.

5. SAFETY

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

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

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

5.4. There are no materials used in this method that have a significant or serious hazard rating. A complete list of materials used in the method can be found in the reagents and standards section. Employees must review the information in the Safety Data Sheet (SDS) for each material prior to using it for the first time, or when there are major changes to the SDS.

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

5.6. When operating the electric chopper or grinder, be sure to keep all aqueous liquids clear to prevent the risk of electrical shock from any spills.

5.7. Avoid inhalation of sample dust. Work in a ventilation hood when necessary to avoid accidental dust inhalation. Wear a dust mask or respirator if the ventilation hood does not provide sufficient dust protection.

5.8. If there is any malfunction in the equipment. De-energize and tag out.

5.9. All noise levels are below OSHA limits.

5.10. Only trained personnel are permitted to use crushing equipment. A list of trained personnel will be maintained with EH&S and QA.

6. EQUIPMENT AND SUPPLIES

6.1. Butcher Paper

6.2. Plastic wrap

6.3. Aluminum foil

6.4. 8 oz. Glass jars with lids

6.5. Top-loading balance.

6.6. Appropriate containers for each subsample

7. REAGENTS AND STANDARDS

7.1. Deionized water: Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of preparation blanks.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Not applicable to this procedure. Sample collection, preservation, and storage are dependent on the requested test method and analytes.

9. QUALITY CONTROL

9.1. Equipment processing blanks might be applicable for some particle size reduction or selection techniques. There is no single blank matrix that is suitable for all analytes, equipment or processes. The blank matrix should be chosen by the client/data user based on the advantages and limitations described below in Section 9. If no blank matrix is selected by the client, reagent water should be used as the default when possible, as noted in Section 9.2.

9.2. Reagent water (or organic solvents) may be used to rinse the equipment surfaces. This liquid is then analyzed for the target analytes. This process is good at monitoring residue on equipment surfaces from previously processed samples. It does not evaluate the potential contribution of the equipment surface material to a solid sample.

9.3. Sand may be run through processing equipment and then analyzed to monitor for both sample carryover residue and contamination from equipment surface erosion. This process is most applicable for organic analytes. Sand always contains metals. These metals concentrations might be too high for suitable blank demonstrations. Also, the sand material is frequently more abrasive than soil and can over estimate sample contamination due to erosion of the equipment surfaces.

9.4. Teflon boiling chips can be suitable to monitor the cleanliness of processing equipment surfaces. This option is between reagent water and sand regarding abrasion of the equipment surfaces. This material is generally non-detect at parts per billion concentrations for most organic and inorganic analytes. The Teflon material does not mimic the behavior of soil in the subsequent sample extraction or digestion procedures.

9.5. Reprocess half of a field sample and look for differing analyte concentrations between the single and double processed sample aliquots. The occurrence of significantly elevated analyte concentrations in the double processed sample can be a good indication of carryover or contamination due to equipment surface erosion. This is most applicable for monitoring metals contamination in soil grinders.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable to this procedure.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

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

11.3. Sample Preparation

11.3.1. The following sections describe a variety of procedures. Additional procedures for sample preparation are available in the Soil and Non-Soil Processing SOPs. The client/data user must select the procedure that is most appropriate for the sample matrix, analytes, and quality objectives. The selection of the procedure(s) can be made by the client in consultation with the appropriate Eurofins TestAmerica representatives during project planning. There is no single default procedure that can be used in the absence of client selection.

11.3.2. Solid Sample Mixing Procedures

11.3.2.1. In jar mixing

11.3.2.1.1. The flowable sample is thoroughly stirred in the sample jar using a wooden blade.

11.3.2.2. Horizontal surface mixing

11.3.2.2.1. The sample is transferred to an aluminum tray or onto a sheet of paper and mixed with a wooden blade.

11.3.3. Solid Sample Subsampling Procedures

11.3.3.1. Multiple increments from a jar

11.3.3.1.1. Select 5-10 small sample increments from various locations within the sample container to make the entire subaliquot. The increments must come from all general areas of the container--top, sides, center, and bottom.

11.3.3.2. Two dimensional slabcake

11.3.3.2.1. Spread the sample to a consistent depth on a clean flat area covered with an appropriate disposable cover (butcher paper, aluminum tray or foil or plastic depending on the analytes of interest).

11.3.3.2.2. Select 30 or more small increments spread evenly over the sample area or as dictated by client data quality objectives.

The increments must be collected with a blunt end spatula or scoop to evenly collect from the top middle and bottom of the slabcake. A coring device of suitable material can also be used if the sample is sufficiently cohesive (e.g. moist soil).

11.3.3.2.3. If the sample has noxious odors or produces dust, the sample spreading and increment collecting should be performed in a hood or large flat bag of appropriate material. The analyst must be protected from potential inhalation hazards from the sample.

11.3.3.3. Alternate scoop

11.3.3.3.1. Wet or dry solid samples can be divided into two or more smaller aliquots. Determine the number of sub-aliquots, and prepare that many empty containers.

11.3.3.3.2. Scoops of the mixed laboratory sample are either placed in the analytical vessel or discarded.

11.3.3.3.3. Three scoops are discarded for every scoop saved. Randomly select an aliquot and place in the first container. Place the next three aliquots in the second container. Repeat as needed for additional aliquot containers.

11.3.3.3.4. Repeat the aliquoting cycle until the original sample is consumed.

11.3.3.3.5. The alternate scoop technique can also be used to subaliquot discrete samples that are to be homogenized into one composite sample.

11.3.3.3.5.1. Determine approximately the ratio of aliquot to discard scoops required to consume the sample and achieve the aliquot size required for homogenization. For example, if a 50 g aliquot is desired from a 250 g sample, a ratio of one scoop used to four scoops discarded will be used.

11.3.3.3.5.2. For each discrete sample, set up two empty containers of appropriate volume.

11.3.3.3.5.3. Stir each discrete sample in its container, or if necessary homogenize on a sheet of butcher paper and return to the jar.

11.3.3.3.5.4. Place one of the empty containers on a balance and tare it. Place one scoop of sample from the top

of the discrete sample jar into this container. This will be the portion used for a homogenized composite later.

11.3.3.3.5.5. Into the second jar, place the three or more (as determined in Section 11.3.3.3.5.1) scoops to be discarded.

11.3.3.3.5.6. Repeat Sections 11.3.3.3.5.4 and 11.3.3.3.5.5 until the sample has been consumed and the desired weight of the subaliquot is in the tared container. Record the weight of the sub-aliquot.

11.3.3.3.5.7. Repeat this process for all of the discrete samples that will be used for the composite, using approximately equal weights of each discrete sample.

11.3.3.3.5.8. After all discrete samples have been sub-aliquoted using the alternate scoop procedure, combine them on a sheet of butcher paper and homogenize. Pour the homogenized sample volume into the labeled sample jar for the composite sample.

11.3.3.4. One dimensional slabcake

11.3.3.4.1. This process is intended to produce large sub-samples from very large dry flowable solid samples, such as those collected using \incremental sampling methodology, dried and then chopped using the process described in Section 1.1.1See Reference 16.1.7.

11.3.3.4.2. Pour the dry soil sample into a long thin pile onto a clean horizontal surface. The pour height should not exceed 20 cm to minimize the formation of a dust cloud.

11.3.3.4.3. Ensure that the sample container makes at least 20 passes back and forth over the “line of sample”.

11.3.3.4.4. Using a rectangular flat-bottomed scoop, remove an increment from the “line of sample”. Ensure that a complete cross cut of the sample line includes the entire depth of that increment. Combine increments as needed to produce the needed sub-sample size.

11.3.3.5. Cone and quarter (for dry flowable samples)

11.3.3.5.1. Pour the sample into a cone on a clean flat area covered with an appropriate disposable cover (butcher paper, aluminum foil, or plastic depending on the analytes of interest).

11.3.3.5.2. Cut the cone in half in two directions to form four quadrants.

11.3.3.5.3. Return opposite quadrants to the original sample container.

11.3.3.5.4. Repeat the process in Sections 11.3.3.5.1 through 11.3.3.5.3 until the needed aliquot size has been obtained.

11.3.4. Liquid Sample Mixing Procedures

11.3.4.1. Closed container shaking

11.3.4.1.1. All liquid samples should be mixed by shaking in the original closed sample container unless a multiple layer sub-aliquoting procedure is used. This applies to emulsifiable layers such as oil and water and suspendable particulates in water. The sample must remain mixed long enough to pour out a representative aliquot. Samples that show noticeable separation in under a minute should be sub-aliquoted using an appropriate technique as described below.

11.3.4.1.2. The shaking process must be vigorous enough to mix and distribute analytes associated with different layers, particulates, or inside container walls.

11.3.5. Liquid Sample Subsampling Procedures

11.3.5.1. Pour

11.3.5.1.1. Samples that are well mixed can be sub-aliquoted by pouring an appropriate volume off the top of the sample.

11.3.5.2. Layer Subsampling

11.3.5.2.1. Some liquid samples with multiple layers separate too quickly to pour a representative sub-aliquot off the top. In some instances it is best to separate the layers and handle them as individual samples. In other instances representative aliquots of each layer must be collected and processed as a single sub-sample.

11.3.5.2.2. Unless directed otherwise, record the phase ratios (or volumes) of the layers.

11.3.5.2.3. Gravity or Centrifuge Settling

11.3.5.2.3.1. Allow the sample layers to separate based on density. Centrifugation can be used to accelerate the process if simple gravity settling is not fast enough.

11.3.5.2.4. Separatory Funnel

11.3.5.2.4.1. Gently pour the sample into a separatory funnel. Allow time for additional layer separation as needed.

11.3.5.2.4.2. Drain the layers out into separate containers one at a time.

11.3.5.2.4.3. Some oils stick to the separatory funnel sides so the draining process must be slow enough to avoid remixing the layers.

11.3.5.2.5. Pipette

11.3.5.2.5.1. Use a pipette of appropriate size to collect a sub-aliquot of a sample layer of interest and transfer to an empty container.

11.3.5.2.5.2. If the entire sample is to be separated, pipette almost all the top layer into a new container. Draw the small volume of the top layer into the pipette along with a small portion of the second layer. Allow the two layers to separate in the pipette (like a separatory funnel). Dispense the bottom layer back into original sample container with the bulk of the bottom layer. Next dispense the remaining top layer into the container that holds the top layer.

11.3.5.2.5.3. Repeat as needed for each layer of interest.

11.3.5.2.6. Coliwasa

11.3.5.2.6.1. A coliwasa is a “coring device” designed for liquid multi-layer samples. It is a long tube with a short valve at the bottom. When designed and used properly it collects representative aliquots of each layer with each sub-aliquoting immersion.

11.3.5.2.6.2. The volume collected is determined by the diameter of the coliwasa and the height of the sample. The larger the tube diameter or taller the sample height, the larger the volume of sample collected.

11.3.5.2.6.3. Place the foot of the valve and its control rod in the multi-layer sample. Slowly slide the coliwasa tube over the control rod and close the ground glass seal of the valve at the bottom.

11.3.5.2.6.4. Lift the coliwasa by the control rod to keep the valve sealed.

11.3.5.2.6.5. Place the coliwasa over the new sample aliquot container. Grasp the top of the coliwasa tube and slowly lower the control rod a few millimeters to open the foot valve and drain the sample into the container.

11.3.5.2.6.6. Repeat Sections 11.3.5.2.6.3 through 11.3.5.2.6.5 until sufficient sample aliquot has been collected.

11.3.6. Multiphase Sample Mixing Procedures

11.3.6.1. All liquid samples should be mixed by shaking unless a multiple layer subaliquoting procedure is used. This applies to emulsifiable layers such as oil and water and suspendable particulates in water. The sample must remain mixed long enough to pour out a representative aliquot. Samples that show noticeable separation in under a minute should be subaliquoted using an appropriate technique as described below.

11.3.6.2. Closed container shaking

11.3.6.2.1. The shaking process must be vigorous enough to mix and distribute analytes associated with different layers, particulates, or inside container walls.

11.3.6.3. Open container stirring

11.3.6.3.1. The sample is stirred or swirled to mix.

11.3.6.4. Wet Sediments

11.3.6.4.1. Aqueous samples for non-volatile compound analysis may contain settleable materials. If the settleable materials are to be included as part of the laboratory sample, and they will remain suspended, or can easily be re-suspended and will remain so during the subsampling operation, the sample should be handled as a liquid sample. These samples should be gently swirled for 15 seconds or slowly inverted six times to reduce heterogeneity.

11.3.6.4.2. If the liquid portion only is to be used, the settleable material must be allowed to sink to the bottom before withdrawing the subsample.

11.3.6.4.3. If the settleable material will not remain suspended and is to be included in the analysis, the sample should be treated as a multilayered sample.

11.3.7. Multi-phase Sample Subsampling Procedures

11.3.7.1. Multi-layered samples may include liquid/liquid layers, liquid/solid samples, or solid/solid samples.

11.3.7.2. If the liquid portion of a sludge sample can be re-mixed with the solid portion and will re-separate over time, the sample should be handled as a solid sample.

11.3.7.3. If the solid portion will remain suspended or can easily be re-suspended, the sample should be treated as a liquid sample. Mixing may occur by inverting the container or with slight shaking

11.3.7.4. Layer Separating

11.3.7.4.1. Gravity/Centrifuge – The solid/liquid phase separation may be achieved by gently centrifuging the unopened container or by allowing it to sit undisturbed until the solid portion is settled.

11.3.7.4.2. Pipette – For liquid/liquid layers, separate the layers using a pipette. Each layer may be either transferred into another container or directly into the analytical vessel. Each separated portion is then handled as a homogeneous liquid sample.

11.3.7.4.3. Filter/Decant – For liquid/solid layers, the liquid subsample may be obtained by filtering or decanting the liquid portion from the solid portion. The liquid portion is then handled as a homogeneous liquid sample. The solid portion is handled as a solid laboratory sample.

11.4. Sample Analysis

11.4.1. Not applicable to this procedure

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable to this procedure.

13. METHOD PERFORMANCE

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

14. POLLUTION PREVENTION

14.1. It is Eurofins TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. Used wood spatulas, aluminum sheets, butcher paper; discard in solid waste.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Eurofins TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. U.S. EPA, 2000. TRW Recommendations for Sampling and Analysis of Soil at Lead (Pb) Sites. EPA-540-F-00-010. OSWER 9285.7-38. April. Available on-line at: http://www.epa.gov/superfund/programs/lead/products/sssiev.pdf

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16.1.3. U.S. EPA, 2003. Superfund Lead-Contaminated Residential Sites handbook. OSWER 9285.7-50. August. Available on-line at: http://www.epa.gov/superfund/programs/lead/products/handbook.pdf

16.1.4. Michigan DEQ SOP #213 Revision #1, Nov. 9, 2004, Soil Fractions Preparation for Lead Analysis (Creating Total, Fine and Coarse Soil Samples). Available on-line at: http://www.deq.state.mi.us/documents/deq-rrd-OpMemo_2_SoilFractionsPrepForLead.pdf

16.1.5. ASTM D 6323-12, Laboratory Subsampling of Media Related to Waste Management Activities, 2012

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

16.1.7. Eurofins TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and Eurofins TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.8. Corporate Quality Management Plan (CQMP), current version

16.1.10 Revision History

Historical File:		Revision 0: 11/27/14		
		Revision 1: 01/23/15		
		Revision 2: 05/31/17		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. Not applicable to this procedure

17.2. Method deviations – None

Title: INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

[Method: EPA Method 200.8, SW846 Methods 6020, 6020A, and 6020B]

Approvals (Signature/Date):

Technology Specialist	11/29/18 Date	Health & Safety Coordinator	01/07/19 Date
Quality Assurance Manager	12/27/18 Date	Technical Director	12/14/18 Date

This SOP was previously identified as SOP No. NC-MT-002, Rev 8, dated 10/27/17

1. SCOPE AND APPLICATION

1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Methods 6020, 6020A, 6020B, and 200.8. The source method lists the following elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Li, Mg. Mn, Ni, K, Ag, Tl, Se, Na, V, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the method.

1.2. The procedure is applicable to the analysis of waters (groundwaters and surface waters), soils, and wastes. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, biological matrices, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

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

2. SUMMARY OF METHOD

2.1. Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a radio frequency inductively coupled plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas, and by means of a water-cooled differentially-pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a resolution less than, or equal to, 0.9 AMU full width at 10% of the peak height. For analysis by Method 200.8, the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged, to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and the constituents of the sample matrix. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Isobaric Interferences: Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most

interferences of this type are corrected for by the instrument software.

4.2. Isobaric Molecular and Doubly Charged Ion Interferences: Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied; and the data flagged to indicate the presence of interferences. Using Collision Cell Technology (CCT) can reduce these interferences. Collision Cell Technology is accomplished by adding an auxiliary gas into the lens chamber. The ions are dissociated into their component atoms/ions or converted into non-interfering species. The transmission of analyte ions is minimally affected. This process is called Kinetic Energy Displacement (KED).

4.3. Physical Interferences: Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.3.1. Generally, the mass of the internal standard should be no more than 50 AMU (Atomic Mass Unit) of the mass of the measured analyte.

4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank.

4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards, which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

4.3.4. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be demonstrated routinely to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014.Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

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

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

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

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. The RF Generator produces strong radio frequency waves--most of which are unshielded. People with pacemakers must not go near the instrument while in operation.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

5.6. The ICPMS plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.7. All work must be stopped in the event of a known or potential compromise to the health

and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Argon gas: High purity grade (99.99%)

6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution less than, or equal to, 0.9 AMU at 5% peak height from a mass range of at least 6-240 and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.3. A three channel peristaltic pump

6.4. Appropriate water-cooling device

6.5. Calibrated adjustable pipettes

6.6. Autosampler with autosampler tubes

6.7. Helium

6.8. Hydrogen

7. REAGENTS AND STANDARDS

7.1. Stock Standards

7.1.1. Stock standards are purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock standard solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017.

7.2. Intermediate / Working Standards

7.2.1. Intermediate / Working standards are prepared as dilutions from the stock standards. Intermediate / working standard solutions are stored according to manufacturer's instructions. Intermediate / working standard solutions must be replaced after 6 months or according to the stock standard expiration date if

less than 6 months. The intermediate / working standard solution must be replaced if verification from an independent source indicates a problem.

7.3. Refer to the LIMS standards and reagents module for further details on preparation of intermediate / working standard solutions.

7.4. Reagent water - ASTM Type I, or equivalent for the elements of interest, generated using an ion-exchange water polishing system.

7.5. Rinse Solution – 2% HNO3 and 1% HCL in reagent grade water.

7.6. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.7. Concentrated hydrochloric acid (HCl), trace metal grade or better

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Aqueous samples are preserved with nitric acid to a pH of < 2, and may be stored in plastic or glass. Preservation must be verified prior to analysis.

8.2. Soil samples do not require preservation, but must be stored at 4° ± 2°C until the time of preparation.

8.3. The analytical holding times for metals are six months from the time of collection to analysis.

8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.

8.5. Samples preserved in the laboratory must be held for 24 hours before digestion.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. Instrument Detection Limit (IDL)

9.1.1.1. The IDL will be determined by calculating the average of the standard deviation of three runs on three non-consecutive days (one day for method 6020B) from the analysis of a reagent blank solution with ten consecutive measurements each day. Each measurement must be performed as though it were a separate analytical sample (i.e., each

measurement must be followed by a rinse at minimum). The IDL must be performed quarterly (annually for Method 6020B). The IDL is calculated by multiplying by three, the average of the standard deviations obtained on three nonconsecutive days. .

9.1.2. Linear Calibration Ranges

9.1.2.1. Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions occurs. In the judgment of the analyst, linear ranges may be lowered based on results obtained during the verification process. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the maximum concentration at which sample results can be reported. The linear range must be verified every six months for Method 6020A and must be within 10% of the true value. For Method 6020B, the upper linear range must be verified daily for samples exceeding the calibration range and must be within 10% of the true value.

9.1.2.2. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards.

9.1.2.3. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value

9.2. Batch Definition

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

9.3. Method Blank (MB)

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

contain any analyte of interest at, or above, the reporting limit (exception: common laboratory contaminants see below) or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10x higher than the blank contamination level).

Note: For Ohio VAP samples, all analytes must be less than the reporting limit unless the sample results are below the requested reporting limit. The exception for 10x blank contamination does NOT apply for OVAP samples.

9.3.2. Corrective Action for MBs

9.3.2.1. If the analyte is a common laboratory contaminant (copper, iron, lead, barium, chromium, manganese, calcium, potassium, magnesium, sodium, or zinc), the data may be reported with qualifiers if the concentration of the analyte in the MB is less than two times the RL. **This is not applicable for Ohio VAP samples.**

9.3.2.2. Re-preparation and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the samples (see exception noted above).

9.3.2.3. If there is no analyte greater than the RL in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action must be addressed in the project narrative.

9.3.2.4. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Methods 6020, 6020A, and 6020B have criterion of 80%-120%. For Method 200.8, LCS limits are 85-115%. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and corrective action must take place before the analysis can be reported.

9.4.2. Corrective Action for LCS

9.4.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.4.2.2. The only exception is if the LCS recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest. **This must be addressed in the project narrative.**

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

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. The spike recovery acceptance limits for each analyte are in the LIMS system. If they are not in control, and all other quality control criteria have been met, then matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the analyst shall determine if the MS/MSD is spiked properly and/or the matrix of the sample is the result of the MS/MSD or RPD failure. If it has been determined that the MS/MSD was not spiked properly and/or the failure is not a result of matrix then the sample along with the MS/MSD will be re-digested and analyzed.

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

9.5.2.2. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is flagged with a “4” in LIMS.

9.5.2.3. For Method 6020A and 6020B, a post digestion spike will be run on a sample if the MS/MSD for the sample falls outside of the percent recovery criteria. A post digestion spike is a matrix spike on the same sample from which the MS/MSD aliquots were prepared, where the spike is added after the sample preparation is completed. The post

digestion spike recovery for Method 6020A should be within 80-120% and for 6020B within 75-125%. If this spike fails, then the dilution test should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. A post digestion spike is not required for Method 200.8 nor Method 6020.

9.6. Sample Duplicate (DU)

9.6.1. A DU is a second aliquot of an environmental sample taken from the same sample container, when possible, that is processed with the first aliquot of that sample. That is, DUs are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.6.2. DUs may be performed in lieu of, or in addition to, MSDs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOP CA-Q-S-006.

9.8.2. MDLs are easily accessible via the LIMs.

9.9. General Corrective Action Requirements: The general requirements for evaluation of QC results and corrective action for failures is described in TestAmerica Policy QA-003. Ohio VAP projects must reference this SOP instead of Policy QA-003 for information on QC Samples.

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Startup: Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / EPA Tune

10.2.1. Tuning the Instrument

10.2.1.1. Tune the Instrument based on manufactures recommendations (See table 4 for recommended values).

10.2.2. EPA Tune

10.2.2.1. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of five times.

10.2.3. Check mass calibration and resolution daily.

10.2.3.1. Mass Calibration Check

10.2.3.1.1. The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.3.2. Mass Resolution Check

10.2.3.2.1. The resolution must be verified to be less than, or equal to, 0.9 amu full width at 5% peak height.

10.3. Initial Calibration

10.3.1. Calibrate the instrument for the analytes of interest according to manufacturer's instructions. The calibration should include a minimum of a blank and one standard. For a linear multi-point calibration curve, the correlation coefficient must be at least 0.995 for Method 200.8, 6020, and 6020B. The correlation coefficient must be at least 0.998 for Method 6020A. Report the average of at least three integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up. Instrument analytical runs may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are

met. Calibration standard concentrations and/or vendors are subject to change.

10.4. Initial and Continuing Calibration Verification (ICV/CCV)

10.4.1. Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a minimum frequency of 10 samples throughout the analytical run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value... Sample results may only be reported when bracketed by valid CCVs.

Note: The only exception is if the ICV/CCV recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.5. Low Level ICV/Low Level CCV (ICVL/CCVL)

10.5.1. The ICVL/CCVL for method 6020A must be within the 70 – 130% recovery range and analyzed at the beginning (ICVL) and end (CCVL) of the analytical sequence. For method 6020B the ICVL must be within 80%-120% and analyzed at the beginning of the analytical sequence. In addition a CCVL can be analyzed on a more frequent basis. If any analyte is outside the range indicated, the CCVL may be re-analyzed once. If the results fall within the required values upon re-analysis, no further corrective action needs to be taken. If still outside the acceptable range, then samples containing the affected analytes at similar concentrations cannot be reported and must be re-analyzed.

Note: The only exception is if the ICVL/CCVL recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest. **This must be addressed in the project narrative.**

10.6. RL Verification Standard (ICVL) Method 6020

10.6.1. An independent standard is analyzed after the ICB to monitor the lab's ability to produce reliable results at RL-level concentrations. There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value. Individual program requirements may vary.

10.7. Initial and Continuing Calibration Blanks (ICB/CCB)

10.7.1. The ICB/CCB solution is prepared with reagent water (ASTM Type I or equivalent) using the same acid matrix as the calibration standards. The ICB must be analyzed immediately following the ICV. The CCB must be analyzed

at a minimum frequency of 10 samples throughout the analytical run. The ICB/CCB must fall within +/- the reporting limit from zero.

Note: The only exceptions are if the ICB/CCB recoveries are biased high and the associated sample is below the requested reporting limit for the parameter(s) of interest or at, or above, 10 % of the measured concentration of that analyte in associated samples, (sample result must be a minimum of 10x higher than the ICB/CCB contamination level). **Note:** The exception for 10x ICB/CCB contamination does NOT apply to OVAP.

This must be addressed in the project narrative.

10.8. Interference Check Solutions (ICSA/ICSAB), ***Methods 6020 and 6020A only***

10.8.1. The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" must be monitored for possible interferences.

10.8.1.1. Control limits of spiked analytes in the ICSA/ICSAB solution are ± 50% of true value. Some projects may require control limits of ± 20% of true value. Control limits of non-spiked analytes are +/- the reporting limit when the reporting limit is greater than 10 ug/L, ± two times the reporting limit when the reporting limit is 1 ug/L to 10 ug/L or less than 1 ug/L when the reporting limit is less than 1 ug/L..

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.

10.9. Internal Standards

10.9.1. The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 120% of the intensity of the calibration blank for Method 6020, 30-150% for Methods 6020A and 6020B, and between 60% and 125% for Method 200.8. If the sample falls outside of these criteria, perform the following procedures. First, evaluate nearby CCVs and CCBs. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples undiluted. If the internal standard recoveries fall outside acceptance criteria and appear to be due to matrix effects, a five fold dilution is performed on the sample to correct for matrix effects and the sample re-analyzed. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal

standard intensities are within acceptance criteria. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported. See Table1 for a list of Internal Standard analytes. See Table 7 for the Internal Standard assignments.

10.9.2. The internal standard for the ICV, ICB, CCV, and CCB should be between 80% to 120% of the intensity of the calibration blank for method 6020 , 50% to 150% for method 6020A, 30% to 150% for method 6020B, and 60% to 125% for method 200.8. If outside these limits, the analyst should check for any instrument anomalies and continue if none are observed.

Note: The internal standards recoveries should never exceed the upper acceptance criteria. If the internal standard recovery exceeds the upper limit for the ICV, ICB, CCV and CCB the associated samples will need to be re-analyzed.

10.10. Serial Dilution, Methods 6020, 6020A, and 6020B only

10.10.1. One serial five-fold dilution must be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit for 6020 and 6020A and a factor of 10 above the RL for 6020B), the serial dilution must agree within 10% of the original analysis (20% limit for 6020B). If not, an interference effect must be suspected; the result is flagged, and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.

10.11. Post-Digestion Spike Addition (PDS), ***Method 6020***

10.11.1. If the serial dilution fails to meet the acceptance criteria, a re-analysis of the serial dilution can be performed on a diluted sample provided that the concentration of the original sample after the dilution is above the requested reporting limit. If the serial dilution is still outside acceptance limits then a post digestion spike must be performed. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference is suspected.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

11.3. Sample Preparation

11.3.1. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.

11.4. Sample Analysis

11.4.1. Flush the system with the rinse blank between samples and standards during the analytical run.

11.4.2. Dilute and re-analyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. The sample should be diluted to the approximate midrange of the linear range unless the dilution is for internal standard recoveries or for sample matrix. To reduce the levels of Total Dissolved Solids (TDS), a two-fold dilution will be performed before analysis on solid digestates including batch QC.

11.4.3. The analytical run sequence must be performed as follows to meet all quality control criteria:

Warm-up
Verify instrument performance
Calibration blank
Calibration standards
ICV
ICB
RL verification standard (ICVL)
Linear Range Verification (6020B only) Linear range can be performed at anytime during the sequence.
ICSA (6020, 6020A, and 6020B only)
ICSAB (6020 and 6020A only)
CCV
CCB
10 Samples
CCV
CCB
RL verification standard (CCVL) for 6020A if applicable

11.5. Analytical Documentation

11.5.1. Record all analytical information in the LIMS, including any corrective actions or modifications to the method.

11.5.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Record all sample results and associated QC in the LIMS. Level I and Level II reviews are performed in the LIMS.

12. DATA ANALYSIS AND CALCULATIONS

Note: The mean of three exposures is used to derive the sample concentrations used in the calculations in this section.

12.1. ICV percent recoveries are calculated according to the equation:

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

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{Found\ (CCV)}}{\mathbf{True\ (CCV)}}\right)$$

12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \mathbf{100\ x}\left(\frac{\mathbf{SSR\ -\ SR}}{\mathbf{SA}}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4. The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$RPD = \mathbf{100\ x}\left[\frac{\mathbf{(DU1\ -\ DU2)}}{\mathbf{(DU1\ +\ DU2)\ /\ 2}}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{\mathbf{(C\ x\ V1\ x\ D)}}{\mathbf{V2}}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V1 = Final volume in liters after sample preparation
V2 = Initial volume of sample digested in liters

12.6. The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result (mg/kg)} = \frac{\mathbf{(C\ x\ V\ x\ D)}}{\mathbf{W}}$$

Where:
C = Concentration from instrument readout, ppb (mean of three exposures)
D = Instrument dilution factor
V = Final volume in liters after sample preparation
W = Weight, in g, of wet sample digested

12.7. Calculation for Hardness

Total Hardness, mg equivalent $CaCO_3$/L, = 2.497 (Ca, mg/L) + 4.118 (Mg, mg/L)

12.8. Calculation for Trivalent Chromium ($Cr^{=3}$)

Cr^{+3} mg/L = Total Chromium mg/L – Hexavalent Chromium (Cr^{+6}) mg/L

12.9. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

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

13.2. Refer to Table 5 for the list of analytes that may be analyzed using this SOP for Methods 6020, 6020A, 6020B, and 200.8. Additional analytes may be analyzed if all method-required QC is acceptable.

13.3. Training Qualifications

13.3.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

15.4. Waste Streams Produced by the Method

15.4.1. Acid waste consisting of sample and rinse solution is generated by this method.

15.4.1.1. Any sample waste generated must be collected and disposed of in the acid waste drum located in the Metals Lab.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update III, Method 6020: Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 0, September 1994

16.1.2. Test Methods for Evaluating Solid Waste, EPA SW-846, Method 6020A Inductively Coupled Argon Plasma - Mass Spectrometry, Revision 1, February 2007

16.1.3. Test Methods for Evaluation Solid Waste, SW846, Method 6020B, Inductively Coupled Plasma-Mass Spectrometry, Revision 2, October 2012

16.1.4. Environmental Monitoring Systems Laboratory, EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, EMMC version

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

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File:		Revision 4.4: 07/30/08		
Revision 0: 08/01/95		Revision 4.5: 07/30/08		
Revision 1: 06/06/01		Revision 4.6: 02/15/11		
Revision 3: 03/26/02		Revision 4.7-A: 04/27/12		
Revision 4: 03/06/03		Revision 5: 04/24/13		
Revision 4.1: 10/01/03		Revision 6: 04/02/14		
Revision 4.2: 01/08/04		Revision 7: 05/31/17		
Revision 4.3: 07/28/07		Revision 8: 10/27/17		

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

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Acid Digestion of Soils, SW846 Method 3050B, NC-IP-010

16.2.3. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, NC-IP-011

16.2.4. Glassware Washing, NC-QA-014

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

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

16.2.7. Standards and Reagents, NC-QA-017

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

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

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. Reporting limits for solids and waters are easily accessible via the LIMS.

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

17.2. Method Deviations

17.2.1. Deviations from Method 6020

17.2.1.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.1.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.1.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.1.4. Internal standard recoveries may be less than 80% in CCVs and CCBs as long as QC criteria are met and that no anomalies are observed by the analyst.

17.2.1.5. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.1.6. The method states that the ICV should be prepared near the midpoint of the linear range. The laboratory prepares the standard near the midpoint of the calibration curve.

17.2.1.7. The method states in Section 10.10 that the dilution test sample result must be at least 100 times the concentration in the reagent blank. The laboratory uses 100 times the reporting limit as the criteria.

17.2.1.8. The ICSA/ICSAB solution is prepared at least every six months, or if expired.

17.2.2. Deviations from Method 200.8

17.2.2.1. Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.2.2. The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.2.3. Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.2.4. The concentration of most analytes in the LCS is 1000 μg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are kept in the laboratory.

17.2.2.5. The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.2.6. The tuning solution and internal standard solution are prepared with 2% nitric acid. The method states 1% nitric acid.

17.2.2.7. The method requires a dilution prior to analysis to adjust the chloride concentration in the sample. Due to newer instrument technology, this dilution is no longer needed.

17.3. Tables and Appendices

Table1: Recommended Internal Standards
Li
Sc
Y
Rh
In
Tb
Ho
Bi
Ge

TABLE 3: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solution criteria which cover a typical mass calibration range.

Element	Concentration (ug/L)
Ce	1
Co	1
Li	1
Mg	1
Tl	1
Y	1

Suggested Response From Tuning Solution (No He Gas based on a 1 ug/L solution)

6 >1000
89 >3000
205 > 2000
156/140 (Oxides) <1.0

Suggested Minimum Response From Tuning Solution (He Gas based on a 1 ug/L solution)

59 >1000 with <5%RSD
51 <200
52 <200
51/59 <10%

TABLE 4: Analyte List

Element
Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Cadmium
Calcium
Chromium
Cobalt
Copper
Iron
Lead
Lithium
Manganese
Magnesium
Molybdenum
Nickel
Potassium
Selenium
Sodium
Silver
Strontium
Thallium
Tin
Titanium
Tungsten
Vanadium
Zinc

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

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

Approvals (Signature/Date):

Technology Specialist	08/05/19 Date	Health & Safety Coordinator	07/30/19 Date
Quality Assurance Manager	07/26/19 Date	Technical Director	07/30/19 Date

This SOP was previously identified as SOP No. NC-MT-014, Rev 8, dated 3/18/19

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW846 Methods 7470A, 7471A, and 7471B, and MCAWW Method 245.1.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants and potassium permanganate has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed; however, Method 7471A is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in surface and saline waters, and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. Methods 7471A and 7471B are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes, biological material, and sludge-type materials. All matrices require sample preparation prior to analysis.

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

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric (aqueous samples), or hydrochloric and nitric acids (soil samples). Organic mercury compounds are oxidized with potassium permanganate (aqueous and soil samples) and potassium persulfate (aqueous samples), and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control (QC) section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.3. Potassium permanganate, which is used to break down organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide (as sodium sulfide) do not interfere with the recovery of inorganic mercury from reagent water.

4.4. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.5. Chlorides can cause a positive interference. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (maximum 25 mL); because during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride

4.6. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.7. Samples containing high concentrations of oxidizable organic materials, as evidenced by high Chemical Oxygen Demand (COD) levels, may not be completely

oxidized by this procedure. When this occurs, the recovery of mercury will be low. Reducing the volume of original sample used can eliminate this problem.

4.8. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. Refer to Appendix B for Contamination Control Guidelines.

5. SAFETY

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

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

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

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Mercury (10PPM in Reagent)	Oxidizer Corrosive Poison	0.1 g/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns

			and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydroxyl-amine Hydro-chloride	Corrosive Poison	None	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Corrosive to the eyes. Irritant and possible sensitizer. May cause burns to the skin.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Note: Always add acid to water to prevent violent reactions.			
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

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

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.

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

5.7. Do not look directly into the beam of the Hg lamp. The Ultra Violet (UV) light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory, and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature-controlled hot block or equivalent

6.2. Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption cell with quartz end windows perpendicular to the longitudinal axis: Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury-specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.2.3. Peristaltic pump which can deliver 1 L/min

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min

6.2.5. Recorder or printer

6.2.6. Drying device to prevent condensation in cell

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

6.3. Plastic bottles – capable of holding 100 mL

6.4. Nitrogen or argon gas supply, welding grade or equivalent

6.5. Calibrated automatic pipettes

6.6. Class A volumetric flasks

6.7. Top-loading balance, capable of reading up to two decimal places

6.8. Thermometer (capable of accurate readings at 95 °C)

6.9. Disposable cups or tubes

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore Deionized Water (DI) system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (10 ppm calibration and ICV) mercury standards are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017. Refer to the reagent module in the Laboratory Information Management System (LIMS) for details on standard preparation.

7.3. Working mercury standard (0.1 ppm): Take 2 mL of the 10 ppm stock standard (Section 7.2) and dilute to 200 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (300 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. Refer to the reagent module in LIMS for details on standard preparation.

7.4. Working ICV standard (0.1 ppm): Take 1 mL of the 10 ppm ICV stock standard (Section 7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. Refer to the reagent module in LIMS for details on standard preparation.

7.5. The calibration standards must be prepared fresh daily from the working standard (Section 7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample preparation bottles for solid samples or by transferring 0, 0.1, 0.25, 0.5, 2.5, and 5.0 mL aliquots of the working mercury standard into sample preparation bottles for aqueous samples and proceeding as specified in Section 11. (A calibration curve is valid for 24 hours from the completion of preparation.) The laboratory control sample (LCS) solution is prepared by transferring 5.0 mL (solids) or 2.5 mL (waters) of working standard into sample preparation bottles and proceeding as specified in Section 11. Refer to the reagent module in LIMS for details on standard preparation.

Note: Alternate approaches to standard preparation may be taken, and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I (Appendix A) are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table 1 (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better

7.10. Sulfuric acid (H_2SO_4), concentrated, traces metal grade or better

7.11. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.12. Stannous chloride solution: Add 50g $\pm$ 0.5g of stannous chloride and 25 mL of concentrated HCl, and bring to a final volume of 500 mL with DI water.

Note: Stannous sulfate may be used in place of stannous chloride. Prepare the stannous sulfate solution according to the recommendations provided by the instrument manufacturer.

7.13. Sodium chloride-hydroxylamine hydrochloride solution: Add 240g $\pm$ 0.5g of sodium chloride and 240g $\pm$ 0.5g of hydroxylamine hydrochloride to every 2000 mL of reagent water.

7.14. Potassium permanganate, 5% solution (w/v): Dissolve 100g of potassium permanganate for every 2000 mL of reagent water.

7.15. Potassium persulfate, 5% solution (w/v): Dissolve 100 g of potassium persulfate for every 2000 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of sample collection to the time of sample analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil samples and biological material do not require preservation, but must be collected in wide-mouth glass jars with PFTE-lined lids and stored at 4° C ± 2° C (and/or freezing for tissues) until the time of analysis.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.2.1. Four aliquots of the laboratory check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.3. A Preparation Batch is a group of up to 20 samples, excluding QC Samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike (MS), Matrix Spike Duplicate (MSD)), that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain an MB, an LCS and an MS/MSD. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes. In some cases, at client request, it may be appropriate to process a MS and sample duplicate (DU) in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.4. Method Blank (MB)

9.4.1. One MB must be processed with each preparation batch. The MB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB must not contain any analyte of interest at, or above, the reporting or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of ten times higher than the MB contamination level).

Note: For Ohio VAP projects, the result must be below the reporting limit or samples must be re-digested and re-analyzed.

9.4.2. Re-digestion and re-analysis of all samples associated with an unacceptable MB is required when reportable concentrations are determined in the

samples (see exception noted above).

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

9.4.4. If the above criteria are not met and re-analysis is not possible due to limited sample quantity, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.5. Laboratory Control Sample (LCS)

9.5.1. One LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits, the system is out of control and corrective action must occur. See Section 12 for the LCS calculation.

9.5.2. For Method 245.1, the LCS must be 85% - 115%. For Methods 7470A, 7471A, and 7471B, the laboratory control sample recovery must be 80%-120%.

9.5.3. Corrective action must be re-digestion and re-analysis of the batch unless the LCS recovery is greater than the upper control limit and the sample results are less than the RL. In that situation the results may be reported with proper narration.

9.6. Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.7.1. One MS/MSD pair must be processed for each preparation batch. An MS is a field sample to which known concentrations of target analytes have been added. An MSD is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and MS. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates (DU) in place of, or in addition to, MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for

MS/MSD analysis. Spiking levels are provided in Table 1 (Appendix I). See Section 12 for the MS/MSD and Relative Percent Difference (RPD) calculation.

Note: for Method 245.1, an MS/MSD pair is required for every 10 samples.

9.7.2. If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. A control limit of, 70 – 130% for Method 245.1, and 20% RPD must be applied to the MS/MSD. A control limit of 80-120% for Methods 7470A, 7471A, and 7471B and 20% RPD must be applied to the MS/MSD.

9.7.3. If the analyte recovery or RPD falls outside the acceptance range, the analyst shall determine if the MS/MSD is spiked properly and/or the matrix of the sample is the result of the MS/MSD or RPD failure. If it has been determined that the MS/MSD was not spiked properly and/or the failure is not a result of matrix then the sample along with the MS/MSD will be re-digested and analyzed.

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

9.7.4. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data are reported with a “4” as a flag. In the event an MS/MSD analysis is not possible, notation in the project narrative is required.

9.8. Control Limits

9.8.1. Control limits are established by the laboratory as described in SOP NC-QA-018

9.8.2. Control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via the LIMS

9.9. Method Detection Limits (MDLs) and MDL Checks

9.9.1. MDLs and MDL Checks are established by the laboratory as described in SOP CA-Q-S-006.

9.9.2. MDLs are easily accessible via the LIMS

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.

10.2. Due to the differences in preparation protocols, separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a calibration blank. One standard must be at, or below, the reporting limit. Analyze standards in ascending order beginning with the calibration blank. Refer to Section 7 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥ 0.995, or the instrument must be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient. NOTE: If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be re-digested.

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

10.7.1. Calibration accuracy is verified by analyzing a second source standard ICV. The ICV result must fall within 5% (for method 245.1) or 10% (for methods 7470A, 7471A, and 7471B) of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within $\pm$ the reporting limit (RL) from zero. See Section 12 for the ICV calculation. If either the ICV or ICB fail to meet criteria, the analysis must be terminated, the problem corrected, and the instrument recalibrated (see Section 11.6.4. for required run sequence). The calibration curve standards are reanalyzed to determine if the failure was instrument related. If the cause of the ICV or ICB failure was not directly instrument-related, the corrective action must include re-digestion of the ICV,

ICB, CRA, CCV, and CCB with the calibration curve. For Ohio VAP, the sample batch must be re-digested.

Note: If the ICV and/or ICB fail criteria on the high side, samples with results below the reporting limit may be reported with proper narration.

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

10.8.1. Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard from the calibration curve.

10.8.2. The CCV result for Methods 7470A, 7471A, and 7471B must fall within 20% of the true value for that solution. For Method 245.1, the criterion is ± 10%. See Section 12 for the CCV calculation.

10.8.3. A CCB is analyzed immediately following each CCV (see Section 11.6.4 for required run sequence). The CCB result must fall within ± RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. If the CCV/CCB is biased high and the sample results associated with the CCV/CCB are below the requested reporting limit, then the results can be reported. Sample results may be reported when bracketed by valid CCV/CCB pairs. If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be re-digested.

Note: If the CCV and/or CCB fail criteria on the high side, sample results that are below the reporting limit may be reported with proper narration.

10.9. Detection Limit Standard (CRA) - A CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. It is recommended that the recovery be ± 50% of the true value. If the CRA recovery is outside of the recommended criterion, correct any problem and re-analyze. Re-calibration may be required. The CRA is only required when requested.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

11.3. Standard and Sample Preparation- Solids

11.3.1. All calibration and calibration verification standards (ICV, ICB, CCV, and CCB) are processed through the digestion procedure as well as the field samples.

11.3.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (Section 7.3) into a series of sample digestion bottles. The ICB/CCB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. For the ICV, transfer a 5 mL aliquot of the working ICV standard to the digestion bottle. The ICV standard must be from a source other than that used for the calibration standards. For the CCV, transfer a 5.0 mL aliquot of the working standard into a sample digestion bottle. Add reagent water to each standard bottle for a total volume of 10 mL.

Note: Alternate volumes and concentrations of standard may be prepared as long as the accuracy and final standard concentrations support laboratory or project reporting limits.

11.3.3. To each LCS standard, add 0.6 g of Teflon chips or other suitable solid matrix, 5 mL of reagent water and 5 mL of the working mercury standard (0.1 ppm) (see Section 7).

11.3.4. To the MB bottle, add 0.6 g of Teflon chips or other suitable solid matrix and 10 mL of reagent water.

11.3.5. For each sample, transfer 0.6 g ± 0.1 g of a well-mixed sample into a clean sample digestion bottle and add 10 mL of reagent water.

11.3.6. Add 5 ml of Aqua Regia to all containers.

11.3.7. Heat for two minutes in a hot block at 90 - 95 ° C.

11.3.8. Add 40 mL of distilled water.

11.3.9. Add 15 mL of potassium permanganate solution. Cover containers with digestion bottle lids.

11.3.10. Heat for 30 minutes in the hot block at 90 - 95 °C.

11.3.11. Record the time on and off of the hotblock in the batch info.

11.3.12. Check the temperature when heating is finished and note in batch information whether temperature requirement was met.

11.3.13. Cool

11.3.14. Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.3.15. Bring each standard, quality control sample, and sample up to a final volume of 100 mL with reagent water.

11.3.16. Samples are ready for analysis (section 11.6).

11.4. Sample preparation for incremental sampling method (ISM) solids

11.4.1. ISM samples are prepped and sub-sampled per SOP requirements for ISM. The Metals laboratory will receive a single sample aliquot from the Pre-Prep department containing approximately 3.0g of each sample inside a 500mL plastic container. The acceptable range for HG sample mass is approximately 2.5-3.5g.

11.4.1.1. 3.0g of Teflon boiling chips or other suitable solid matrix are weighed into a 500mL bottle for both the MB and LCS. Preparatory method for QC samples will be the same as for the client samples.

11.4.1.2. The laboratory control sample (LCS) is spiked with 25mL of the HG Calibration solution. Matrix spike (MS) and matrix spike duplicate (MSD) are spiked with 5mL of the HG Calibration solution.

11.4.1.3. Add 50mL of deionized water to each sample container except the LCS. Add 25mL of the reagent water into the LCS container for an even volume.

11.4.1.4. To each sample container, including MB and LCS, add 25mL of Aqua Regia.

11.4.1.5. Place each sample into individual sample slots inside the water bath. Heat samples for two minutes at 90-95 degrees Celsius.

11.4.1.6. Add 200mL of deionized water into each sample container.

11.4.1.7. Add 75mL of potassium permanganate solution.

11.4.1.8. Cover 500mL containers with its bottle lids.

11.4.1.9. Digest for 30 minutes inside the water bath at 90-95 degrees Celsius.

11.4.1.10. Add 30 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.4.1.11. Bring each standard, quality control sample, and sample up to a final volume of 500 mL with reagent water.

11.4.1.12. Samples are ready for analysis (section 11.6).

11.5. Standard and Sample Preparation Waters

11.5.1. All calibration and calibration verification standards (ICV, ICB, CCV, and CCB) are processed through the digestion procedure as well as the field samples. Transfer 0, 0.1, 0.25, 0.5, 2.5 and 5.0 mL aliquots of the working standard (Section 7.3) into a series of sample digestion bottles containing 50 mL of reagent water. For the ICV, transfer a 2.5 mL aliquot of the working standard to the digestion bottle containing 50 mL of reagent water. The ICV standard must be from a source other than that used for the calibration standards. For the CCV, transfer a 2.5 mL aliquot of the working standard into a sample digestion bottle containing 50 mL of reagent water.

11.5.2. The Method Blank (MB) consists of 50 mL of reagent water. The LCS consists of 2.5 mL of the HG working standard, and 50 mL of reagent water.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations support laboratory or project reporting limits.

11.5.3. Transfer 50 mL of well-mixed sample or standard to a clean sample digestion bottle. Continue preparation as described under Section 11.6.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

Note: Spiking is done before the addition of acids or reagents.

11.5.4. Add 2.5 mL of concentrated H_2SO_4 and 1.25 mL of concentrated HNO_3.

11.5.5. Add 7.5 mL of potassium permanganate solution. For samples high in organic materials or chlorides, 7.5 mL may be insufficient to fully break down all organic mercury compounds. If the purple color does not persist for at least 15 minutes after the addition of potassium permanganate, the sample must be discarded and re-prepped at a dilution.

11.5.6. Add 4 mL of potassium persulfate solution, cover, and heat for two hours in a hot block at 90 - 95 °C.

11.5.7. Cool samples.

11.5.8. Add 3 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.5.9. Bring each standard, quality control sample and sample up to a final volume of 75mL with reagent water.

Note: The final volume for water samples is 50 mL prior to the addition of digestion reagents. After all prep reagents are added and the samples are digested, reagent water is added to bring each sample to a consistent 75 mL volume. The calibration curve and samples are prepared in the exact same manner. To avoid result and limit calculation errors, the 50 mL volume is recorded as the final sample volume in the preparation log in LIMS.

11.5.10. Samples are ready for analysis (section 11.6).

11.6. Sample Analysis

11.6.1. Automated determination: Refer to the instrument manual for details on instrument setup.

11.6.2. Create a calibration curve by plotting response of calibration standards vs. concentrations of mercury. Determine the mercury concentration in the samples from the linear fit of the calibration curve. The calibration acceptance criteria are listed in Section 10.6. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.6.3. All measurements must fall within the defined calibration range to be valid. Dilute and re-analyze all samples for analytes that exceed the highest calibration standard.

Note: For Method 245.1, the measurement must fall within 90% of the highest standard. Sample measurements that exceed 90% of the highest standard must be diluted and reanalyzed.

11.6.4. The following analytical sequence is consistent with Methods 7470A, 245.1, 7471A and 7471B.

Instrument Calibration
ICV

ICB
CRA if required
CCV
CCB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete the run
CCV
CCB

11.6.5. Refer to Quality Control Section 9.0 for quality control criteria.

Note: Samples include the MB, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.6.6. To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data be reviewed periodically throughout the run.

11.6.7. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.

11.7. Analytical Documentation

11.7.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.7.2. Record all standards and reagents in the LIMS Reagents module. All standards and reagents are assigned a unique number for identification.

11.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.7.4. Record all sample results and associated QC in LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

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

12.2. CCV percent recoveries are calculated according to the equation:

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

12.3. Matrix spike (MS) recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
Matrix Spike (MS) = determined spiked sample concentration
Matrix Spike Duplicate (MSD) = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

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

Where:
C = Concentration (ug/L) from instrument readout
V = Volume of digestate (L)
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the "S" factor must be omitted from the above equation.

12.6. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.7. The Laboratory Control Sample (LCS) percent recovery is calculated according to the following equation:

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

12.8. Appropriate factors must be applied to sample values if dilutions are performed.

12.9. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.1.

13.2. Training Qualification

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

14. POLLUTION PREVENTION

14.1. It is Eurofins TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste must be disposed of in accordance with Federal, State, and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by this Method

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

15.2.1.1. Acid Waste: This waste disposed of in the designated container labeled "Acid Waste".

15.2.1.2. Acid waste/aqueous waste generated by the analysis: Samples are disposed of in the acid waste drum located in the Metals lab. The contents of the drum are neutralized and released to the POTW.

16. REFERENCES

16.1. References

16.1.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury)

16.1.2. "Methods for the Chemical Analysis of Water and Wastes", Rev. 3.0 (1994)

16.1.3. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A

(Mercury)

16.1.4. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Revision 2, February 2007, Method 7471B (Mercury)

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

16.1.6. Eurofins TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and Eurofins TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.7. Corporate Quality Management Plan (CQMP), current version

16.1.8. Revision History

Historical File: (formerly Corp-MT-0007NC, NC-MT-011, and NC-MT-013)				
Revision 1.1: 04/17/97		Revision 2: 03/20/13		
Revision 2.2: 02/06/01		Revision 3: 06/05/13		
Revision 2.3: 05/15/01		Revision 4: 06/06/15		
Revision 2.4: 10/28/02		Revision 5: 06/15/15		
Revision 2.5: 11/24/04		Revision 6: 06/23/16		
Revision 0: 12/12/07 (011)		Revision 7: 02/13/18		
Revision 1: 01/07/09 (011)		Revision 8: 03/18/19		
Revision 0: 01/07/09 (013)				
Revision 0: 09/27/10 (014)				
Revision 1-A: 04/17/12				

**4/9/19: changed logo and copyright information. No changes made to revision number or effective date.*

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

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

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

16.2.5. Standards and Reagents, NC-QA-017

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

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

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from Reference Method

17.1.1. Modifications from Method 7471A

17.1.1.1. Chapter 1 of SW846 specifies the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2. Modifications from both Methods 7470A and 245.1

17.1.2.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.2.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, “Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.”

17.1.3. Modifications from Method 7470A

17.1.3.1. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit if the samples associated with the method blank are equal to or above the reporting limit.

17.1.4. Modifications from Method 245.1

17.1.4.1. Method 245.1 states that standards are not heated. Eurofins TestAmerica Canton prepares heated standards for this method.

17.1.4.2. Stannous Chloride is prepared in hydrochloric acid, instead of sulfuric acid, per instrument manufacturer recommendations.

17.1.4.3. Section 9.3.4 of the method states that the CCB must be less than the MDL. The laboratory uses the criteria that the CCB result must fall within ± RL from zero.

17.2. Tables and Appendices

APPENDIX A - TABLES

TABLE 1. MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD AND SPIKING LEVELS

Soil RL (mg/kg)	0.1
Standard Aqueous RL (mg/L)	0.0002
TCLP RL (mg/L)	0.002
Std 0 (mg/L)	0
Std 1/CRA (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L)	0.010
ICV (mg/L)	0.005
CCV/Laboratory Control Sample (LCS) (mg/L)	0.005
LCS (mg/L)	0.005
Matrix Spike (MS) (mg/L)	0.001
TCLP Matrix Spike (MS)	0.005

APPENDIX B - CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by Deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas should be kept clean.

Powdered Gloves should not be used in the metals laboratory since the powder contains zinc, as well as other metallic analytes. Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

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

Improper cleaning of glassware can cause contamination.

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

Title: pH ELECTROMETRIC METHOD

[Methods: SW846 Methods 9040B, 9040C, 9041A, 9045C and 9045D, and SM4500 H^+B]

Approvals (Signature/Date):

Technology Specialist	07/19/19 Date	Health & Safety Coordinator	07/23/19 Date
Quality Assurance Manager	07/22/19 Date	Technical Director	07/30/19 Date

This SOP was previously identified as SOP NC-WC-010, Rev 15 dated 7/27/17

Facility Distribution No. _____ Distributed To:_____
The controlled copies of this SOP are the PDF copy of the SOP that is posted to the laboratory's SOP Directory and, where applicable, the copy of the SOP that is printed and placed in the General Chemistry SOP binder. Printed or electronic copies of this SOP distributed outside of the facility are considered uncontrolled.

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of pH in waters, drinking waters, wastewaters, and solids. It is based on SW846 Methods 9040B, 9040C. 9041A, 9045C, 9045D, SM4500 H^+B, Method 9040B/9040C should be used if the aqueous phase constitutes at least 20% of the total volume of the waste. Method 9045C/9045D should be used for measuring pH in soils and waste samples. If water is present, it must constitute less than 20% of the total volume of the sample. See Section 11 for details on determining the correct method.

1.2. The approximate working range is 1 - 14 pH units.

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

2. SUMMARY OF METHOD

2.1. The pH is determined electrometrically by using an electrode. The pH meter is calibrated with a series of pH buffers.

2.2. For Method 9041A, an aliquot of sample is analyzed for pH using pH paper. Samples are mixed with water prior to analysis.

3. DEFINITIONS

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

4. INTERFERENCES

4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low sodium error electrode.

5. SAFETY

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

5.2. There are no materials used in this method that have a serious or significant hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the Safety Data Sheet (SDS) for each material before using it for the first time or when there are major changes to the SDS.

5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other

gloves will be cleaned immediately

5.4. Exposure to chemicals must be minimized as much as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

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

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

6. EQUIPMENT AND SUPPLIES

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

6.2. Disposable beakers: various

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

6.4. Stir plate and stir bars

6.5. Shaker or mechanical tumbler

6.6. Autotitrator

6.7. Centrifuges tubes

6.8. pH paper: Various pH ranges

6.9. Disposable snap top containers

7. REAGENTS AND STANDARDS

7.1. Standards

7.1.1. A commercially available control standard (LCS)

7.1.2. Target Calibration Standards

7.1.2.1. pH 2, 4, 7, 10, and 12 buffers--purchased

7.1.2.1.1. Fresh buffers are poured and used each working day.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at 4°C ± 2°C.

8.3. Samples should be analyzed as soon as possible after sampling, but not to exceed one day after sampling.

9. QUALITY CONTROL

9.1. Batch Definition

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

9.2. Sample Duplicate

9.2.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, a sample duplicate pair is processed as two independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process.

9.2.2. Sample duplicates are performed at a frequency of 10% per matrix, and must meet laboratory-specific limits for precision. For 9041A, all samples will be analyzed in duplicate.

9.3. Laboratory Control Sample (LCS)

9.3.1. One second source aqueous LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. A commercially available (Environmental Resource Associates or equivalent) control standard will be analyzed. Recovery must be within +/-3% of true value.

9.3.3. Corrective Action for LCS

9.3.3.1. If the pH is outside the established control limits the system is out of control and corrective action must occur.

9.3.3.2. Corrective action consists of identification and correction of the cause for the out of control situation and reanalysis of all effected samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. Refer to the manufacturer's manual for instrumental calibration.

10.1.2. The following procedure is applicable for use with the Orion Star A211 pH meter.

10.1.2.1. Five pH buffers will be used for calibrating this meter, 2, 4, 7, 10, and 12.

10.1.2.2. After calibration, run a pH 7, then an LCS, allowing the electrode to stabilize for each. Record results on analytical logsheet.

10.1.3. The pH meter must be calibrated daily. The calibration date is recorded on the analytical logsheet.

10.1.4. If the pH meter has been turned off, it must be calibrated prior to use.

10.1.5. The calibration slope must be 95 – 105 %. If the slope does not meet criteria, perform maintenance and recalibrate.

10.1.5.1. Maintenance can include, but is not limited to, changing the solution in the probe, cleaning the probe, or refreshing the buffer solutions.

10.2. An NCM will be created for samples with results outside of the calibration range.

10.3. Continuing Calibration

10.3.1. A pH 7 buffer is analyzed before sample analysis, every ten samples, and at the end of the analysis to ensure the calibration remains linear.

10.3.2. The pH meter must be recalibrated if the reading for the pH 7 buffer deviates by more than ±0.10 pH units. If this range is exceeded, re-analyze all samples analyzed since the last pH buffer that met criteria.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of QA, operations supervisor, or designee to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo.

11.2. Sample Preparation

11.2.1. At the time of sample receipt, the sample must be inspected to determine the correct method reference. General Chemistry staff members will determine the percent of aqueous phase present and notify the Project Management staff if a method change is needed. Methods 9040B and C should be used if the aqueous phase constitutes at least 20% of the total volume of the waste. Method 9045C and 9045D should be used for measuring pH in soils and waste samples with less than 20% water present (as percent of total sample volume).

Note: The analyst will note in the comments section in LIMS which method was used and if a method change was required.

11.2.2. Waters and aqueous wastes where the aqueous phase constitutes at least 20% of the total volume of the waste

11.2.2.1. No preparation necessary for waters and wastewaters.

11.2.3. Solids and Sludges

11.2.3.1. Place 10 g (± 0.5 g) of sample in a beaker or other suitable container.

11.2.3.2. Add approximately 10 mL of reagent water and mix for five minutes in a shaker or mechanical tumbler.

11.2.3.3. Allow sample to stand for about one hour to allow the solids to settle out.

11.2.4. Non-aqueous Waste and liquids

11.2.4.1. Place 10 g (± 0.5 g) of sample in a beaker or other suitable container.

11.2.4.2. Add approximately 10 mL of reagent water and mix for five minutes in a shaker or mechanical tumbler.

11.2.4.3. Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension. Filter or centrifuge and decant off aqueous phase for pH measurement.

Note: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned gently with acetone if it becomes coated with an oily material.

11.2.5. Method 9041A Sample Preparation (solids, sludges, and oils)

11.2.5.1. Place 10 g (± 0.5 g) of sample in a snap top container.

11.2.5.2. Add approximately 10 mL of reagent water to the sample and mix.

11.2.5.3. If the sample is multiphasic decant the oily phase and analyze only the

aqueous layer.

11.2.5.4. Allow the sample and water layers to separate and carefully decant the water layer into another snap cap for analysis. If it is not possible to decant without decanting some of the sample (in the case of oils or oily sludges), it is permissible to use a disposable transfer pipette to remove the water layer for analysis.

11.3. Sample Analysis

11.3.1. Manual Procedure

11.3.1.1. Waters and aqueous wastes where the aqueous phase constitutes at least 20% of the total volume of the waste

11.3.1.1.1. Place the sample in a clean beaker using a sufficient volume to cover the sensing elements of the electrode(s). Allow the pH to stabilize (swirling or stirring may quicken stabilization). Record the pH in LIMS. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 7 buffer when not in use.

11.3.1.1.2. For 9040B and 9040C,– Continuously stir the sample while obtaining a stable reading.

11.3.1.1.3. For Method 9040B and 9040C note and record the sample pH of the first aliquot. Repeat the measurement on successive aliquots of sample until the values differ by < 0.1 pH units. Two or three volume changes are usually sufficient. If more than three measurements are required, contact the Group Leader.

11.3.2. Solids and Non-aqueous Waste and liquids

11.3.2.1. Immerse the pH electrodes in the supernatant layer of the sample - be careful not to stir up solids. Allow pH to stabilize and record the value in LIMS. Remove and rinse the electrodes between each measurement. Store the electrode in the pH 7 buffer.

Note: If the sample contains oil or other substances that will coat and damage the electrodes analyzing the pH by pH Paper Method 9041A should be considered.

11.3.3. Automated Procedure (aqueous samples only)

11.3.3.1. Load the appropriate schedule on the autotitrator starting with the pH calibration.

11.3.3.2. Pour a homogenized sample into the centrifuge tubes and place the tubes in the appropriate position on the autosampler. Remember to include a pH 7 buffer check after every ten positions.

11.3.3.3. Start the autotitrator.

11.3.4. Method 9041A Sample Analysis Procedure (aqueous samples)

11.3.4.1. Immerse the wide range pH paper into the decanted water layer of the sample for several seconds. Remove the paper and determine the pH range from the manufacturer's pH chart. Using the appropriate narrow range pH paper read the sample pH and record the pH in LIMS. Reading with the narrow range pH paper will be done in duplicate.

11.3.4.2. pH paper used for analysis will also be checked against certified buffers and the lot of pH paper recorded in the batch information.

Note: The initial pH range check that is performed with the wide range pH paper does **not** count as a duplicate analysis.

11.4. Analytical Documentation

11.4.1. Record all analytical information in LIMS, including any corrective actions or modifications to the method.

11.4.2. Record all standards and reagents in the LIMS reagents module. All standards and reagents are assigned a unique number for identification.

11.4.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

11.4.4. Record all sample results and associated QC directly into LIMS. Level I and Level II reviews are performed in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Method validation information (where applicable) in the form of analyst demonstrations of capabilities are maintained for this method in the analysts' training files.

13.2. Training Qualifications

13.2.1. Each analyst must have initial demonstration of competence (IDOC) data on file and corresponding continuing DOCs.

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

14. POLLUTION PREVENTION

14.1. It is Eurofins TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage, and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

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

15.2.1.1. Acidic and alkaline sample waste and exhausted buffer solutions can be poured down the drain if the pH is between 5 and 10. Any sample waste generated that is not in this pH range is collected in a designated container identified as "Acid Waste".

15.2.1.2. Exhausted soil or oil samples analyzed by the method. The liquid layer is decanted and disposed of in a designated container identified as "Acid Waste". The remaining solid layer is disposed of by placing it in a container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of Eurofins TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, pH Electrometric Measurement, Method 9040B, Revision 2, January 1995

16.1.2. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Soil pH, Method 9045C, Revision 3, January 1995.

16.1.3. SW846, Test Methods for Evaluating Soil Waste, Soil and Waste pH Method 9045D, Revision 4, November 2004

16.1.4. SW846, Test Methods for Evaluating Solid Waste, pH Electrometric Measurement , Method 9040C, Revision 3, November 2004.

16.1.5. SW846, Test Methods for Evaluating Solid Waste, Third Edition, pH paper, Method 9041A, Revision 1, July 1992

16.1.6. Standard Method for pH Electrometric Method, SM4500 H^+B, 2000

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

16.1.8. Eurofins TestAmerica Corporate Environmental Health and Safety Manual, CW-E-M-001, and Eurofins TestAmerica Canton Facility Addendum and Contingency Plan, current version

16.1.9. Corporate Quality Management Plan (CQMP), current version

16.1.10. Ohio EPA Laboratory Manual for Chemical Analyses of Public Drinking Water 2000

16.1.11. Revision History

Historical File:		Revision 9: 05/26/10		
Revision 4.0: 01/04/99		Revision 10: 11/24/10		
Revision 4.1: 11/28/00		Revision 11: 04/16/12		
Revision 5: 02/05/03		Revision 12: 03/21/13		
Revision 6: 10/27/04		Revision 13: 03/13/14		
Revision 7: 03/23/06		Revision 14: 06/15/15		
Revision 8: 04/30/08		Revision 15: 07/27/17		

**4/15/19: changed logo and copyright information. No changes made to revision number or effective date.*

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

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

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. A minimum reporting limit of 0.1 SU (standard units) is listed in LIMS. Units are reported as “SU”.

17.2. Method Deviations

17.2.1. Method 9041A requires a procedure to identify interferences. The laboratory does not perform this procedure.

17.2.2. Method 9041A requires each batch of pH paper to be calibrated versus certified pH buffers or a pH meter which has been calibrated with certified pH buffers. The pH paper is not calibrated by the laboratory.

17.2.3. Method 9041A does not call for any kind of sample preparation; however, due to the various matrices encountered, the laboratory preps the samples as described in section 11.2.5.

Attachment C
Scope of Work Approval Form

USEPA ID Number: MID 005 356 621
Revision Number 0
September 2019
Prepared by: GHD
Prepared for: RACER Trust Site

Approved By: _____ Date: October 11, 2019
Project Manager - GHD
John-Eric Pardys

Approved By: _____ Date: October 11, 2019
QA Officer - GHD
Ruth Mickle

Approved By: _____ Date: October 15, 2019
Deputy Cleanup Manager – RACER
Dave Favero

Approved By: _____ Date: Oct 14, 2019
Project Manager – Eurofins TestAmerica North Canton, Ohio
Denise Heckler

Approved By: _____ Digitally signed by ZACHARY SASNOW Date: 2019.10.18 08:49:43 -05'00' Date: _____
USEPA Region 5 Project Manager
Zachary Sasnow