AECOM

Supplemental Soil Characterization Work Plan

Pines Area of Investigation

AOC II

Docket No. V-W-'04-C-784

November 2014

Appendix A

Statistical Property Number Determination

Appendix A

Calculations of Representative Number of Properties to Sample

As discussed in Section 1.3.4 of the Supplemental Soil Characterization (SSC) Work Plan, the data from the gamma surveys and the coal combustion by-product (CCB) verification studies will be compiled and evaluated to aid in the identification of appropriate properties for soil sampling. A statistical procedure has been used to determine the number of properties to sample in order to provide a representative subset, as described in this appendix.

Approach

While there are numerous statistical methods available to estimate sample sizes, most are not directly applicable to the circumstances of this plan. For example, most methods assume an infinite number of possible samples rather than being designed to select a subset from a fixed, finite population (the total number of properties in this case). There are also a number of methods that estimate sample size based on cost constraints. The method used here is based on stratified sampling, and was one of the few methods based on a finite population that was identified (U. S. Environmental Protection Agency (USEPA), 2002).

The number of properties based on stratified sampling is dependent on the statistical characteristics (for example mean and standard deviation) of the parameter being measured, in this case, concentrations of constituents of potential concern (COPCs) as identified in the Human Health Risk Assessment (AECOM, 2012). Since the statistical characteristics can be different for different parameters, the calculated number of properties can also be different. The statistical calculations were conducted using those COPCs for which detected results were available, and for which the maximum detected concentration was above the site-specific Preliminary Remediation Goals (PRGs) developed for the project (see Table 1 of the main text of the SSC Work Plan). Therefore, statistical calculations were performed using the following constituents:

- Arsenic
- Iron
- Thallium
- Lead-210
- Radium-226
- Radium-228
- Uranium-238

The following constituents, while identified as COPCs, were not included in the statistical calculations because their concentrations in all the municipal water service extension (MWSE) samples were below site-specific PRGs: aluminum, chromium (total), cobalt, thorium-228, thorium-230, thorium-232, uranium-234, uranium-235, and vanadium. Hexavalent chromium is also a COPC, but it was not included in the statistical calculations because the concentrations in all the MWSE samples were nondetect.

Methodology and Calculations

Equations for estimating sample sizes for stratified sampling designs were taken from USEPA guidance QA/G-5S: Guidance for Choosing a Sampling Design for Environmental Data

Collection (USEPA, 2002). For stratified sampling, the population or area to be sampled is divided into groups (strata) that have different characteristics with the end goal of calculating a mean per group. Examples of strata include land use characteristics (industrial/commercial, urban, agricultural, forest, etc.). Although the sampling program is not designed to calculate an overall mean across properties, the results are still usable as described in the Results section below, and are generally consistent with results based on the only other statistical method that was found to use a finite population: item sampling with judgemental samples.

For the purposes of the SSC Work Plan, there are a total of 94 private properties that were identified as potentially having coal combustion by-products (CCBs) based on visual inspections in rights-of-ways and other historical information. Of these properties, CCBs were confirmed through visual inspections on 45 properties. CCBs were confirmed not present on 27 properties, and access was not granted on 22 properties. Thus, the 94 properties can be divided into two strata: properties where CCBs were confirmed not present (27), and properties where CCBs were confirmed present or may be present but were not inspected (45+22=67).

USEPA guidance (USEPA, 2002) provides equations for calculating the number of samples (in this case, number of properties) in each stratum to provide a representative sampling subset:

$$n = \frac{z^2_{1-\frac{\alpha}{2}}\left(\frac{\sum_{h=1}^{L} W_h s_h^2}{d}\right)}{1+z^2_{1-\frac{\alpha}{2}}\left(\frac{W_h s_h^2}{d^2 N}\right)}$$

Where

$d = margin\ of\ error$

$L = number\ of\ strata$

$n = number\ of\ properties\ to\ be\ sampled$

$N = total\ number\ of\ properties\ across\ all\ strata$

$s_h = prior\ known\ standard\ devation\ in\ concentrations\ in\ strata\ 1\ through\ h$

$Z_{1-\frac{\alpha}{2}} =\ cumulative\ normal\ distribution\ with\ probability\ of\ 1-\frac{\alpha}{2}$

$W_h = \frac{number\ of\ properties\ in\ strata}{number\ of\ properites\ across\ all\ strata}\quad in\ strata\ 1\ through\ h$

For this project, there are a total of 94 properties (N) divided into two strata (L). The first stratum will be called “Group 1” and consists of the 67 properties where CCBs were confirmed or may be present. Group 2 consists of the 27 properties where CCBs were confirmed to not be present. The concentrations of the parameters in Group 1 are based on the concentrations in the MWSE samples (Table A-2), representing the presence of CCBs. Concentrations in Group 2 are based on background soil samples (Table A-3), representing background locations where no CCBs are present. The standard deviations were calculated from the concentrations of these previously-obtained samples. The calculations were performed at the 95% confidence level (α=0.05).

Table A-1 presents the inputs to the calculations for arsenic, iron, thallium, lead-210, radium-226, radium-228, and uranium-238. Standard deviations were calculated on either straight concentrations or log transformed concentrations based on the distribution of concentrations. Non-detect values were included in the calculations using a surrogate value of the reporting limit. Concentration distributions were evaluated using the Shapiro Wilk Test in Stata/IC 11.0 (Stata Corporation, 2009). The probabilities associated with the Shapiro Wilk Tests are show in Table A-4. If the probability associated with the Shapiro Wilk test on log transformed concentrations was greater than 0.05 for both Groups 1 and 2, then both groups were treated as lognormally-distributed, and the standard deviation was calculated using log transformed concentrations for both Groups 1 and 2. This was the case for arsenic, lead-210, radium-226, and radium-228. None of the parameters were normally-distributed for both groups. Of the remaining three parameters, iron concentrations were lognormally-distributed in Group 1 and normally-distributed in Group 2; thallium was neither normally nor lognormally-distributed in both groups; and uranium-238 concentrations were lognormally-distributed in Group 1 and neither normally nor lognormally-distributed in Group 2. Therefore, the standard deviations for these parameters were calculated using both log transformed concentrations and straight concentrations, and the equation for calculating number of samples was run twice. Calculated results (i.e., the number of properties to be sampled) were typically not integers, so the result was rounded up to the nearest integer, representing the number of properties to be sampled (for example, a result of 7.02 for arsenic was rounded up to 8 properties).

Results

The results of the calculations for the number of properties based on concentrations of arsenic, iron, thallium, lead-210, radium-226, radium-228, and uranium-238 are summarized in Table A-5. The appropriate number of properties to sample ranges from 5 to 10. For iron, thallium, and uranium-238 the calculated number of samples based on straight and log transformed concentrations were similar.

The statistical method for stratified sampling used here and outlined in the USEPA guidance (USEPA, 2002), is based on the assumption that calculated number of samples (in this case, properties) would be divided between the two strata, and would be randomly selected within each strata. However, to be conservative, the sampling plan proposes that all properties be selected from Group 1, that is, properties where CCBs are confirmed or may be present, and that the specific properties be selected not randomly, but based on criteria such as the results of the gamma surveys and CCB visual inspections as described in the SSC Work Plan.

Although the statistical method based on stratified sampling is intended to calculate a mean concentration, the sampling to be conducted is judgemental and biased to evaluate likely worst-case situations, that is, properties most likely to have the greatest human health risks posed by CCBs. If the calculated number of properties is sufficient to calculate the means of each group, then the same number of properties selected from only one of the groups is more than sufficient to estimate worst-case conditions for that group.

The number of properties (9) selected for judgemental sampling was also run through the algorithm for item sampling with judgemental samples in the visual sample plan (VSP) from Pacific Northwest National Laboratory (VSP Development Team, 2014). Item sampling with judgemental samples is another method based on a finite population. The number of properties calculated from item sampling with judgemental samples indicates that nine judgemental properties are sufficient to characterize the properties where CCBs have been observed. In fact, using inputs based on best professional judgement, the number of properties based on item sampling with judgemental samples in the VSP indicates that three judgement properties would be sufficient. These results are generally consistent with those from the statistical procedure based on stratified sampling that is used in this appendix.

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References:

AECOM. 2012. Human Health Risk Assessment (HHRA). Pines Area of Investigation. July 2012.

Stata Corporation. 2009. Intercooled Stata 11 for Windows. College Station, TX.

USEPA. 2002. Guidance on Choosing a Sampling Design for Environmental Data Collection for Use in Developing a Quality Assurance Project Plan. EPA QA/G-5S.

VSP Development Team, 2014. Visual Sample Plan: A Tool for Design and Analysis of Environmental Sampling. Version 6.5. Pacific Northwest National Laboratory. Richland, WA. http://vsp.pnnl.gov

Tables

Table A-1: Inputs Used To Calculate Optimal Number of Properties to Sample

Parameter	Arsenic (Log Transformed)	Iron	Iron (Log Transformed)	Thallium	Thallium (Log Transformed)	Lead-210 (Log Transformed)	Radium-226 (Log Transformed)	Radium-228 (Log Transformed)	Uranium- 238	Uranium-238 (Log Transformed)
N (Number of Properties Across Groups)	94	94	94	94	94	94	94	94	94	94
Number of Properties in Group 1 (Inspections Conducted, CCBs Suspected/ No Access Granted)	67	67	67	67	67	67	67	67	67	67
Number of Properties in Group 2 (Inspections Conducted, CCBs Not Identified)	27	27	27	27	27	27	27	27	27	27
s_1^2 (s_1 = Standard Deviation of Concentrations in Group 1)	0.57	782058552	0.29	1.49	0.69	0.08	0.15	0.15	0.83	0.34
s_2^2 (s_2 = Standard Deviation in Concentrations in Group 2)	1.05	179549286	0.83	0.42	0.30	0.90	0.31	0.320	0.77	0.63
α (statistical significance level)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
$Z_{1-\alpha/2}$ (Cumulative Normal Distribution With Probability of 1-α/2)	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98
Preliminary Remediation Goal	30.1	76,436	76,436	1.35	1.35	8.44	0.975	1.17	4.5	4.5
d (Desired Margin of Error)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
$W_h s_h^2$ added for Groups 1 through h	0.71	608997380.20	0.45	1.18	0.58	0.32	0.19	0.20	0.81	0.42

Table A-2: MWSE CCB Samples Used To Calculate Standard Deviation in Group 1

Location	Sample	Date
Metals Samples		
TP001	TP001BCB091004S	9/10/04
TP002	TP002BCB091004S	9/10/04
TP003	TP003BCB091004S	9/10/04
TP004	TP004BCB091304S	9/13/04
TP005	TP005BCB091304S	9/13/04
TP006	TP006BCB091304S	9/13/04
TP008	TP008BCB092204S	9/22/04
TP009	TP009BCB092204S	9/22/04
TP010 *	TP010BCB092204D	9/22/04
TP010	TP010BCB092204S	9/22/04
TP011	TP011BCB092204S	9/22/04
TP012	TP012BCB092204S	9/22/04
TP013	TP013BCB092404S	9/24/04
TP014	TP014BCB092404S	9/24/04
TP015	TP015ECB100104S	10/1/04
TP016	TP016ECB100104S	10/1/04
TP017	TP017BCB100104S	10/1/04
TP018	TP018BCB100104S	10/1/04
TP019	TP019BCB100104S	10/1/04
TP020 *	TP020CCB100604D	10/6/04
TP020	TP020CCB100604S	10/6/04
TP021	TP021CCB100604S	10/6/04
TP022	TP022BCB100604S	10/6/04
TP023	TP023ACB100604S	10/6/04
TP026	TP026CCB112904S	11/29/04
TP027	TP027CCB112904S	11/29/04
TP028	TP028CCB112904S	11/29/04
TP033	TP033CCB032305S	3/23/05
TP034 *	TP034CCB032305D	3/23/05
TP034	TP034CCB032305S	3/23/05
TP035	TP035CCB032305S	3/23/05
TP036	TP036CCB032305S	3/23/05
TP037	TP037ACB032305S	3/23/05
TP039	TP039CCB082405S	8/24/05
TP040	TP040ACB082405S	8/24/05
TP041	TP041ACB082405S	8/24/05
TP042	TP042BCB082405S	8/24/05

Location	Sample	Date
Radionuclide Samples		
TP002	TP002XCB040908S	9/10/04
TP004	TP004XCB040908S	9/13/04
TP011	TP011XCB040908S	9/22/04
TP012	TP012XCB040908S	9/22/04
TP014	TP014XCB040908S	9/24/04
TP018	TP018XCB040908S	10/1/04
TP020	TP020XCB040908S	10/6/04
TP026	TP026XCB040908S	11/29/04
TP035	TP035XCB040908S	3/23/05
TP041 *	TP041XCB040908D	8/24/05
TP041	TP041XCB040908S	8/24/05

*Duplicate sample. Results were averaged with parent sample and treated as one sample for calculation of standard deviation. All samples were not necessarily analyzed for all parameters.

Table A-3: CCB-Free Background Samples Used To Calculate Standard Deviation in Group 2

Location	Sample*	Sample Date
SS003	SS003ASS111512S	11/15/2012
SS005	SS005ASS110212S	11/2/2012
SS008	SS008ASS111512S	11/15/2012
SS011	SS011ASS111512S	11/15/2012
SS012	SS012ASS111512S	11/15/2012
SS014	SS014ASS050107S	5/1/2007
SS015	SS015ASS111512S	11/15/2012
SS016	SS016ASS043007S	4/30/2007
SS017	SS017ASS050107S	5/1/2007
SS018	SS018ASS050107S	5/1/2007
SS023	SS023ASS110212S	11/2/2012
SS026	SS026ASS110212S	11/2/2012
SS027	SS027ASS110212S	11/2/2012
SS028	SS028ASS110212S	11/2/2012
SS029	SS029ASS110212S	11/2/2012
SS030	SS030ASS110212S	11/2/2012
SS030*	SS030ASS110212D	11/2/2012
SS031	SS031ASS110212S	11/2/2012
SS033	SS033ASS110212S	11/2/2012
SS034	SS034ASS110212S	11/2/2012
SS034*	SS034ASS110212D	11/2/2012
SS035	SS035ASS110212S	11/2/2012
SS038	SS038ASS111512S	11/15/2012
SS040	SS040ASS111512S	11/15/2012

*Duplicate sample. Results were averaged with parent sample and treated as one sample for calculation of standard deviation.

Table A-4: Probabilities Associated with Shapiro Wilk Test For Normality on Concentrations Used for Calculations of Known Standard Deviation in Groups 1 and 2

Parameter	Shapiro Wilk Test Probability for Group 1	Shapiro Wilk Test Probability for Group 2
Arsenic	0.00002	0.00002
Log Transformed Arsenic	0.99276	0.36363
Iron	0.588827	0.00024
Log Transformed Iron	0.00001	0.08677
Thallium	0.00003	0.00005
Log Transformed Thallium	0.0309	0.00133
Pb 210	0.23059	0.00891
Log Transformed Pb 210	0.30244	0.49842
Ra-226	0.41005	0.00472
Log Transformed Ra-226	0.18498	0.29016
Ra-228	0.14234	0.00059
Log Transformed Ra-228	0.07371	0.18821
U-238	0.84429	0.00004
Log Transformed U-238	0.41313	0.02514

Note: A probability >0.05 suggests there is not enough evidence to reject the hypothesis that a dataset is normal.

Table A-5: Results of Optimal Number of Property Calculations

Parameter	Number of Properties To Be Sampled
Arsenic (Log Transformed)	8
Iron	10
Iron (Log Transformed)	7
Thallium	8
Thallium (Log Transformed)	7
Lead-210 (Log Transformed)	6
Radium-226 (Log Transformed)	5
Radium-228 (Log Transformed)	5
Uranium-238	8
Uranium-238 (Log Transformed)	6

Appendix B

Quality Assurance Project Plan Addendum

Supplemental Soil Characterization Work Plan

Appendix B

Quality Assurance Project Plan Addendum

Pines Area of Investigation

AOC II

Docket No. V-W-’04-C-784

November 2014

QAPP Approvals

Quality Assurance Project Plan Addendum
Supplemental Soil Characterization Work Plan
Pines Area of Investigation
Revision 2
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Prepared for: Brown Inc. and NIPSCO

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Acronyms

ALS	The ALS Group
AOC II	Administrative Order on Consent, 2004; Docket No. V-W-'04-C-784
bgs	below ground surface
°C	degrees Celsius
CAS	Chemical Abstracts Service
CCB	Coal Combustion By-product
CCBK	Continuing Calibration Blank
COC	Constituent of Concern
DOE	Department of Energy
DQL	Data Quality Level
EM	Electron Multiplier
EML	Environmental Measurements Laboratory
FS	Feasibility Study
FWHM	Full Width at Half Maximum
GEL	General Engineering Laboratory
HASL	Health and Safety Laboratory
IC	Inductively Coupled
ICBK	Initial Calibration Blank
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
IDL	Instrument Detection Limit
keV	kiloelectron volt
LCS	Laboratory Control Sample
LOI	Loss on Ignition
MDC	Minimum Detectable Concentration
MDL	Method Detection Limit
mg/kg	milligram per kilogram
mL	milliliter
MRL	Method Reporting Limit

MS/MSD	Matrix Spike/Matrix Spike Duplicate
NA	Not Applicable
NIPSCO	Northern Indiana Public Service Company
NIST	National Institute of Standards and Technology
NORM	Naturally Occurring Radioactive Material
ORP	Oxidation-Reduction Potential
oz	ounce
pCi/g	Picocuries per gram
PLM	polarized light microscopy
PRG	Preliminary Remediation Goal
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
%R	Percent Recovery
RI	Remedial Investigation
RI/FS	Remedial Investigation and Feasibility Study
RJ Lee	RJ Lee Group
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
RSL	Regional Screening Level
SOP	Standard Operating Procedure
SOW	Statement of Work
SR	Sample Result
SSC	Supplemental Soil Characterization
TOC	Total Organic Carbon
ug/L	micrograms per liter
USEPA	United States Environmental Protection Agency
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Standard Chemical Abbreviations

Ac	Actinium
Al	Aluminum
Am	Americium
As	Arsenic
Ba	Barium
Be	Beryllium
Bi-	Bismuth
Co	Cobalt
Cs	Cesium
Cr	Chromium
Fe	Iron
K	Potassium
Pa	Protactinium
Pb	Lead
Ra	Radium
Th	Thorium
Tl	Thallium
U	Uranium
V	Vanadium

Disclaimer

This document is a draft document prepared under a federal administrative order on consent. This document has not undergone formal review by U.S. Environmental Protection Agency (USEPA), however, this document has incorporated comments provided by USEPA on the previous draft version of the report (see Appendix D of the Supplemental Soil Characterization (SSC) Work Plan). The opinions, findings, and conclusions expressed are those of the author and not necessarily those of USEPA.

A.0 Project Management

A.1 Introduction

In April 2004, the United States Environmental Protection Agency (USEPA) and the Respondents (Brown Inc., Ddalt Corp., Bulk Transport Corp., and Northern Indiana Public Service Company (NIPSCO)) signed an Administrative Order on Consent (AOC II) (Docket No. V-W-'04-C-784) to conduct a Remedial Investigation and Feasibility Study (RI/FS) at the Pines Area of Investigation, located in the environs of the Town of Pines, Indiana, as set forth in Exhibit I to II (AOC II, 2004). AOC II (Section VII. 22) and its attachment, the Statement of Work (SOW) (Task 8), require the Respondents to conduct a Feasibility Study (FS) as part of the RI/FS process. As documented in the FS (AECOM, 2014a), additional soil investigations will be conducted. A Supplemental Soil Characterization (SSC) Work Plan (AECOM, 2014b) provides the details for conducting this work.

This Quality Assurance Project Plan (QAPP) Addendum incorporates the RI/FS QAPP (AECOM, 2005) by reference and was prepared to reflect the scope of work described in the SSC Work Plan, and is provided as Appendix B of the SSC Work Plan.

A.2 Project Schedule

The project schedule is presented in Section 6.0 of the SSC Work Plan.

A.3 Distribution List

The QAPP Addendum, and any subsequent revisions, will be distributed to the personnel shown on the Distribution List that immediately follows the approval page.

A.4 Project/Task Organization

The lines of authority and communication specific to the Quality Assurance (QA) program for this additional soil investigation are presented in Figure A-1.

A.5 Problem Definition and Background

Background and the objectives specific to the additional soil investigation are provided in Sections 1.1 and 1.2, respectively, of the SSC Work Plan.

A.6 Project/Task Description

To meet the objectives defined in the SSC Work Plan, three data collection tasks will be conducted:

1. Gamma count rate and gamma dose rate surveys
2. Coal combustion by-product (CCB) visual inspection confirmation sampling
3. Soil sampling of selected properties for specific constituents

The number of field and quality control (QC) samples that will be collected for each analytical parameter is presented in Table A-1. A summary of analytical parameters by medium is presented in Table A-2. Target compounds and analytical parameters for all matrices are presented with their respective laboratory detection limits and data quality levels (DQLs) in Tables A-3 (Metals) and A-4 (primary radionuclide target analytes), and in Attachment B (gamma spectroscopy library).

All data generated from field activities or from the analytical program will be reviewed internally through a tiered review process and validated prior to reporting. All of the data will be validated as limited validation (refer to the RI/FS QAPP [AECOM, 2005] for a detailed description of validation procedures).

A.7 Quality Objectives and Criteria for Measurement Data

The objectives for precision, accuracy, and sensitivity are provided in Table A-5.

B.0 Measurement/Data Acquisition

B.1 Sampling Process Design

The rationale for the sample design is provided in Section 3.0 of the SSC Work Plan.

B.2 Sampling Methods Requirements

B.2.1 Field Measurements

Field measurements will include a gamma walk-over survey and a gamma dose rate survey. These procedures are described in Sections 3.2.1 and 3.2.2 of the SSC Work Plan. Standard operating procedures (SOPs) are included in Appendix C of the SSC Work Plan.

B.2.2 Sampling Procedures

The SOPs that will be utilized for CCB visual inspection, confirmation sampling, and private property soil sampling (Sections 3.3 and 3.4 of the SSC Work Plan, respectively) are provided in Appendix C of the SSC Work Plan.

B.3 Sample Handling and Custody

B.3.1 Sample Containers, Preservation, and Holding Times

A summary of sample container, preservation, and holding time requirements is presented in Table B-1.

B.3.2 Sample Labeling

Labeling of sample containers is described in Section 4.2.2.2 and Appendix G of the SSC Work Plan.

B.4 Analytical Methods

Analyses will be performed by laboratories that have been utilized for previous investigations at the Pines Area of Investigation and approved by USEPA. Chemical analyses of soil samples for metals (including hexavalent chromium), except total uranium will be performed by The ALS Group (ALS; formerly Columbia Analytical Services, Inc.) in Rochester, NY. Gamma spectroscopy analyses for the radioisotopes and inductively coupled plasma – mass spectroscopy (ICP-MS) for total uranium (calculated from U-235 and U-238) will be performed by General Engineering Laboratories, LLC (GEL) in Charleston, SC. Particulate matter analyses will be performed by RJ Lee Group (RJ Lee) in Monroeville, PA.

B.4.1 Laboratory Analytical Procedures

B.4.1.1 Metals

A list of the ALS and GEL SOPs for metals analyses is provided in Table B-2. The SOPs are included in Attachment A.

B.4.1.2 Particulate Matter

The particulate matter analysis by RJ Lee will consist of polarized light microscopy (PLM), X-ray diffraction (XRD), X-ray fluorescence (XRF), and loss on ignition (LOI). The PLM analysis will be used to identify crystalline and non-crystalline glassy and organic phases in the sample and to identify particles with fly ash or bottom ash morphologies. The PLM analyses will be performed in general accordance to EPA 600/R-93/116, *Test Method for the Determination of Asbestos in Bulk Building Materials*. The SOPs for the particulate matter analysis are not included in Attachment A because RJ Lee considers them to be proprietary. The SOPs are available for review at the RJ Lee facility. A summary of the procedures are presented below.

The sample will be spread on a grid on one or more glass slides, and 400 random points on that grid are observed. Particles will be identified by the microscopist as either fly ash or bottom ash and these particles will be counted. If one particle of fly ash is counted in any of those 400 grid squares, the sample will be reported as containing 0.25% fly ash. If a single fly ash article is observed in the light microscopy field, but it is not contained in any of the 400 grid squares randomly selected for counting, a result of “trace” will be reported, which quantitatively is <0.25% fly ash. The same method will apply to the bottom ash results.

Particle Counting Interpretations Observations on a 400-point Grid

Result	Observations on a 400-point Grid
ND	No particles observed within or outside of the grid
<0.25%	No particles observed within the grid, but particle(s) observed upon review of the entire slide
0.25%	1 particle observed within the grid
0.5%	2 particles observed
0.75%	3
1%	4
1.5%	6
2%	8

The XRD analysis will be used to identify the crystalline phases present in the samples and will be performed in general accordance to ASTM D934, *Standard Practices for Identification of Crystalline Compounds in Water-Formed Deposits by X-ray Diffraction.* The LOI analysis (based on ASTM D7348, *Standard Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues*) will be used to determine the weight of percent organic and volatile constituents in the sample and to prepare the samples for XRF analysis by removing the carbonaceous material, carbon dioxide, and water content. The XRF analysis will be used to determine the elemental composition of the residual material in the sample. XRF will be performed in general accordance to ASTM D4326, *Standard Method for Analysis of Coal and Coal Ash by X-ray Fluorescence.*

B.4.1.3 Radionuclides

A list of the GEL SOPs is provided in Table B-2. The SOPs are included in Attachment A.

For the radionuclides by gamma spectroscopy, GEL will dry and prep samples according to their SOPs and seal samples in a 100 cc “tuna can” sample container for a minimum of 28-days prior to analyses. The samples will be counted using the more sensitive detector (N-type) and will be counted for a sufficient amount of time, to a maximum count time of 1000 minutes, in order to meet the minimum detectable concentration (MDC) requirements in Table A-4. The laboratory gamma spectroscopy library includes those isotopes that are used to directly or indirectly quantify the primary radionuclide target analytes. These isotopes are also listed in Table A-4 as primary target analytes with MDCs. Due to the parent/progeny relationship with the isotopes in the gamma spectroscopy library and Table A-4, MDCs are not established for all isotopes on the library list. MDCs in Table A-4 establish the detection limits for the primary radionuclide target analytes. The radionuclides that will be reported for the soil samples will be based on the gamma spectroscopy library that is provided in Attachment B.

The following limits on sensitivity parameters will be applied for gamma spectroscopy analysis:

- Energy Tolerance: 1.5 kiloelectron volts (keV)
- Peak Sensitivity: 3.0
- Abundance Limit: 75%

GEL will conduct a thorough review of 'Unidentified Peaks' and note such peaks with comments in the batch narrative. Any nuclides identified in the 'Unidentified Peaks' report that are not already being reported may be added to the library following approval by the AECOM project manager. For each radionuclide in the gamma library, GEL will report the concentration along with its sample specific uncertainty for each sample as obtained during analysis even if the concentration is less than the MDC or is negative (Section 16.6 in MARLAP, 2004).

USEPA plans to collect split samples for independent analysis. The specific procedures for sample selection, collection, and shipment will be provided by USEPA and will be accommodated in the field.

B.4.2 List of Project Target Constituents and Detection Limits

A listing of project target constituents and reporting limits (RLs) or MDCs for each analyte group listed in Table B-2 can be found in Tables A-3 (metals) and A-4 (primary radionuclide target analytes) and in Attachment B (gamma spectroscopy library).

B.5 Quality Control

Table B-3 summarizes the QC for the analytical methods. Field QC will include field duplicates, equipment blanks, and matrix spike/matrix spike duplicate (MS/MSD) samples, as appropriate for the analytical method. Table A-5 presents the limits for each field QC sample. Procedures and frequencies will be consistent with those described in the RI/FS QAPP.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance

B.6.1 Field Instrument Maintenance

The maintenance schedule and trouble-shooting procedures for field instrument are indicated in Table B-4.

B.7 Laboratory Instrument Preventative Maintenance

Table B-5 provides the frequency with which components of key analytical instruments will be serviced. Table B-6 provides a summary of the monitoring of laboratory equipment.

B.8 Instrument/Equipment Calibration and Frequency

B.8.1 Field Instruments

Calibration of field instruments will be performed according to the manufacturer's instructions and the SOPs included in Appendix C of the SSC Work Plan. A summary of calibration procedures and frequencies is provided as Table B-7.

B.8.2 Analytical Instrumentation

The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria, and the conditions that will require recalibration. This information is summarized in Table B-8. The SOPs are included as Attachment A.

C.0 Project Assessment/Oversight

No audits of field activities or the laboratory analyses associated with the investigation to be conducted under the SSC Work Plan are planned.

D.0 Data Validation and Usability

All chemical and radiochemical data will be subjected to limited validation. The elements of limited validated are described in the RI/FS QAPP (AECOM, 2005). Consistent with the RI/FS QAPP, all metals and radionuclide data packages will be submitted by the laboratories as Level IV data deliverables in the event that a more thorough data validation is required at a later date.

References

AECOM. 2005. Remedial Investigation/Feasibility Study Work Plan, Volumes 1-7. September 16, 2005.

AECOM. 2014a. Feasibility Study. Pines Area of Investigation. July 2014.

AECOM. 2014b. Supplemental Soil Characterization Work Plan. Pines Area of Investigation. November 2014.

MARLAP. 2004. Multi-Agency Radiological Laboratory Analytical Protocols Manual. July 2004.

Tables

Table A-1 Sample Summary

Matrix	Number of Locations (Samples)	Field Parameters	Analytical Parameters	Equipment Blanks[1]	Field Duplicates[2]	MS/ MSDs[3]
Soil (Quadrant Sampling)	• 9 properties • 4 quadrants per property[4] (up to 7 quadrants if special uses) • 1 composite (from 5 locations) per quadrant • 3 depths[5]: 0 - 6 inches below ground surface (bgs), 6 -18 inches bgs, and 1.5 - 5 feet bgs. Total samples 72 - 189	None	Aluminum Arsenic Chromium (total) Hexavalent Chromium Cobalt Iron Thallium Total uranium Vanadium Radionuclides[6]	9	9	9 pairs
Soil/CCB Mixture (CCB VI Verification Sampling)	15	None	Particulate matter (PLM, XRF, XRD, LOI)	NA	0	NA

[1] Equipment rinsate blanks will be collected when non-disposable or non-dedicated equipment is used.
[2] Collected at a frequency of one per 10 samples submitted for analysis for the CCB/soil mixture samples, and a frequency of one per property sampled for the soil samples.
[3] Collected at a frequency of one per property sampled, except not applicable to radionuclides.
[4] Up to 7 quadrants may be established based on the property size and to address three specific property uses, as defined in the SSC Work Plan.
[5] Samples collected at the 1.5 - 5 foot horizon will be submitted for analysis only if CCBs are visually observed in at least 1 of the 5 samples to be composited from a single quadrant.
[6] Refer to Table A-4 and Attachment B (gamma spectroscopy library) for the specific list of radionuclides.

bgs – below ground surface
CCB – Coal Combustion By-product
LOI – Loss on Ignition
NA – Not Applicable
MS/MSD – Matrix Spike/Matrix Spike Duplicate
PLM – Polarized Light Microscopy
SSC – Supplemental Soil Characterization
XRF – X-ray Fluorescence
XRD –X-ray Diffraction

Table A-2 Laboratory Parameters by Sample Medium

Parameter	Soil[4] (Quadrant Sampling)	Soil/CCB Mixtures[4] (CCB VI Verification Sampling)
Metals[1]	X	
Hexavalent chromium	X	
Percent moisture	X	
Radionuclides[2]	X	
Particulate matter[3]		X

[1] Refer to Table A-3 for the specific list of analytes.
[2] Refer to Table A-4 and Attachment B (gamma spectroscopy library) for the specific list of radionuclides.
[3] PLM, XRF, XRD, LOI
[4] Note that particulate matter analyses will be conducted on samples collected from locations where CCBs were previously identified to be present. CCBs may also be present in the soil samples identified for collection in Table A-1, however, those samples will be collected without biasing the sample locations based on the presence or absence of CCBs.

CCB – Coal Combustion By-product
LOI – Loss on Ignition
PLM – Polarized Light Microscopy
XRD – X-Ray Diffraction
XRF – X-Ray Fluorescence

Table A-3 Target Analytes, Reporting Limits, and Data Quality Levels for Metals

Analytes	CAS Number	MDL[1] or IDL[1] (mg/kg)	RL[1] (mg/kg)	DQL – USEPA May 2014 Residential RSL (mg/kg)[2,3]	
Metals by ICP-AES					
Aluminum	7429-90-5	2.8	10	7700	nc
Cobalt	7440-48-4	0.053	5	2.3	nc
Iron	7439-89-6	5.23	10	5500	nc
Metals by ICP-MS					
Arsenic	7440-38-2	0.003	0.10	0.67	c
Chromium (total)	7440-47-3	0.00438	0.20	12000	nc
Thallium	7440-28-0	0.00239	0.10	0.078	nc
Uranium (total)	7440-61-1	see below		23	nc
U-235	see total uranium	0.002	0.014	see total uranium	
U-238	see total uranium	0.0132	0.040	see total uranium	
Vanadium	7440-62-2	0.0164	0.20	39	nc
Hexavalent Chromium					
Chromium (hexavalent)	18540-29-9	0.057	0.40	0.3	c

1 Laboratory RLs, MDLs (GEL), and IDLs (ALS) are updated periodically and are dependent on aliquot weight and percent moisture of the samples. MDLs and IDLs are updated periodically; the current MDLs and IDLs at the time of analyses will be used.

2 Nondetects for ICP-AES and ICP-MS analyses will be reported at the MDLs or IDLs to ensure achievement of the DQL.

3 Regional Screening Levels for Chemical Contaminants at Superfund Sites. May 2014. http://www.epa.gov/region09/superfund/prg/index.html. Values for residential soil. If RSL is based on a noncancer endpoint (nc), the RSL is adjusted to a hazard quotient of 0.1 by multiplying the RSL by 0.1. The risk level is 1E-6 if the RSL is based on a cancer endpoint (c).

CAS – Chemical Abstracts Service
DQL – Data Quality Level
ICP-AES – Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS – Inductively Coupled Plasma-Mass Spectrometry
IDL – Instrument Detection Limit
MDL – Method Detection Limit
mg/kg – milligrams per kilogram
RSL – Regional Screening Level
RL – Reporting Limit
USEPA – United States Environmental Protection Agency

Table A-4 MDC and Data Quality Levels for Primary Radionuclide Target Analytes

Radionuclides[1]	MDC[2] (pCi/g)	DQL – Residential Soil PRG (pCi/g) [3]
Potassium-40	0.5	8.36E-02
Cobalt-60	0.1	3.20E-02
Barium-137m	0.1	1.60E+05
Cesium-137[4]	-[4]	-[4]
Thallium-208	0.1	2.05E+04
Lead-210	1.0	1.90E-02
Bismuth-211	-[5]	2.69E+06
Lead-211	-[5]	3.95E+01
Bismuth-212	0.5	1.70E+01
Lead-212	0.1	6.44E-01
Bismuth-214	0.1	6.43E+01
Lead-214	0.1	4.73E+01
Radon-219	-[5]	7.04E+07
Francium-223	-[5]	2.11E+00
Radium-223	-[5]	6.65E-02
Thorium-227	-[5]	3.35E-01
Actinium-228	0.2	8.58E+00
Protactinium-231	-[5]	8.86E-02
Thorium-231	-[5]	7.36E+00
Protactinium-234m	4.5	1.03E+07
Thorium-234	4.5	6.95E-01
Uranium-235	0.2	1.07E-01
Americium-241[4]	-[4]	-[4]

[1] The radionuclides listed in this table are based on the USEPA approved gamma spectroscopy library presented in Attachment B.

[2] MDCs are based upon sample volume, instrument background, detector efficiency, count time and other statistical factors, as well as specific isotopic values such as abundance and half-life.

[3] USEPA Preliminary Remediation Goals for Radionuclides. Updated November 2014. As the download tables were not available as of 11/6/2014, the on-line calculator was used to derive PRGs for the residential scenario using all defaults from the calculator. http://epa-prgs.ornl.gov/radionuclides/download.html. DQLs for which Residential Soil PRGs are available for the isotope and its progeny. The DQL represents the lower of the Residential Soil PRGs for the isotope and its progeny.

[4] Cs-137 and Am-241 will be reported for each sample, but the results will be used by the laboratory as QC checks on instrument calibration (i.e., efficiency and energy). These radionuclides are not naturally occurring radioactive material (NORM), but are in the environment due to world-wide nuclear activities.

[5] The laboratory gamma spectroscopy library includes those isotopes that are used to directly or indirectly quantify the primary target radionuclides listed above. Due to the parent/progeny relationship with the isotopes in the gamma spectroscopy library, MDCs are not established for all isotopes on the library list. MDCs establish the detection limits for the primary radionuclide target analytes.

pCi/g – picoCuries per gram

DQL – Data Quality Level

MDC – Minimum Detectable Concentration

Radionuclides[1]	MDC[2] (pCi/g)	DQL – Residential Soil PRG (pCi/g) [3]
NORM – Naturally Occurring Radioactive Material PRG – Preliminary Remediation Goal QC – Quality Control		

Table A-5 Quality Control Performance Criteria for Soil Samples

Analytes or Radionuclides	Field and Lab Blanks	Field Duplicate %RPD[1]	LCS % R^2	Matrix Spike % R^2	Duplicate % RPD[2]
Metals by 3050/6010C/6020A & 3060/7199					
Aluminum	<RL	30	47 – 152[3]	75-125	20
Arsenic	<RL	30	82.3 - 117[3]	75-125	20
Chromium (total)	<RL	30	81.8 - 118[3]	75-125	20
Chromium (hexavalent)	<RL	30	80 - 120[3]	85-115	20
Cobalt	<RL	30	83.2 -116[3]	75-125	20
Iron	<RL	30	50.6 -149[3]	75-125	20
Thallium	<RL	30	78.2 -120[3]	75-125	20
Uranium (total) (calculated from U-235 and U-238)					
Uranium-235	<RL	30	75-125	75-125	20
Uranium-238	<RL	30	75-125	75-125	20
Vanadium	<RL	30	73.5 -126[3]	75-125	20
Radionuclides by Gamma Spectroscopy					
Potassium-40	<MDC	30	75-125	NA	20
Cobalt-60	<MDC	30	75-125	NA	20
Barium-137m	<MDC	30	75-125	NA	20
Cesium-137[4]	<MDC	30	75-125	NA	20
Thallium-208	<MDC	30	75-125	NA	20
Lead-210	<MDC	30	75-125	NA	20
Bismuth-211	<MDC	30	75-125	NA	20
Lead-211	<MDC	30	75-125	NA	20
Bismuth-212	<MDC	30	75-125	NA	20
Lead-212	<MDC	30	75-125	NA	20
Bismuth-214	<MDC	30	75-125	NA	20
Lead-214	<MDC	30	75-125	NA	20
Radon-219	<MDC	30	75-125	NA	20
Francium-223	<MDC	30	75-125	NA	20
Radium-223	<MDC	30	75-125	NA	20
Thorium-227	<MDC	30	75-125	NA	20
Actinium-228	<MDC	30	75-125	NA	20
Protactinium-231	<MDC	30	75-125	NA	20
Thorium-231	<MDC	30	75-125	NA	20
Protactinium-234m	<MDC	30	75-125	NA	20

Analytes or Radionuclides	Field and Lab Blanks	Field Duplicate %RPD[1]	LCS % R[2]	Matrix Spike % R[2]	Duplicate % RPD[2]
Thorium-234	<MDC	30	75-125	NA	20
Uranium-235	<MDC	30	75-125	NA	20
Americium-241[4]	<MDC	30	75-125	NA	20

[1] RPD criteria when results are less than 5x RL < 60%.
[2] Control limits current at the time of analyses will be used.
[3] Represent the limits on the Certificate of Analysis supplied by the vendor or limit supplied by the laboratory.
[4] Cs-137 and Am-241 will be reported for each sample, but the results will be used by the laboratory as QC checks on instrument calibration (i.e., efficiency and energy). These radionuclides are not NORM, but are in the environment due to world-wide nuclear activities.
[5] The gamma spectroscopy analysis will quantify gamma-emitting radionuclides provided in Table A-4. Many of these radionuclides are decay progeny of parent radionuclides that are Pines Area of Investigation constituents of concern (COCs) and they will be used to directly quantity the activity of the parent COC. Parent COC concentrations are equivalent to or a constant factor of the progeny radionuclides given that the decay chains will be in secular equilibrium following a 28-day buildup time.

LCS – Laboratory Control Sample
MDC – Minimum Detectable Concentration (radionuclides only)
NA – Not Applicable
NORM – Naturally Occurring Radioactive Material
QC – Quality Control
RL – Reporting Limit
% R - Percent Recovery
RPD – Relative Percent Difference

Table B-1 Summary of Sample Container, Preservation, and Holding Time Requirements for Soil and CCB/Soil Mixture Samples

Parameter	Container [1, 2]	Preservation	Holding Time [3]
Metals – Al, As, Co, Cr, Fe, Tl, U (total), and V	Wide-mouth 500-mL glass or plastic jar[4]	Cool, 0 - 6°C	180 days
Hexavalent chromium	Wide-mouth 500-mL glass or plastic jar[4, 5]	Cool, 0 - 6°C	24 hours for ORP, pH, and ferrous iron 30 days to extraction, 7 days from extraction to analysis for hexavalent chromium
Radionuclides[6]	Wide-mouth 500 mL glass or plastic jar[4]	None required	None required
Particulate matter (PLM, XRD, XRF, LOI)	Wide-mouth 4-oz glass jar[4]	None required	None established

[1] Additional volume will be collected for MS/MSD samples (metals only).
[2] Laboratory may provide alternate containers as long as the containers meet the requirements of the method and allow the collection of sufficient volume to perform the analyses.
[3] Holding time begins from date and time of sample collection.
[4] Glass containers will be placed in zipper-lock bags prior to shipping.
[5] In association with the hexavalent chromium analyses, additional parameters will be analyzed. These parameters either confirm the reducing/oxidizing tendency of the samples or are indirect indicators of the reducing/oxidizing tendency, and include pH, oxidation reduction potential (ORP), Total Organic Carbon (TOC), sulfides, and ferrous iron. To ensure adequate volume, a separate container from other metals will be collected. These results will be used qualitatively.
[6] Refer to Table A-4 and Attachment B (gamma spectroscopy library) for the list of radionuclides that will be reported for this program.

mL – milliliter
oz – ounce
°C – degrees Celsius
CCB – Coal Combustion By-product
LOI – Loss on Ignition
MS/MSD – Matrix Spike/Matrix Spike Duplicate
ORP – Oxidation Reduction Potential
PLM – Polarized Light Microscopy
TOC – Total Organic Carbon
XRD – X-Ray Diffraction
XRF – X-Ray Fluorescence

Table B-2 Analytical Methodologies

Analyte Group[1]	Laboratory SOP Number[2]	Equivalent Method Number
Metals		
Metals by ICP-AES (Al, Co, Fe)	MET-3050B, Rev.5 MET-200.7/6010C, Rev. 14	USEPA SW-846 Method 3050B USEPA SW-846 Method 6010C
Metals by ICP-MS (As, Cr, Tl, V)	MET-3050B, Rev.5 MET-6020A/200.8, Rev. 2	USEPA SW-846 Method 3050B USEPA SW-846 Method 6020A
Uranium (Total) (calculated from U-235 and U-238)	GL-MA-E-009, Rev. 22 GL-MA-E-014, Rev. 25	USEPA SW-846 Method 3050B USEPA SW-846 Method 6020A
Hexavalent Chromium	GEN-3060, Rev. 3 GEN-7199, Rev. 6	USEPA SW-846 Method 3060A USEPA SW-846 Method 7199
Radionuclides		
Radionuclides by Gamma Spectroscopy	GL-RAD-A-013, Rev. 25 GL-RAD-A-021, Rev. 20 GL-RAD-I-001, Rev 19	DOE EML HASL 300
Particulate Matter		
PLM	See Section B.4.1.2	Modified, EPA 600/R-93/116, *Test Method for the Determination of Asbestos in Bulk Building Materials*.
XRD	See Section B.4.1.2	ASTM D934, *Standard Practices for Identification of Crystalline Compounds in Water-Formed Deposits by X-ray Diffraction*
XRF	See Section B.4.1.2	ASTM D4326, *Standard Method for Analysis of Coal and Coal Ash by X-ray Fluorescence*
LOI	See Section B.4.1.2	ASTM D7348, *Standard Test Methods for Loss on Ignition (LOI) of Solid Combustion Residues*

[1] See Tables A-3 and A-4 and Attachment B (gamma spectroscopy library) for the analytes in each analyte group.
[2] The version of the SOP that is current at the time of sample analysis will be utilized. Any modification to the approved SOP will require USEPA notification and concurrence.

DOE – Department of Energy
EML – Environmental Measurements Laboratory

Analyte Group[1]	Laboratory SOP Number[2]	Equivalent Method Number
HASL – Health and Safety Laboratory ICP-AES – Inductively Coupled Plasma-Atomic Emission Spectroscopy ICP-MS – Inductively Coupled Plasma-Mass Spectrometry LOI – Loss on Ignition NA – Not Available PLM – Polarized Light Microscopy SOP – Standard Operating Procedure USEPA – United States Environmental Protection Agency XRF – X-ray Fluorescence XRD – X-ray Diffraction		

Table B-3 Analytical Quality Control Checks

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Metals 6010C	Reagent/prep/ ICBK blanks	One per preparation batch	No analytes above RL	Repreparation/reanalysis of entire prep batch
	MS samples	One per preparation batch	One per preparation batch	Analyze post-digestion spike
	Duplicate samples	One per preparation batch	Refer to Table A-5	Check analytical system, flag results
	LCS	One per preparation batch	Vendor limits (refer to Table A-5)	Repreparation/reanalysis of entire prep batch
	Dilution test	One per preparation batch	Within 10% of original sample results	Flag results
	Interference check	Beginning of each analytical run	20% of true values	Recalibrate and reanalyze any sample with interfering elements
Metals 6020A	Reagent/Prep/ ICBK/CCBK blanks	1 per analytical batch of 20 samples or less, CCBs every 10 samples in analytical run	No analytes above RL	Repreparation/reanalysis of entire prep batch
	MS Samples	1 per analytical batch of 20 samples or less	Refer to Table A-5	Analyze post digestion spike
	MS Duplicate Samples	1 per analytical batch of 20 samples or less	Refer to Table A-5	Check analytical system, flag results
	LCS	1 per analytical batch of 20 samples or less	Vendor limits (refer to Table A-5)	Repreparation/reanalysis of entire prep batch
	Dilution Test	1 per analytical batch of 20 samples or less	10% (results >4 x RL)	Flag results
	Interference check	Beginning of each analytical run	80-120% R	Recalibrate, reanalyze any sample with interfering elements
Hexavalent Chromium 7199	Reagent/prep blanks	One per analytical batch of 20 samples or less	Not detected above MRL	Repreparation/reanalysis of entire batch
	MS samples	One per analytical batch of 20 samples or less	Refer to Table A-5	Repreparation/reanalysis of entire batch
	Duplicate samples	One per analytical batch of 20 samples or less	Refer to Table A-5	Check analytical system, flag results
	LCS	One per analytical batch of 20 samples or less	Vendor limits (refer to Table A-5)	Repreparation/reanalysis of entire batch

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Radionuclides Gamma spectroscopy	Reagent/prep blanks	One per preparation batch	Not detected above MDC	Repreparation/reanalysis of entire batch
	Duplicate samples	One per preparation batch	RPD <20; RPD<100 if SR <5x MDC; RPD NA if SR <MDC	Check analytical system, flag results
	LCS	One per preparation batch	75-125% R	Repreparation/reanalysis of entire batch
Particulate Matter	Duplicate samples	One per preparation batch	RPD <20 or current laboratory limits	Check results, flag results

[1] Preparation Batch defined as maximum of 20 field samples of a similar matrix unless otherwise specified.

CCB – Coal Combustion By-product
CCBK – Continuing Calibration Blank
ICBK – Initial Calibration Blank
LCS – Laboratory Control Sample
MDC – Minimum Detectable Concentration
MRL – Method Reporting Limit
MS – Matrix Spike
NA – Not Applicable
%R – Percent Recovery
QC – Quality Control
RL – Reporting Limit
RPD – Relative Percent Difference
SR – Sample Result

Table B-4 Maintenance Procedures and Schedule for Field Instruments

Instrument	Maintenance Procedures/Schedule	Spare Parts in Stock
Portable radiation detection instruments	Physical check of instrument/daily Check the battery and change/recharge if necessary/daily High voltage check/daily Response correlation check/beginning of the program	Batteries Source standard

Table B-5 Maintenance Procedures and Schedule for Analytical Instruments

Instrument	Spare Parts	Activity	Frequency
ICP-AES (SW-846 Method 6010C)	Gases O-rings Tubing	Check gases Check argon tank pressure Check aspiration tubing Check vacuum pump gauge Check cooling water system Check nebulizer Check capillary tubing Check peristaltic pump tubing Check high voltage switch Check exhaust screens Check torch, glassware, aerosol injector tube, bonnet Clean plasma torch assembly Clean nebulizer and drain chamber Clean filters Replace tubing Check o-rings	Daily Daily Daily Daily Daily Daily Daily Daily Daily Daily Daily Monthly or as needed Monthly or as needed Monthly or as needed Monthly or as needed Monthly or as needed
ICP-MS (SW-846 Method 6020A)	Gases O-rings Tubing	Clean nebulizer tip after use Replace peripump sample introduction tubing Change pump hoses on drain systems Check drain waste collection containers, and empty as necessary Check Neslab water level and add water if required Clean/replace interface cones Clean/replace nebulizer Clean/replace torch Check/replace water filter	As needed As needed As needed As needed As needed As needed As needed As needed As needed
		Change oil in interface rotary pump (or as needed). Clean ion lenses 4-6 months (or as needed).	Quarterly Quarterly
		Clean air filters	6 months
		Change pump oil in backing rotary pump Evaluate/replace EM	12 months
Ion Chromatography Method (SW-846 Method 7199)		Rinse IC pump and valves Lubricate pump	Weekly Every 6 months
Gamma Spectrometer (DOE EML HASL 300)		Energy and FWHM calibration Efficiency calibration Instrument check Background Liquid nitrogen fill Software backups Filter cleaning	Annual Annual Daily Weekly Weekly Monthly Quarterly

Instrument	Spare Parts	Activity	Frequency
DOE – Department of Energy EM – Electron Multiplier EML – Environmental Measurements Laboratory FWHM – Full Width at Half Maximum HASL – Health and Safety Laboratory IC – Ion Chromatograph ICP-AES – Inductively Coupled Plasma-Atomic Emission Spectroscopy ICP-MS – Inductively Coupled Plasma-Mass Spectrometry			

Table B-6 Laboratory Equipment Monitoring

Equipment Type	Activity	Frequency
Ovens	Temperature monitoring Electronics serviced	Daily As needed
Refrigerators	Temperature monitoring Refrigerant system and electronics serviced	Twice daily As needed
Balances	Calibration Manufacturer cleaning and servicing	Daily or before use Annually
High-purity water system	Conductance monitoring	Daily

Table B-7 Field Instrument Calibration

Parameter	Calibration Frequency	Calibration Standards	Acceptance Criteria
Gamma Walk-over Survey (Ludlum Model 44-10 detector)	Annually: At least once per year and after repairs have been performed, if applicable.[1]	NIST Traceable sources	Calibrated by the manufacturer or a rental vendor with detector efficiency optimized for gamma energies associated with Ra-226 and its decay progeny
	Daily: Field response check	Exempt sealed gamma source	Within 20% of source activity
Gamma Dose Rate Survey (Thermo Scientific™ Micro Rem r)	Annually: At least once per year and after repairs have been performed, if applicable.	NIST Traceable sources	Calibrated by the manufacturer or a rental vendor
	Daily: Field response check	Exempt sealed gamma source	Within 20% of source activity

[1] Note that the detector will be correlated to a source block set (4 stacked blocks) with known total radium concentration; a 10 pCi/g total radium source block set is located at the former Kerr McGee Rare Earths Facility in West Chicago, Illinois.

NIST – National Institute of Standards and Technology
pCi/g – picoCurie/gram
SSC – Supplemental Soil Characterization

Table B-8 Analytical Instrument Calibration

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
Metals by ICP-AES SW-846 6010C	Initial: Daily	Initial: Per manufacturer's instructions. Minimum of one standard and calibration blank and instrument blank.	Initial: Highest standard within 10% of true value. % RSD 20 < RL
	Continuing: Every 10 samples	Mid-level of each metal and instrument blank	±10% of true value % RSD 20 < RL
	Ending	Mid-level of each metal and instrument blank	±10% of true value % RSD 20 < RL
Metals by ICP-MS SW-846 6020A	Instrument tune: Daily	Per manufacturer: tune solution of 10 ug/L, Be, Mg, Co, In, Pb	Manufacturer's recommended tune criteria as specified in SOP.
	Initial: Daily	Initial per manufacturer's instructions – minimum of one calibration standard, one calibration blank and interference check standards ICS-A, ICS-AB	±10% true value % RSD 20 <RL ±20% recovery
	Continuing: every 10 samples	One calibration standard and one calibration blank	±10% true value % RSD 20 <RL
	Ending	If required: run MRL standard , ICS-A and ICS-AB interference check standards, one calibration standard, one calibration blank	±20% recovery ±10% true value % RSD 20 <RL

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
Hexavalent chromium by SW-846 7199	Initial: Daily	3 standards plus blank	r ≥ 0.999 ±10% of true value < RL
	Continuing: Every 10 injections, or 24 hours, whichever is more frequent	Mid-level plus blank	±10% of true value < RL
	Ending	Mid-level plus blank	±10% of true value < RL
Radionuclides by Gamma Spectroscopy (DOE EML HASL 300)	Daily checks using a check source with multiple radionuclides	NIST Traceable standards	Within 2-3 sigma control limits
	Monitor FWHM and efficiency	NIST Traceable standards	Within 2-3 sigma control limits
	Peak centroid	NIST Traceable standards	+/- 2 keV
	Weekly or monthly background checks	NA	Within 2-3 sigma control limits

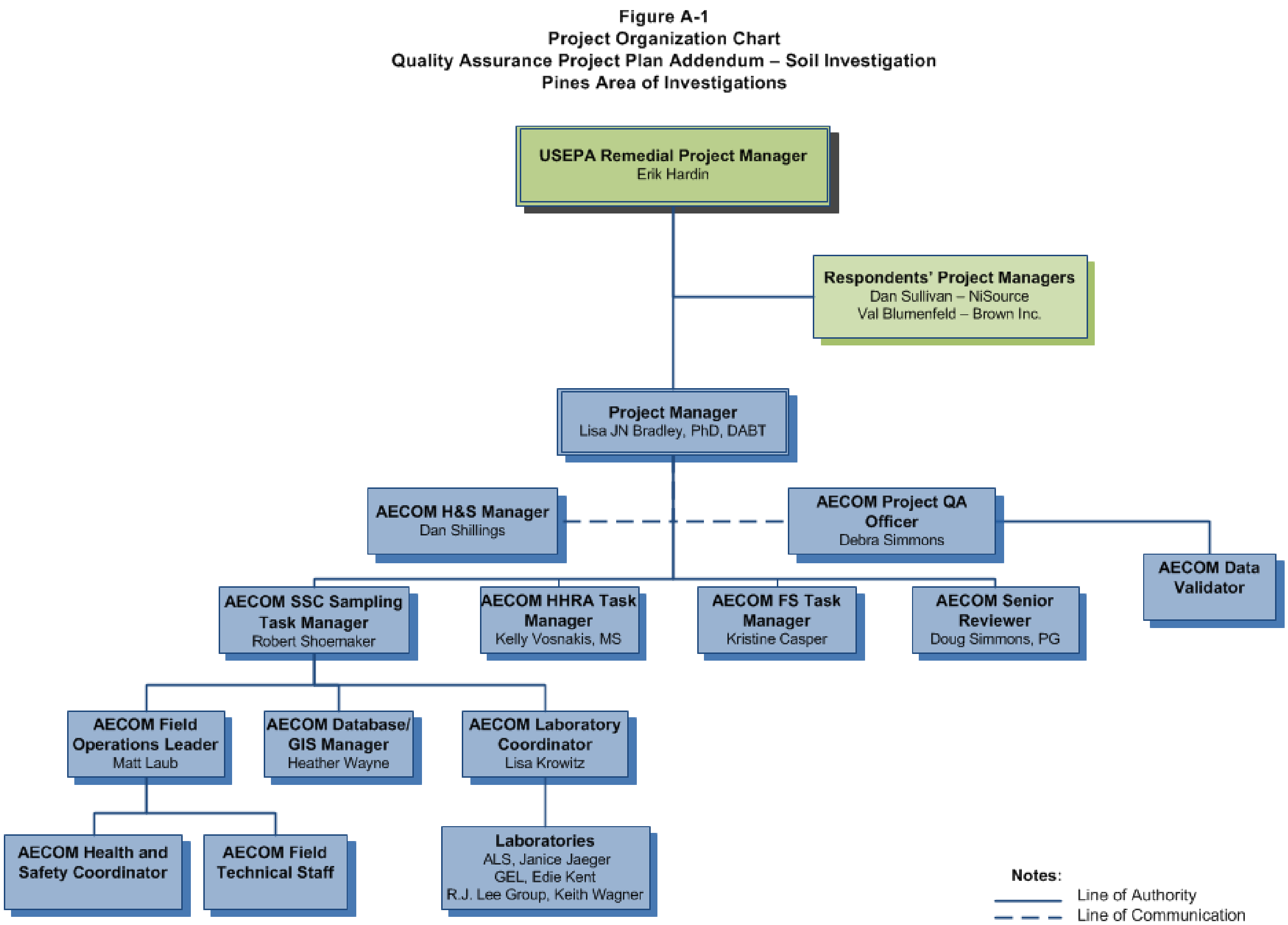
[1] If criteria are not met, corrective actions as specified in the laboratory SOPs (Attachment A) are taken.

DOE – Department of Energy
EML – Environmental Measurements Laboratory
FWHM – Full Width at Half Maximum
HASL – Health and Safety Laboratory
ICP-AES – Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS – Inductively Coupled Plasma-Mass Spectrometry
ICS – Interference Check Sample
KeV – kiloelectron volt
MRL – Method Reporting Limit
NA – Not Applicable
NIST – National Institute of Standards and Technology
RL – Reporting Limit
RSD – Relative Standard Deviation
SOP – Standard Operating Procedure
ug/L – micrograms per Liter

Figure

Figure

Figure A-1 Project Organization Chart



Attachment A

Laboratory Standard Operating Procedures

SOP Change Form

SOP Title: Determination of Metals and Trace Elements by ICP-MS	
SOP Code: MET-6020A/200.8	
SOP Revision No.: 2	
SOP Date: 11/4/13	
SOP Section(s) Affected by Change: 11.1, Appendix	

Description of Change:
Add to 11.1: "The daily operating and evaluation criteria are discussed in 11.3-11.6. An example of further instrument conditions is found in the Appendix of this SOP."

Add the attached to the Appendix.

Reason(s) for Change(s):

PJLA Audit

Change(s) Submitted by: Vicky Collom	Date: 12/5/13

Approvals:

Technical Reviewer Signature: [signature]	Date: 12/5/13
QA Signature: [signature]	Date: 12/5/13
Laboratory Director Signature: [signature]	Date: 12/9/13

Change(s) Effective Date:

Distribution: Original filed with original SOP   Photocopy attached to each controlled copy

Quantitative Method Report

File Name: 6020a.mth
File Path: c:\elandata\Method\6020a.mth

Timing Parameters

Sweeps/Reading:	10
Readings/Replicate:	1
Number of Replicates:	3
Tuning File:	epa.tun
Optimization File:	epa2.dac
QC Enabled:	Yes
Settling Time:	Normal

	Analyte	Mass	Scan Mode	MCA Channels	Dwell Time	Integration Time
>	Li	6.015	Peak Hopping	1	100.0 ms	1000 ms
	Be	9.012	Peak Hopping	1	100.0 ms	1000 ms
	Al	26.982	Peak Hopping	1	100.0 ms	1000 ms
>	Sc	44.956	Peak Hopping	1	100.0 ms	1000 ms
	V	50.944	Peak Hopping	1	100.0 ms	1000 ms
	Cr	51.941	Peak Hopping	1	100.0 ms	1000 ms
	Cr	52.941	Peak Hopping	1	100.0 ms	1000 ms
	Mn	54.938	Peak Hopping	1	100.0 ms	1000 ms
	Co	58.933	Peak Hopping	1	100.0 ms	1000 ms
	Ni	59.933	Peak Hopping	1	100.0 ms	1000 ms
	Ni	61.928	Peak Hopping	1	100.0 ms	1000 ms
	Cu	62.930	Peak Hopping	1	100.0 ms	1000 ms
	Cu	64.928	Peak Hopping	1	100.0 ms	1000 ms
	Zn	65.926	Peak Hopping	1	100.0 ms	1000 ms
	Zn	66.927	Peak Hopping	1	100.0 ms	1000 ms
	Zn	67.925	Peak Hopping	1	100.0 ms	1000 ms
>	Ge	71.922	Peak Hopping	1	100.0 ms	1000 ms
	As	74.922	Peak Hopping	1	100.0 ms	1000 ms
	Se	76.920	Peak Hopping	1	500.0 ms	5000 ms
	Se	81.917	Peak Hopping	1	500.0 ms	5000 ms
	Kr	82.914	Peak Hopping	1	100.0 ms	1000 ms
	Sr	85.909	Peak Hopping	1	100.0 ms	1000 ms
	Sr	87.906	Peak Hopping	1	100.0 ms	1000 ms
	Y	88.905	Peak Hopping	1	100.0 ms	1000 ms
	Mo	94.906	Peak Hopping	1	100.0 ms	1000 ms
	Mo	96.906	Peak Hopping	1	100.0 ms	1000 ms
	Mo	97.906	Peak Hopping	1	100.0 ms	1000 ms
	Rh	102.905	Peak Hopping	1	100.0 ms	1000 ms
	Ag	106.905	Peak Hopping	1	100.0 ms	1000 ms
	Ag	108.905	Peak Hopping	1	100.0 ms	1000 ms
	Cd	110.904	Peak Hopping	1	100.0 ms	1000 ms

|	Cd	113.904	Peak Hopping	1	100.0 ms	1000 ms
|>	In	114.904	Peak Hopping	1	100.0 ms	1000 ms
|	Sb	120.904	Peak Hopping	1	100.0 ms	1000 ms
L	Sb	122.904	Peak Hopping	1	100.0 ms	1000 ms
Γ	Ba	134.906	Peak Hopping	1	100.0 ms	1000 ms
|	Ba	136.905	Peak Hopping	1	100.0 ms	1000 ms
L>	Tb	158.925	Peak Hopping	1	100.0 ms	1000 ms
Γ>	Ho	164.930	Peak Hopping	1	100.0 ms	1000 ms
|	Tl	202.972	Peak Hopping	1	100.0 ms	1000 ms
|	Tl	204.975	Peak Hopping	1	100.0 ms	1000 ms
|	Pb	207.977	Peak Hopping	1	100.0 ms	1000 ms
|	Pb	205.975	Peak Hopping	1	100.0 ms	1000 ms
L	Pb	206.976	Peak Hopping	1	100.0 ms	1000 ms
Γ>	Bi	208.980	Peak Hopping	1	100.0 ms	1000 ms
|	Th	232.038	Peak Hopping	1	100.0 ms	1000 ms
L	U	238.050	Peak Hopping	1	100.0 ms	1000 ms

Signal Processing

Detector Mode:	Dual
Measurement Units:	Cps
AutoLens:	On
Spectral Peak Processing:	Maximum
Signal Profile Processing:	Maximum
Blank Subtraction:	After Internal Standard
Baseline Readings:	0
Smoothing:	Yes, Factor 5

Equations

Analyte	Mass	Corrections
V	50.944	-3.127*(ClO 53-(0.113*Cr 52))
As	74.922	-3.127*(ArCl77-(0.873*Se82))
Se	81.917	-1.0087*Kr83
Sr	85.909	- 1.505657 * Kr 83
Mo	97.906	- 0.110588 * Ru 101
Cd	110.904	-1.073*(MoO 108 - (0.712*Pd 106))
Cd	113.904	- 0.026826 * Sn 118
In	114.904	- 0.014032 * Sn 118
Sb	122.904	- 0.127189 * Te 125
Pb	207.977	+1*Pb 206 + 1*Pb 207

Calibration Information

Analyte	Mass	Curve Type	Sample Units	Std Units	Std 1	Std 2	Std 3	Std 4
Li	6.015	Linear Thru Zero	ug/L	ug/L				
Be	9.012	Linear Thru Zero	ug/L	ug/L	1	20	100	
Al	26.982	Linear Thru Zero	ug/L	ug/L	10	20	100	
Sc	44.956	Linear Thru Zero	ug/L	ug/L				

V	50.944	Linear Thru Zero	ug/L	ug/L	2	20	100
Cr	51.941	Linear Thru Zero	ug/L	ug/L	2	20	100
Cr	52.941	Linear Thru Zero	ug/L	ug/L	2	20	100
Mn	54.938	Linear Thru Zero	ug/L	ug/L	1	20	100
Co	58.933	Linear Thru Zero	ug/L	ug/L	1	20	100
Ni	59.933	Linear Thru Zero	ug/L	ug/L	1	20	100
Ni	61.928	Linear Thru Zero	ug/L	ug/L	1	20	100
Cu	62.930	Linear Thru Zero	ug/L	ug/L	1	20	100
Cu	64.928	Linear Thru Zero	ug/L	ug/L	1	20	100
Zn	65.926	Linear Thru Zero	ug/L	ug/L	5	20	100
Zn	66.927	Linear Thru Zero	ug/L	ug/L	5	20	100
Zn	67.925	Linear Thru Zero	ug/L	ug/L	5	20	100
Ge	71.922	Linear Thru Zero	ug/L	ug/L			
As	74.922	Linear Thru Zero	ug/L	ug/L	1	20	100
Se	76.920	Linear Thru Zero	ug/L	ug/L	2	20	100
Se	81.917	Linear Thru Zero	ug/L	ug/L	2	20	100
Kr	82.914	Linear Thru Zero	ug/L	ug/L			
Sr	85.909	Linear Thru Zero	ug/L	ug/L	1	20	100
Sr	87.906	Linear Thru Zero	ug/L	ug/L	1	20	100
Y	88.905	Linear Thru Zero	ug/L	ug/L			
Mo	94.906	Linear Thru Zero	ug/L	ug/L	1	20	100
Mo	96.906	Linear Thru Zero	ug/L	ug/L	1	20	100
Mo	97.906	Linear Thru Zero	ug/L	ug/L	1	20	100
Rh	102.905	Linear Thru Zero	ug/L	ug/L			
Ag	106.905	Linear Thru Zero	ug/L	ug/L	1	20	100
Ag	108.905	Linear Thru Zero	ug/L	ug/L	1	20	100
Cd	110.904	Linear Thru Zero	ug/L	ug/L	1	20	100
Cd	113.904	Linear Thru Zero	ug/L	ug/L	1	20	100
In	114.904	Linear Thru Zero	ug/L	ug/L			
Sb	120.904	Linear Thru Zero	ug/L	ug/L	1	20	100
Sb	122.904	Linear Thru Zero	ug/L	ug/L	1	20	100
Ba	134.906	Linear Thru Zero	ug/L	ug/L	1	20	100
Ba	136.905	Linear Thru Zero	ug/L	ug/L	1	20	100
Tb	158.925	Linear Thru Zero	ug/L	ug/L			
Ho	164.930	Linear Thru Zero	ug/L	ug/L			
Tl	202.972	Linear Thru Zero	ug/L	ug/L	1	20	100
Tl	204.975	Linear Thru Zero	ug/L	ug/L	1	20	100
Pb	207.977	Linear Thru Zero	ug/L	ug/L	1	20	100
Pb	205.975	Linear Thru Zero	ug/L	ug/L	1	20	100
Pb	206.976	Linear Thru Zero	ug/L	ug/L	1	20	100
Bi	208.980	Linear Thru Zero	ug/L	ug/L			
Th	232.038	Linear Thru Zero	ug/L	ug/L	1	20	100
U	238.050	Linear Thru Zero	ug/L	ug/L	1	20	100

Analyte	Mass	Std 5	Std 6	Std 7	Std 8	Std 9	Std 10	Std 11	Std 12
Li	6.015								
Be	9.012								

Al	26.982
Sc	44.956
V	50.944
Cr	51.941
Cr	52.941
Mn	54.938
Co	58.933
Ni	59.933
Ni	61.928
Cu	62.930
Cu	64.928
Zn	65.926
Zn	66.927
Zn	67.925
Ge	71.922
As	74.922
Se	76.920
Se	81.917
Kr	82.914
Sr	85.909
Sr	87.906
Y	88.905
Mo	94.906
Mo	96.906
Mo	97.906
Rh	102.905
Ag	106.905
Ag	108.905
Cd	110.904
Cd	113.904
In	114.904
Sb	120.904
Sb	122.904
Ba	134.906
Ba	136.905
Tb	158.925
Ho	164.930
Tl	202.972
Tl	204.975
Pb	207.977
Pb	205.975
Pb	206.976
Bi	208.980
Th	232.038
U	238.050

AS Pos	Sample Flush	Sample Flush	Read Delay	Read Delay	Wash	Wash

Blank	1	20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 1	2	20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 2	3	20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 3	4	20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 4		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 5		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 6		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 7		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 8		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 9		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 10		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 11		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 12		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 13		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 14		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 15		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 16		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 17		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 18		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 19		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 20		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 21		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 22		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 23		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 24		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 25		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 26		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 27		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 28		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 29		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm
Standard 30		20 s	-36 rpm	30 s	-26 rpm	120 s	-36 rpm

Reporting Options

Report Template for Printing: c:\elandata\ReportOptions\6020a qc report.rop
Send to Printer: Yes
Report Template for File: c:\elandata\ReportOptions\lims export.rop
Send to File: Yes
Report Filename: i:\instdata\metals\elan_xf\120213.rep
Create NetCDF File: No
Send to Serial Port: No
Port: COM1

Sampling Devices

Peristaltic Pump Control: Yes
Autosampler: AS-93plus
Autosampler Tray File: c:\elandata\Autosampler\as-93\as93f.try

Sampling Device Type: None
Dil. Factor: 10
Dil. to Vol. (mL): 10
1st Dil. Pos.: 1
Probe Purge Pos.: 10

FIAS Program

Step	Read	Time	Pump 1	Pump 2	Valve	A/S Loc.	Sw 2	Sw 3	Sw 4

Repeat Statement

HGA Program

Description:
Sample Volume: uL
Injection Temperature: C
Injection Speed:
Read delay: s
Closure delay: s
Modifier #1:
Modifier #2:

Step	Cell Temp	Ramp	Hold	Int. Flow	Gas Norm.	Gas Alt.	To Vent	To ICP	Read

Pipet Seq.	Mod#1	Mod#2	Sample	Start Step	Wash	Rep. From	End S Wash	Rep. To	# R

ALS Standard Operating Procedure

DOCUMENT TITLE:	DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY (ICP-MS)
REFERENCED METHOD:	EPA 200.8, SW 6020A
SOP ID:	MET-6020A/200.8
REV. NUMBER:	2
EFFECTIVE DATE:	11/4/2013

ALS Environmental

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY (ICP-MS)
EPA 200.8, SW 6020A

SOPID:	MET-6020A/200.8	Rev. Number:	2	Effective Date:	11/4/2013

Approved By: [signature] Date: 11/1/13
Department Supervisor – Christine Kutzer

Approved By: [signature] Date: 11/1/2013
QA Manager – Lisa Reyes

Approved By: [signature] Date: 11/1/13
Laboratory Director – Michael Perry

Archival Date:		Doc Control ID#:	13-MET-01 ooc 11/4/13	Editor:	

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DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROSCOPY (ICP-MS)

1) Scope and Applicability

This SOP uses EPA SW846 Method 6020A for the determination of the concentrations of certain elements in water, soil, aqueous and non-aqueous wastes, and sediment samples. This SOP also uses EPA 200.8 for the determination of the concentrations of certain elements in drinking water, ground water, and surface water. The scope of this document does not allow for the in-depth descriptions of the relevant spectroscopic principles required for gaining a complete level of competence in this scientific discipline.

The analytes and reporting limits are listed in Table 1.

2) Summary of Procedure

2.1 Prior to analysis, samples must be digested using appropriate sample preparation methods unless otherwise specified by the client. The preparation for soils is described in MET-3050 and the preparation for waters is described in MET-CLP-DIG. The digestate is analyzed for the elements of interest using ICP spectrometry.

2.2 This method is for the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences 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 constituents of the sample matrix.

2.3 Method Modifications

2.3.1 The concentration of interfering elements in the ICSA and ICSAB solutions are spiked at levels recommended by the manufacturer due to instrument sensitivity.

2.3.2 6020A says that IDLs should be determined every 3 months to monitor noise and response changes. Blanks and MRL standards are analyzed with every run and can be used for monitoring.

3) Definitions

3.1 Initial Calibration - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the detector to the element.

3.2 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification.

3.4 Initial Calibration Verification (ICV) (also called Second Source Calibration Verification) – ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the initial calibration.

3.5 Continuing Calibration Verification Standard (CCV) - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration. For the LLCCV, see MRL Standard below.

3.6 Matrix Spike (MS) – An aliquot of an environmental sample to which known quantities of all of the elements of client interest are added to a sample matrix prior to sample digestion and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for each of the analytes detected.

3.7 Duplicate (DUP) - A laboratory duplicate. Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.8 Laboratory Control Sample (LCS) - A matrix blank spiked with all of the elements of client interest. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate measurements. LCS-Soil is purchased from a vendor.

3.9 Method Blank (MB) - The MB is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire preparation and analytical procedure.

3.10 Instrument Blank (ICB/CCB) - The instrument blank (also called initial or continuing calibration blank) is a volume of reagent water acidified with the same acid matrix as in the calibration standards. This blank is the zero standard and has a reagent composition identical to the digestates. The purpose of the ICB/CCB is to determine the levels of contamination associated with the instrumental analysis.

3.11 Batch – A group of no more than 20 samples analyzed together on the same day with the same reagents. See the SOP for Batches and Sequences (ADM-BATCH) for more detail.

3.12 Calibration Blank – A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to the calibrate the instrument.

3.13 Internal Standard - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.14 Linear Range - The concentration range over which the instrument response to an analyte is linear.

3.15 Limit of Detection (LOD) – An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory – dependent. For DOD, the smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%.

3.16 Limit of Quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target that can be reported with a specified degree of confidence. For DOD, the lowest concentration that produces a quantitative result within specified limits of precision and bias. The LOQ shall be set at or above the concentration of the lowest initial calibration standard.

3.17 Interference Check Solution (ICS) - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria. This is used for 6020A.

3.18 MRL Standard – Standard prepared with a known concentration of elements to check accuracy at the quantitation limit. This is also known as Low-level calibration check standard (LLCCV or LLICV). This standard is not digested.

3.19 LOQ Standard – also called LLQC – Standard prepared at the LOQ that undergoes digestion and preparation procedures.

3.20 HLCCV2 – A standard prepared slightly higher than the calibration range for metals. This is an "upper range limit" standard used to verify the upper limit of the linear dynamic range of the instrument.

3.21 Tune – The analysis of a standard element to verify that the mass spectrometer meets standard mass spectra abundance criteria prior to sample analysis.

3.22 Matrix – the predominant material, component, or substrate (e.g., surface water, soil, etc.) of which the sample to be analyzed is composed.

4) Health and Safety Warnings

4.1 All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as safety glasses, lab coat and the correct gloves.

4.2 Chemicals, reagents and standards must be handled as described in the Company safety policies, approved methods and in MSDSs where available. Refer to the Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

4.3 Hydrochloric and Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids and safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

4.4 The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

4.5 High Voltage - The RF generator supplies up to 2000 watts to maintain an ICP. The power is transferred through the load coil located in the torch box. Contact with the load coil while generator is in operation will likely result in death. When performing maintenance on the RF generator, appropriate grounding of all HV capacitors must be performed as per manufacturer.

4.6 UV Light - The plasma is an intense source of UV emission, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available when direct viewing of the plasma is necessary.

4.7 Refer to the Safety Manual for further discussion of general safety procedures and information.

4.8 Waste Management and Pollution Prevention

It is the laboratory's practice to minimize the amount of acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when disposed of properly.

The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the EH&S Manual.

Samples with analyte concentrations exceeding TCLP regulatory limits are disposed of as hazardous waste, see the SOP for Sample Disposal (SMO-SPLDIS).

5) Cautions

Preventive maintenance activities listed below should be performed when needed as determined by instrument performance (i.e. stability, sensitivity, etc.) or by visual inspection. Other maintenance or repairs may, or may not require factory service, depending on the nature of the task.

- cone removal and cleaning
- removal and cleaning of ICP glassware and fittings
- checking air filters and cleaning if necessary
- checking the rotary pump oil and adding or changing if necessary
- removal and cleaning of extraction lens
- removal and cleaning of ion lens stack

6) Interferences

6.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Attention should be given to circumstances where very high ion currents at adjacent masses may contribute to ion signals at the mass of interest. Matrices exhibiting a significant problem of this type may require resolution improvement, matrix separation, or analysis using another isotope.

6.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Refer to Method 6020A for further discussion.

6.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Total solid levels below 2000 mg/L have been recommended to minimize solid deposition on the nebulizer tip. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes.

6.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate these interferences.

7) Personnel Qualifications and Responsibilities

7.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

7.2 Training – see CE-QA003.

8) Sample Collection, Containers, Preservation, and Storage

8.1 Solid samples require no preservation prior to analysis other than storage at 0-6˚C. Sample containers may be glass or plastic. When the laboratory provides the sample containers, the containers are glass soil jars with Teflon-lined lids.

8.2 For aqueous samples, glass or plastic sample containers are acceptable. When the laboratory provides the sample containers, the containers are certified clean 500 mL plastic bottles. Sample volume should be acid preserved with (1+1) nitric acid to pH <2. Samples are held at room temperature (although refrigeration is acceptable also).

8.3 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Samples should be filtered prior to acidification, because acidification changes the sample (usually by dissolving particulates that would be filtered out). Acidified samples received at the lab that require lab filtration must be noted in the case narrative. See digestion SOPs for filtration procedure.

8.4 Samples are generally received in the ICP-MS laboratory as 1% Nitric Acid digestates. Digestates are stored at room temperature in hotblock cups or B-cups. There is no specific holding time from digestion to analysis. Client samples must be analyzed within 6 months of collection.

8.5 Following analysis, digestates are stored until all results have been reviewed. Digestates are diluted and disposed of through the sewer system in approximately 90 days after receipt of sample.

8.6 For more information about custody, sample handling, and storage procedures, see SMO-GEN and SMO-ICOC.

9) Equipment and Supplies

Instrument ID	Instrument Configuration	Manufacturer Part	Serial Number	Year Acquired
ICPMS (R-ICP-MS-01)	SCIEX ICP/MS	Perkin Elmer Elan 9000	PO370203	2002
	Autosampler	PE AS93Plus		
	Computer Workstation	Dell Optiplex GX150		
	Analytical Software	ELAN v.2.4		

The system has a mass range from at least 6 to 240 amu and a data system which allows corrections for isobaric interferences and the application of the internal standard technique.

9.1 Peristaltic Pump and pump tubing

9.2 15 and 50 mL autosampler tubes

9.3 Pipettes (Eppendorf) – calibrated according to ADM-PCAL.

9.4 Volumetric flasks, class A

10) Standards and Reagents

10.1 Standards Preparation General Information and Disclaimers

All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 mg/L standard may be made by adding 1 mL of 200 mg/L to 10 mLs or may be made by adding 4 mL of 50 mg/L to 10 mL. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used.

Vendors and vendors' products are sometimes listed for the ease of the analyst using this SOP, but products and purchased concentrations are examples only and subject to change at any time. All purchased standards are certified by the vendor. Certificates of Analysis are kept in the department until the standards are no longer being used – at which time they are filed with QA. Certificates of Analysis are available upon request. Purchased standards are routinely checked against an independent source for both analyte identification and analyte concentration.

All Standards must be traceable using the laboratory lot system (CE-QA007).

All preparatory information for the standards and QC samples are provided in the Controlled Forms section of the Rochester Intranet in the Metals Standards Logbooks. They are all stored in plastic at room temperature.

10.2 Argon – 99.99% purity

10.3 Trace metals grade chemicals shall be used in all tests. Each lot of acid used is to be analyzed to demonstrate that it is free of interference before use (CE-GEN007). All acids are stored at room temperature. Acids expire per the recommendations in Expiration Policy (CE-QA012) if no other indication is given.

- Hydrochloric acid (conc.), HCl. Purchased commercially
- Nitric acid (conc.), HNO3. Purchased commercially.

10.4 Reagent Water. All references to water in this SOP refer to the water produced by the laboratory water system.

10.5 Standards

10.5.1 Mixed Calibration Standards are prepared by combining appropriate volumes of the stock solutions in volumetric flasks. Matrix match with the appropriate acid and dilute to 500 mL with water. Calibration standards should be verified using a second source quality control sample (LCS or ICV). Calibration standards expire in 1 month.

10.5.2 Initial Calibration Verification (ICV) Standard is prepared by combining compatible analytes at concentrations equivalent to the midpoint of their respective calibration curves. The ICV standard should be prepared from a separate source independent from that used in the calibration standards. ICV standard expires in 48 hours.

10.5.3 Continuing Calibration Verification (CCV) Standard is prepared by combining compatible analytes at concentrations equivalent to the midpoint of their respective calibration curves. The CCV standard is prepared from a separate source as that used in the calibration standards. CCV standard expires in 48 hours.

10.5.4 MRL Standard is prepared to contain known concentrations of elements at the MRL. MRL standard expires in 1 month.

10.5.5 Interference Check Solutions A and AB are prepared to contain known concentrations of interfering analytes that will provide an adequate test of the correction factors. Used for 6020A only. ICSA / ICSAB standards expire in 1 week.

10.5.6 The spiking solutions for the Laboratory Control Sample and Matrix Spike are purchased as custom mixes at the concentrations recommended in the method. Solutions expire per manufacturer recommended expiration date. The LCS and MS are spiked at digestion according to the preparation SOP. All target analytes are spiked in the LCS and MS.

10.5.7 Internal Standards Solutions-high purity grade solutions are purchased and diluted to final concentration of 1000-5000 ppb. Diluted solutions expire in 6 months.

10.6 Blanks

10.6.1 Method Blanks must contain all the reagents and in the same volumes as used in the preparation of samples. The method blanks are blank matrix samples carried through the complete procedure and contain the same acid concentration in the final solution as the samples.

10.6.2 The Calibration Blank is prepared by acidifying reagent water to the same concentrations of acid found in the standards and samples.

11) Method Calibration

11.1 Refer to method 6020A (Section 11.0) and the instrument manuals for detailed instruction on implementation of the following procedures preceding an analytical run. All of the following are done daily prior to initial calibration unless otherwise specified.

11.2 Initiate plasma and allow a warm up of at least 30 minutes. The tuning procedures may be carried out during warm-up.

11.3 Open the EPA Tune Method

11.3.1 Aspirate 10 ppb tuning solution

11.3.2 Click on Tune Mass Spec button in Tuning Window

11.3.3 Check mass calibration. Measured mass must be within 0.05 amu of actual mass. The resolution must be <0.9 amu full width at 10% peak height. Save and print tune. Put one copy of the tune with the analytical run and another copy in the tune binder.

11.4 Open EPA Daily Method

11.4.1 Aspirate the 10 ppb tuning solution

11.4.2 Click on the Analyze button to acquire

11.4.3 Check that the RSDs for the five replicates are less than 5%

11.4.4 Monitor daily performance measures as recommended by Perkin Elmer for Rh sensitivity, background, % double charged, and % oxide levels.

- Rh>150000 cps for 10 ppb
- Background @ mass 220<30cps (once initial operating conditions have changed, i.e. voltage on detector, RF power, etc, background should be <100 cps. Ensure that desired signal to noise ratio is achieved.)

- % double charged <4%
- % oxides <4%

Oxides and double charged levels can be reduced by slightly decreasing the nebulizer flow rate.

11.4.5 If the tune and Daily Performance checks do not meet criteria, retune the instrument and reanalyze tuning solution. The tune and Daily must pass before proceeding.

11.5 Open the EPA Lens Calibration method and perform the autolens calibration using 10 ppb tuning solution. This is done as needed.

11.5.1 Clear old calibration

11.5.2 Get analytes

11.5.3 Optimize (Takes about 6 minutes)

11.5.4 Save file

11.6 Open the Neblens power oxides workspace and optimize the following parameter using the 10 ppb tuning solution containing Be, Mg, Co, Rh, In, Ba, Ce, Pb

11.6.1 Set RF power to desired level

- 1500 watts

11.6.2 Optimize the nebulizer argon flow – done as needed

11.6.3 Optimize the static lens voltage – done as needed

11.6.4 Save the optimization file

11.7 Open the EPA 6020 Dual Detector calibration method and aspirate a solution twice the calibration range. All elements plus internal standard elements should be present.

Note: This procedure is required when detector voltages or a new detector is installed. The laboratory does periodically.

11.7.1 Clear old calibration

11.7.2 Get analytes

11.7.3 Optimize (Takes about 20 minutes)

11.7.4 Save file

11.8 Initial Calibration – follow ADM-ICAL. If these instructions conflict with ADM-ICAL, follow the instructions in this SOP.

11.8.1 Number of Calibration standards – 3 standards and a calibration blank are analyzed daily before samples or QC. The correlation coefficient must be greater than 0.998 for each analyte. If the correlation is less than 0.998, recalibrate the instrument prior to analyzing any samples.

11.8.2 The use of internal standards, ICAL calculation, and sample calculation is in the Calculation Section.

12) Sample Preparation and Analysis

12.1 Digest samples with the appropriate digestion method. For waters, use MET-CLPDIG. For soils, use MET-3050. Digestates originating from soil samples are diluted prior to instrumental analysis to avoid interferences and allow the analysis to achieve maximum sensitivity which results in optimum Reporting Limits.

12.2 Analytical Run

12.2.1 For soil digestates - Dilute 1 mL of digestate to 5 mL with matrix matched reagent water prior to internal standard addition and analysis.

12.2.2 Each 5 mL aliquot of blanks, standards, samples, and sample dilutions are spiked with 50 uL of internal standard solution prior to analysis. Load samples on the autosampler according to the analytical sequence.

12.2.3 Open desired method. Enter sample information. Enter pump control speeds for all samples and save sample file. Re-open the sample file (this must be done for batch QC to run properly) and highlight the row numbers to be analyzed. Select “analyze batch.”

12.2.4 Calibration is done daily using 3 standards and a blank for each analyte. Analyze QC as per the frequency described in the QC Section. See ADM-BATCH for further detail.

12.3 Sample Analysis and Evaluation

12.3.1 Sensitivity, LOD, LOQ, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

12.3.2 Dilute and reanalyze samples which are above the linear range of the instrument or measure an alternate, less-abundant isotope (if calibrated). See ADM-DIL for more instruction on preparing and documenting sample dilutions.

12.3.3 Evaluate QC according to the QC Section. Repeat samples associated with non-compliant QC whenever possible.

12.3.4 If sample concentration for Ag is greater than 100 ug/L, sample should be redigested at a dilution until the sample solution contains less than 100 ug/L.

13) Troubleshooting –

Maintenance log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by ALS staff. The laboratory maintains a service contract with the instrument manufacturer that allows for an unlimited number of service calls and full reimbursement of all parts and labor. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The data file name of the first acceptable run after maintenance is to be documented in the maintenance log.

See instrument manual or maintenance log for help in solving specific analytical or instrument problems.

14) Data Acquisition

Data is electronically transferred from the instrument software to LIMS. The preparation information entered to LIMS is used by LIMS to calculate the final results – see Calculation Section.

15) Calculations and Data Reduction Requirements

15.1 Calculate sample results using the data system printouts and digestion information. The digestion and dilution information is entered into the data system. The data system then uses the calculations below to generate a sample result.

15.2 **Aqueous samples** are reported in μg/L:

$$\mu g / L\ (Sample) = \frac{C^{*}\ x\ Dilution\ Factor\ x\ FinalDigestateVolume(ml)}{InitialVolumeDigested(ml)}$$

C*= Concentration of analyte as measured at the instrument in ug/L (in digestate).

15.3 **Solid samples** are reported in ug/Kg:

$$ug/Kg\ \ (Sample) = C^{*}\ x\ PostDigestionDilutionFactor\ \ x \frac{Digestion\ Vol(ml)}{Sample\ \ wt.(g)}\ x \frac{1L}{1000ml}\ x \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in ug/L (in digestate).

15.4 Internal standards are identified by a caret and are bracketed by elements with which they are associated.

15.5 Table 2 has the recommended Isotopes. The actual mass used is on the Quantitation report.

15.6 ELAN software assumes that all elements within a standard group are similarly affected by instrument drift or matrix interferences. Changes in measured intensity of the Internal standard are used to create the ratios for correcting measured intensities of an element. A blank (called "Blank Intensity" on quantitation report) is analyzed prior to the ICAL to establish Internal standard intensities. A ratio is calculated from the measured intensity of the sample and the blank intensity for a given Internal standard. This ratio is applied to the measured intensity of the target element and adjusts the measured intensity based on performance of the sample matrix. The adjusted intensity is used to plot the ICAL. Sample concentrations are calculated from adjusted intensities.

15.7 $$Adjusted\ Intensity = \frac{I_B}{I_{IS}} * I_E$$

Where:

I_B = Intensity of Internal Standard in Blank Solution

I_{IS} = Intensity of Internal Standard in Measured Solution

I_E = Intensity of Element in Measured Solution

15.8 The adjusted intensity of the standards is plotted against concentration using the linear regression equation of a line and forced through zero intensity and zero concentration. This calibration curve is assuming that the relationship between concentration (the X values) and intensity (the Y values) is linear and that the following equation describes this relationship:

Y=MX

Where:

X=concentration

Y= adjusted intensity

M=slope of the calibration curve

The intercept is forced to be zero.

Given 2 or more data points, the values for M are calculated using the following equation.

$$M = \frac{\sum_{n}^{i=1} (X_i Y_i)}{\sum_{n}^{i=1} (X_i^2)}$$

Where: n=number of standards (includes the blank)

In this equation, the blank is subtracted from all solutions and included in the calculation of the calibration curve

15.9 To avoid bias at the low end of the curve, the curve is forced through zero. Forcing the curve through zero may favor the low end of the curve therefore a MRL standard and high level CCV (HLCCV2) are analyzed to verify both ends of the curve.

15.10 Common isobaric interferences are corrected using equations equivalent to those listed in EPA Methods 6020A and 200.8. Monitoring of multiple isotopes for a single element provides a mechanism for identifying isobaric interferences. If an element has more than one monitored isotope, examination of the concentration calculated for each isotope will provide useful information in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the sample concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes. Refer to the Interferences section of EPA Method 6020A and 200.8 for additional descriptions of possible interferences and the mechanisms required for adequately compensating for their effects.

15.11 The ArCl correction equation adds artificial signal to the As result when selenium is high. Check to see if there is ArCl interference on As by comparing 52Cr and 53Cr (ClO interferes on 53Cr). If they look about the same, turn the correction equation off and reprocess the data. The data is valid if the QC passed before the equation was turned off. If there is Cl interference, qualify the As result as estimated or report it by ICP.

15.12 Data is reviewed according to ADM-DREV.

16) Quality Control, Acceptance Criteria, and Corrective Action

16.1 Initial Calibration Verification Standard – midlevel (ICV) Analyzed immediately after the calibration using a second source standard to verify the standards in the calibration curve. The results for each analyte must agree within 10% of the expected value. If not, the analyses should be terminated and instrument recalibrated. Investigate the sources and preparation procedures of the standards.

16.2 Continuing Calibration Verification Standard – midlevel (CCV) Analyzed after every 10 samples and at the end of the analytical sequence. The results of the CCV must agree within ±10% of the expected value. If the control limits are exceeded, correct the problem and reanalyze the CCV. If that fails, recalibrate the instrument. Repeat samples bound by the out of control CCV unless the CCV is high and the sample concentration is less than the reporting limit.

16.3 Initial and Continuing Calibration Blank (ICB/CCB) The ICB is analyzed at the beginning of the run. The CCB is analyzed after every 10 samples (immediately following the CCV) and at the end of the run. The CCB must be less than the reporting limit (less than the LOD for DOD). If the control limits are exceeded, correct the problem and reanalyze the CCB. If that fails, recalibrate the instrument. Repeat any samples bound by the out of control CCB. If CCB results are exceeded, these associated data shall be flagged unless the sample concentration is less than the reporting limit.

16.4 MRL Standard (MRL) - A standard at or near the MRL is analyzed at the beginning and end of each analytical run but not before the ICV. If the MRL is at the MRL, the limit is 70-130% of the true value for 6020A. (DOD requires a limit of +/- 20%). If the MRL standard is near the MRL, the limit is 80-120%. If the limits are not met the analysis is stopped and the instrument is recalibrated.

16.5 LOQV (LLQC) – This digested standard spiked at the reporting limit must be analyzed quarterly for DOD (6020A requires “as needed”). The limits are 70-130% for 6020A and LCS limits for DOD. If this QC does not meet these limits, determine the source of the problem. Achieve an acceptable LOQV before continuing.

16.6 HLCCV – analyzed once per daily run. The limit is +/- 10%. If it is out of control, client data above the high ICAL standard should be re-analyzed.

16.7 DUP –

16.7.1 Frequency for 200.8 – 1/10 or one per batch, whichever is greater.

16.7.2 Frequency for 6020A – 1/20 or per batch, whichever is greater.

16.7.3 Limits - The control limits are listed in the Data Quality Objectives Table. Client specific QC recoveries may supercede the limits listed in the QA manual.

16.7.4 Corrective Action - If the control limits are exceeded, the data will be reported with a qualifier.

16.8 MS –

16.8.1 Frequency for 200.8 - 1/10 or one per batch, whichever is greater

16.8.2 Frequency for 6020A - 1/20 or per batch, whichever is greater

16.8.3 Limits - The control limits are listed in the Data Quality Objectives Table. These limits are 75-125% for 6020A and 70-130% for 200.8. Client specific QC recoveries may supercede the limits listed in the QA manual.

16.8.4 Corrective Action - If the control limits are exceeded, analyze a post-digestion spike. DOD requires project-specific DQOs be examined or contact the client for additional measures. See Table F-8.

16.9 LCS is prepared at a frequency of one per preparation batch, not to exceed 20 samples. The % recovery must be within the limits in the Data Quality Objectives Table. These limits are 80-120% for 6020A waters, 85-115% for 200.8, and per the Manufacturer's Certificate of Analysis for soils. Client specific QC recoveries may supercede these limits. If the control limits are exceeded, the associated batch of samples will be redigested and reanalyzed for the out of control elements or the data is to be flagged. Exception – if the LCS recovery fails high, elements which are less than the reporting limit may be reported.

16.10 Linear Range Study – performed every 6 months. A high level check standard (HLCCV2) must be within 5% of the expected value. If it is not, repeat the linear range study or reduce the linear range and analyze a new high level check standard.

16.11 Ongoing verification of the detection and quantitation limits is required. See CE-QA011 for requirements.

16.12 Method Blank (MB) Method Blanks must be prepared with each batch of 20 or fewer samples of the same matrix. MB values must not exceed the LOQ (1/2 LOQ for DOD). Fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable MB values have been obtained. If detections are greater than the limit, the batch needs to be redigested if sample concentration is less than 10 times the concentration found in the method blank. If the sample concentration is less than the reporting limit the sample does not require redigestion.

16.13 Internal standards–

16.13.1 Limits – Evaluate the intensity of each internal standard in each standard and QC compared to the intensity of the internal standards in the initial calibration.

- 200.8: 60-125%
- 6020A: > 70%

16.13.2 Corrective Action - If these limits are not met in the samples, verify that the instrument is not drifting by evaluating the internal standards in the CCBs and dilute the sample five fold and reanalyze with the proper addition of internal standards. Repeat this procedure until the internal standard intensities fall within the limits. If the internal standards are not acceptable for the QC, terminate the analysis, correct the problem, recalibrate, and reanalyze any associated samples.

16.14 Dilution Test (serial dilution) – One dilution test must be performed for each prep batch of 20 or fewer samples. To perform the Dilution Test, choose a sample which has a concentration within the linear range of the instrument and dilute it 1/5. The result of the dilution must agree within 10% of the original sample determination when concentrations exceed 50X LOQ. If it does not, an interference effect must be suspected and should be noted in the case narrative. (DOD requires post-digestion spike addition if the dilution test fails.)

16.15 Post digestion spike – Perform when the MS fails or, for DOD, if no samples had concentration >50xLOQ. (For DOD, Perform when dilution test fails or analyte concentration for all samples <50 times LOQ) The spike addition should produce a concentration of 10-100 times the LOQ. The Post Digestion Spike recovery should be 75-125% of the true value. If it is not the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree within 10% of the original determination. The use of standard-addition may also be used to compensate for this effect, or samples may be flagged.

16.16 Interference Check Standard (ICS) – not required for 200.8

16.16.1 Frequency - Solutions A and AB are analyzed at the beginning of each analytical run or every 12 hours, which ever is more frequent.

16.16.2 Limits –

- ICS-A - the absolute value of concentration for all non-spiked analytes must be less than the LOD (unless they are a verified trace impurity from one of the spiked analytes).
- ICS-AB - The analytes in ICS-AB should recover within 20% of the expected value. If the analytes are not present, monitor concentration for possible interferences.

16.16.3 Corrective action – Terminate analysis, locate and correct the problem, reanalyze ICS, reanalyze all affected samples. If corrective action fails, qualify the associated sample data.

17) Data Records Management

See CE-GEN003 and ADM-ARCH.

18) Contingencies for Handling Out-Of-Control Data

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, flag and narrate appropriately.

19) Method Performance

19.1 This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional available method performance data.

19.2 Detection and Quantitation Limits are determined for all masses utilized for each type of matrix commonly analyzed. See CE-QA011 for determination and verification of detection and quantitation limits.

19.3 Demonstration of Capability is performed according to the SOP for Training (CE-QA003).

20) Summary of Changes

- Updated to new ALS format
- Removed copies of standards log and referenced Controlled Forms
- Incorporated Change form for background mass typo.
- Changed the limits for internal standards.

21) References and Related Documents

- USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update IV, Method 6020A, Revision 1, February 2007.
- Method 200.8 - Determination of Trace Elements in Waters and Wastes By Inductively Coupled Plasma-Mass Spectrometry, USEPA-EMSL, Revision 5.4, 1994.
- Perkin Elmer Instrument Manuals
- DOD Quality Systems Manual for Environmental Laboratories – Version 4.2, October 2010.

22) Appendix

- DOD Summary
- Table 1 Analytes and Reporting Levels
- Table 2 Recommended Isotopes for Selected Elements
- Table F-8 DOD Data Quality Objectives from QSMv4.2

DOD SUMMARY

For work for the Department of Defense – the DOD Quality Systems Manual must be followed. The DOD Manual is based on the NELAC Standards with some additional requirements. The exact wording is in Table F-8 (attached). The following are the requirements which are different or additional to routine analysis and must be followed for DOD work:

- The CCB must be less than the LOD.
- The Method Blank must be less than ½ the reporting limit (<RL for common laboratory contaminants).
- Apply J flag to all hits between LOD and LOQ.
- The limits for LCS and MS are 80-120%. All targets are spiked and evaluated.
- The IDL must be less than the LOD. The IDL study is only required by DoD at set-up and after significant change.
- Low Level Check Standard (MRL standard) must be spiked at or below the reporting limit and it must have a recovery of 80-120% of the true value when analyzed at the beginning of the run.
- ICS-A absolute value of concentration for all non-spiked analytes must be <LOD (unless they are a verified trace impurity from one of the spiked analytes).
- Serial Dilution Test
- Only for samples >50 times LOQ
- Corrective Action – If the limits are not met, perform a post digestion spike addition.
- Post digestion spike – Perform when dilution test fails or analyte concentration for all samples <50 times LOQ.
- Method of Standard Additions – use when matrix interference is suspected. Document use in the case narrative.

TABLE 1

Analyte	MRL / LOQ (ug/L)	MRL/LOQ (ug/kg)
Antimony	1	0.50
Arsenic	1	0.50
Barium	1	0.50
Beryllium	1	0.50
Cadmium	1	0.50
Chromium	2	1.0
Cobalt	1	0.50
Copper	1	0.50
Lead	1	0.50
Manganese	1	0.50
Molybdenum	1	0.50
Nickel	1	0.50
Platinum	1	0.50
Selenium	2	1.0
Silver	1	0.50
Strontium	1	0.50
Thallium	1	0.50
Uranium	1	0.50
Vanadium	2	1.0
Zinc	5	2.5

TABLE 2
RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	Mass(es)
Aluminum	**27**
Antimony	121, **123**
Arsenic	**75**
Barium	138, 137, 136, **135**, 134
Beryllium	**9**
Bismuth (IS)	209
Cadmium	**114**, 112, **111**, 110, 113, 116, 106
Calcium (I)	42, 43, **44**, 46, 48
Chlorine (I)	35, 37, (77, 82)[a]
Chromium	**52**, **53**, **50**, 54
Cobalt	**59**
Copper	**63**, **65**
Germanium (IS)	74
Holmium (IS)	165
Indium (IS)	**115**, 113
Iron (I)	**56**, **54**, **57**, 58
Lanthanum (I)	139
Lead	**208**, **207**, **206**, 204
Lithium (IS)	6[b], 7
Magnesium (I)	24, **25**, **26**
Manganese	**55**
Mercury	202, **200**, 199, 201
Molybdenum (I)	98, 96, 92, **97**, 94, (108)[a]
Nickel	58, **60**, 62, **61**, 64
Potassium (I)	**39**
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, **78**, **82**, **76**, **77**, 74
Silver	**107**, **109**
Sodium (I)	**23**
Terbium (IS)	159
Thallium	**205**, 203
Vanadium	**51**, **50**
Tin (I)	120, **118**
Yttrium (IS)	89
Zinc	64, **66**, **68**, **67**, 70

[a] These masses are also useful for interference correction (Sec. 4.2).
[b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

NOTE: Method 6020 is recommended for only those analytes listed in Sec.1.2. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

Table F-8. Trace Metals Analysis by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) (Method 6020)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analytical capability	Prior to using any test method and at any time there is a change in instrument type, personnel, test method, or sample matrix.	QC acceptance criteria published by DoD, if available; otherwise method-specified criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria (see Section C.1.f).	NA.	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure in Appendix C. No analysis shall be allowed by analyst until successful demonstration of capability is complete.
LOD determination and verification (See Box D-13)					
LOQ establishment and verification (See Box D-14)					
Instrument detection limit (IDL) study	At initial set-up and after significant change in instrument type, personnel, test method, or sample matrix.	IDLs shall be ≤ LOD.	NA.	NA.	Samples may not be analyzed without a valid IDL.
Tuning	Prior to ICAL.	Mass calibration ≤ 0.1 amu from the true value; Resolution < 0.9 amu full width at 10% peak height; For stability, RSD ≤ 5% for at least four replicate analyses.	Retune instrument then reanalyze tuning solutions.	Flagging criteria are not appropriate.	No analysis shall be performed without a valid MS tune.
Initial calibration (ICAL) for all analytes (minimum one high standard and a calibration blank)	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r ≥ 0.995.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.

Table F-8. Trace Metals Analysis by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) (Method 6020) (continued)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Second source calibration verification	Once after each ICAL, prior to beginning a sample run.	Value of second source for all analytes within ± 10% of true value.	Verify second source standard. Rerun second source verification. If that fails, correct problem and repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Continuing calibration verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	All analytes within ± 10% of true value.	Correct problem, rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Low-level calibration check standard	Daily, after one-point ICAL.	Within ± 20% of true value.	Correct problem, then reanalyze.	Flagging criteria are not appropriate.	No samples may be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the reporting limit.
Linear dynamic range or high-level check standard	Every 6 months.	Within ±10% of true value.	NA.	NA.	
Method blank	One per preparatory batch.	No analytes detected > ½ RL and greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL (see Box D-1).	Correct problem, then see criteria in Box D-1. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Calibration blank	Before beginning a sample run, after every 10 samples, and at end of the analysis sequence.	No analytes detected > LOD.	Correct problem. Re-prep and reanalyze calibration blank. All samples following the last acceptable calibration blank must be reanalyzed.	Apply B-flag to all results for specific analyte(s) in all samples associated with the blank.	

Table F-8. Trace Metals Analysis by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) (Method 6020) (continued)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Interference check solutions (ICS-A and ICS-AB)	At the beginning of an analytical run and every 12 hours.	ICS-A: Absolute value of concentration for all non-spiked analytes < LOD (unless they are a verified trace impurity from one of the spiked analytes); ICS-AB: Within ± 20% of true value.	Terminate analysis, locate and correct problem, reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the ICS.	
LCS containing all analytes to be reported	One per preparatory batch.	QC acceptance criteria specified by DoD, if available; see Box D-3 and Appendix G.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available (see full explanation in Appendix G).	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Matrix spike (MS)	One per preparatory batch per matrix (see Box D-7).	For matrix evaluation, use QC acceptance criteria specified by DoD for LCS.	Examine the project-specific DQOs. If the matrix spike falls outside of DoD criteria, additional quality control tests (dilution test and post-digestion spike addition) are required to evaluate matrix effects.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix (see Box D-7).	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS. MSD or sample duplicate: RPD < 20% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Dilution test	One per preparatory batch.	Five-fold dilution must agree within ± 10% of the original measurement.	Perform post-digestion spike addition.	Flagging criteria are not appropriate.	Only applicable for samples with concentrations > 50 x LOQ.

Table F-8. Trace Metals Analysis by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) (Method 6020) (continued)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Post digestion spike addition	When dilution test fails or analyte concentration for all samples < 50 x LOD.	Recovery within 75-125% (see Table B-1).	Run all associated samples in the preparatory batch by method of standard additions (MSA) or see flagging criteria.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	Spike addition should produce a concentration of 10 – 100 x LOQ.
Method of standard additions (MSA)	When matrix interference is confirmed.	NA.	NA.	NA.	Document use of MSA in the case narrative.
Internal standards (IS)	Every sample.	IS intensity within 30-120% of intensity of the IS in the ICAL.	Reanalyze sample at 5-fold dilution with addition of appropriate amounts of internal standards.	Flagging criteria are not appropriate.	
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

ALS Standard Operating Procedure

DOCUMENT TITLE:	METALS DIGESTION, SOILS, SEDIMENTS, AND SLUDGE FOR ICP-AES AND ICP-MS ANALYSIS
REFERENCED METHOD:	EPA SW846 3050B
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ALS Environmental

METALS DIGESTION, SOILS, SEDIMENTS, AND SLUDGE FOR ICP-AES AND ICP-MS ANALYSIS

EPA SW846 3050B

SOPID:	MET-3050	Rev. Number:	5	Effective Date:	11/4/13

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METALS DIGESTION, SOILS, SEDIMENTS, AND SLUDGE FOR ICP-AES AND ICP-MS ANALYSIS

1) Scope and Applicability

Method 3050 is an acid digestion procedure used to prepare matrices such as soils, sludges, or sediments for analysis by ICP-AES or ICP- MS using SW846 methods 6010 and 6020.

2) Summary of Procedure

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide (and Hydrochloric for ICP-AES). Hydrochloric acid is used as a final reflux acid for ICP-AES analyses. Nitric Acid is used as the final reflux acid for ICP-MS analyses.

3) Definitions

3.1 Laboratory Duplicates - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 Laboratory Control Sample (LCS) - An aliquot of a purchased soil with known quantities of the method analytes. If the purchased soil (LCSS) does not contain all of the target elements needed, the laboratory prepares an LCS with the missing elements by spiking Teflon chips. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.3 Matrix Spike - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 Method Blank (MB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample from digestion to analysis including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The MB is used to determine if method analytes or other interferences are present.

3.5 Digestion Batch - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day. See ADM-BATCH.

3.6 Limit of Detection (LOD) – An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory – dependent.

3.7 Limit of Quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target that can be reported with a specified degree of confidence.

4) Health and Safety Warnings

4.1 All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

4.2 Chemicals, reagents, and standards must be handled as described in the company safety policies, approved methods and in the MSDSs where available. Refer to the Environmental Health and Safety Manual and the appropriate MSDS prior to beginning this method.

4.3 Nitric and Hydrochloric Acids are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

4.4 Waste Management and Pollution Prevention

4.4.1 It is the laboratory's practice to minimize the amount of acids and reagents used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when disposed of properly.

4.4.2 The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the EH&S Manual.

4.4.3 For further information refer to SMO-SPLDIS.

5) Cautions

5.1 All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

6) Interferences

6.1 Elements bound in silicate structures are not normally dissolved by this method. Such bound elements would not be mobile in the environment and are not normally of interest.

6.2 See appropriate analysis SOP for applicable interferences

7) Personnel Qualifications and Responsibilities

7.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

7.2 Training – see CE-QA003.

8) Sample Collection, Preservation and Storage

For solids and non-aqueous samples, glass or plastic sample containers are acceptable. Typically our lab uses purchased, precleaned 4 or 8 oz glass jars. Samples are to be stored at 0-6°C from collection to digestion. Samples are analyzed within 6 months of sample collection. Additional sample handling policies, storage and custody procedures are in SMO-GEN and SMO-ICOC.

9) Equipment and Supplies

9.1 Hot Plate Digestion

- 9.1.1 Digestion vessel = 250 and 100 mL beakers
- 9.1.2 Ribbed watch glasses
- 9.1.3 Hot plates
- 9.1.4 Funnels
- 9.1.5 Filter paper

9.2 Hot Block Digestion

- 9.2.1 Digestion vessel = Graduated block digestor cups
- 9.2.2 Reflux cap
- 9.2.3 Hot Block Digestor with ETR-3200 Controller by Environmental Express, LTD
- 9.2.4 CPI MOD Block Digestor
- 9.2.5 Block Digestor Filters.

9.3 Graduated cylinders

9.4 Eppendorf Pipettors –Calibrated according to ADM-PCAL.

9.5 Mortar and pestle

9.6 Tongue depressors

10) Standards and Reagents

10.1 Standards Preparation General Information and Disclaimers

10.1.1 All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 mg/L standard may be made by adding 1 mL of 200 mg/L to 10 mL or may be made by adding 4 mL of 50 mg/L to 10 mL. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used

10.1.2 Vendors and vendors' products are sometimes listed for the ease of the analyst using this SOP, but products and purchased concentrations are examples only and subject to change at any time. All purchased standards are certified by the vendor. Certificates of Analysis are kept in the department until the standards are no longer being used – at which time they are archived with QA. Certificates of Analysis are available upon request. Purchased standards are routinely checked against an independent source for both analyte identification and analyte concentration.

10.1.3 Standards and Reagent expire per the Expiration Policy (CE-QA012) unless otherwise specified.

10.1.4 All Standards must be traceable using the laboratory lot system (CE-QA007).

10.2 Reagent water – laboratory produced deionized water.

10.3 Purchased Reagents and standards – Store at room temperature.

10.3.1 Concentrated nitric acid (Baker Instra-Analyzed 69-70%): Acid should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store in the dark.

10.3.2 Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%): Acid should be demonstrated to be free of impurities at levels which would interfere with sample determinations.

10.3.3 Hydrogen peroxide (30%) - H_2O_2. Should be demonstrated to be free of impurities at levels which would interfere with sample determinations.

10.3.4 ERA Soil Laboratory Control Sample (LCSS) - Concentrations and Performance Acceptance Limits distributed through vendor

10.3.5 Metals spiking solutions – Purchased commercially. See Table 1. All target elements needed for client samples in the batch are added to the LCS and MS.

10.4 LCS – use ERA Soil Laboratory Control Sample (LCSS) as above. If the LCSS does not contain all of the target elements needed, create a second LCS sample and spike Teflon chips with the elements missing from the ERA Soil (see Table 1 for appropriate spiking solutions). Digest as a sample.

10.5 MS – Add appropriate spiking solutions (see Table 1) to client sample prior to the addition of heat or reagents. Digest as a sample.

10.6 Method Blank – Digest Teflon chips as a sample.

11) Method Calibration

11.1 The uniformity of the temperature of the hotplates and hotblocks is monitored by randomly moving a temperature blank around to different positions with each run. The temperature blank is DI in a digestion vessel and the temperature is read with a thermometer held in the DI when the samples should be at the required temperature. If positions become unreliable (not within the required temperature of digestion), those positions must not be used and the unit should be serviced or replaced.

11.2 The graduations on the hot block cups are verified for volume whenever a new lot number of cups is received. To verify the volume, tare a cup on a toploader balance, add DI to the desired graduation (all graduations used for measuring volume must be checked) and record the mass. Repeat on 10 cups. The mean mass must be within 3% of the marked volume. The RSD must be ≤ 3%. If criteria is not met, the lot of cups is either rejected and removed from service or a correction factor must be employed

12) Sample Preparation

12.1 Be sure there is a current LOD and the analyst has a current Demonstration of Capability.

12.2 Be sure the hot block cups have been verified for volume. Record the lot number of the cups used in the batch through the Standards Log in LIMS.

12.3 Set the temperature on the Hot Plate or Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

12.4 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor. The temperature of the batch is monitored by randomly placing a vessel with DI in the block or on the hotplate. Record the temperature and the ID of the hotplate or hotblock in the Comments section of the MB on the prep sheet.

12.5 Label digestion vessel with appropriate sample IDs for digestion.

12.6 See ADM-SPLPREP for instructions of how to homogenize and subsample and how to handle standing water and extraneous materials. Make note of any special sample handling in the comments section of the prep sheet.

12.7 Weigh (to the nearest 0.01g) 1.00g to 1.05g of sample into the digestion vessel. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. Record the sample weight, sample color, and sample texture directly into LIMS in real time – do not handwrite on anything to be later entered. Add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents. Record the spike volumes, spiking solutions, and reagents directly into LIMS.

12.8 Unless specified by project or state requirements, add the following to each sample and QC sample: 10 mL of 1:1 HNO3 and, for ICP-AES and Silver or Antimony by ICP-MS, add 1.0 mL of 1:1 HCl. Place digestion vessel on hotplate or in hotblock. Cover with a ribbed watch glass or reflux cap and reflux for 15 minutes. The sample temperature should be 90-95oC. Allow the sample to cool. Add 5 mL of concentrated HNO3, cover and reflux for 30 minutes. Repeat the addition of 5 mL of HNO3 and reflux to 5 mL. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

12.9 Cool the sample and add 2 mL of DI and 3 mL of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the digestion vessel.

12.10 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

12.11 If the sample is being prepared for analysis by ICP-AES or Silver or Antimony by ICP-MS, add 10 mL 1:1 HCL. If the sample is being prepared for analysis by ICP-MS, no HCl is added and the sample is evaporated to approximately 5 mL.

12.12 Cover and reflux the ICP-AES and Silver or Antimony by ICP-MS samples for 15 minutes without boiling. Allow to cool.

12.13 Prepare filters by rinsing with 1:1 nitric acid and DI.

12.14 Filter if particulates are suspended. If particulates have settled, no filtering is necessary. Filtering is usually required if analyzed on the same day as digestion. If filtering, record the lot number of the filters through the Standards Log in LIMS. If the entire batch is filtered, also filter the QC samples. If only some of the samples are filtered, note which samples are filtered in the comments section of the benchsheet and filter an undigested LCS and MB to demonstrate the acceptability of the filters.

12.15 Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and watch glass or reflux cap with DI into the filter. Rinse the filter with DI. If not filtering, quantitatively transfer digestate to a graduated cylinder rinsing beaker with DI. All samples are diluted to 100 mL with DI. Document the final volume in LIMS. Pour into a labeled B-cup.

12.16 Print out one copy of the Preparation Information Benchsheet. The prep sheets are reviewed and signed by a peer or supervisor within 48 hours of preparation. This prep sheet is filed in the appropriate binder (logbook). A copy remains with the samples through analysis. Copies made for client folders are to include all review signatures.

13) Troubleshooting

None

14) Data Acquisition

Preparation volumes are entered manually into the LIMS Prep Sheet and are used to calculate final results

15) Calculation and Data Reduction Requirements

Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

16) Quality Control, Acceptance Criteria, and Corrective Action

16.1 LCS - Digest one laboratory control sample (LCS) per digestion batch.

16.2 MB - Digest one Method blank per digestion batch.

16.3 DUP/MS - Digest one spiked sample and one duplicate sample (or matrix spiked duplicate if specified by client) with each digestion batch.

16.4 See appropriate analytical SOP for applicable QC limits and corrective action.

17) Data Records Management

See CE-GEN003 and ADM-ARCH

18) Contingencies for Handling Out Of Control Data

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, flag and narrate appropriately.

19) Method Performance

- Detection and Quantitation limits are determined according to the requirements in CE-QA011. The supporting information is filed with the QA office.
- Demonstration of Capability is performed according to CE-QA003.

20) Summary of Changes

- Updated to ALS format – removed CAS throughout
- Removed references to GFAA methods and CLP
- Incorporated change form for reduction of HCl

21) References and Related Documents

- "Test Methods For Evaluating Solid Waste, Physical/Chemical Methods". EPA SW846, Third Edition, December 1996.

22) Appendix

- Table 1 Spike Concentrations
- Digestion Log Benchsheet
- SW846 Method 3050 Flow Chart

Table 1 Spiking Concentrations for LCS and MS Samples

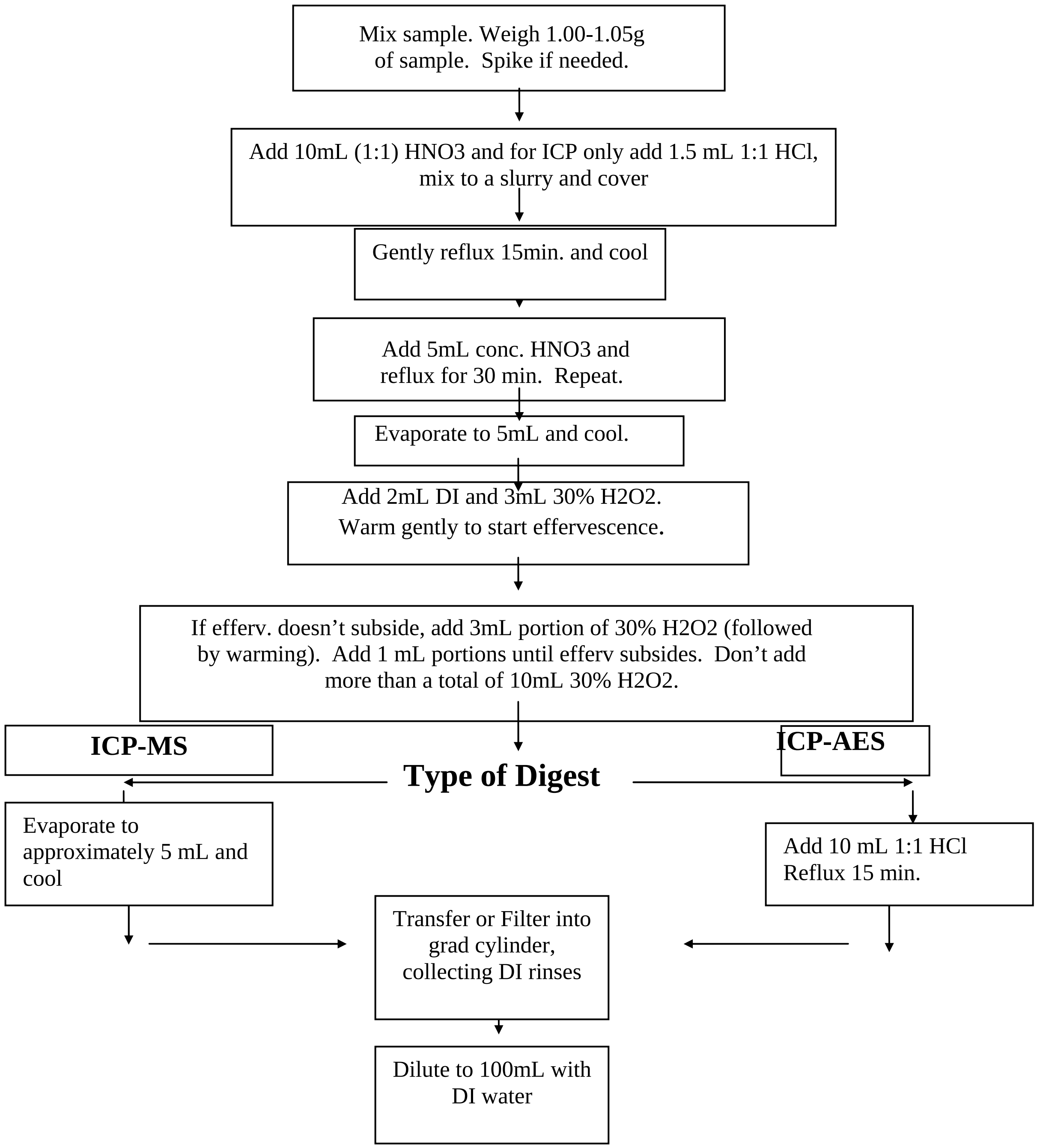
SPIKE SOLUTION A			1.00ml Spk A	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
AL	200		**NI**	50
AS	4		**SE**	1
BA	200		**AG**	5
BE	5		**TL**	200
CD	5		**V**	50
CR	20		**ZN**	50
CO	50		**B**	100
CU	25		**CA**	200
FE	100		**MG**	200
PB	50		**NA**	2000
MN	50		**K**	2000

SPIKE SOLUTION B			1.00ml Spk B	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SB	50		**TI**	50
MO	50		**-**	-

INDIVIDUAL METALS	0.10ml Spk. to Final Volume of 100ml		**INDIVIDUAL METALS**	0.5ml Spk. to Final Volume of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SE	1000		**SN**	1000

SW846 Method 3050
Flow Chart

Soils, Sediments and Sludges



ALS Standard Operating Procedure

DOCUMENT TITLE:	DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY (ICP)
REFERENCED METHOD:	EPA 200.7 AND SW 846 6010C
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ALS Environmental

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY (ICP)

EPA 200.7 AND SW 846 6010C

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Approved By: [signature] Date: 11/1/13
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DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY (ICP)

1) Scope and Applicability

This SOP uses EPA methods 200.7 and 6010C for the determination of trace metals in solution by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. The Reporting Limits are listed in Table 1. The reporting limit may be adjusted if required for specific project requirements, however, the capability of achieving other reporting limits must be demonstrated.

2) Summary of Procedure

Sample preparation and digestion is found in the appropriate extraction and digestion SOPs. Examples include MET-3010A, MET-3050B, MET-TCLP, MET-TZHE, MET-SPLP, and MET-SPLPZHE.

This method uses multiple elemental determinations by ICP-AES using sequential or simultaneous optical systems and both axial and radial viewing of the plasma (dual view). The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in the Interferences Section should also be recognized and appropriate corrections made.

3) Definitions

3.1 **Initial Calibration** - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the detector to the element.

3.2 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Dissolved Analyte** - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification.

3.4 **Initial Calibration Verification (ICV)** (also called Second Source Calibration Verification) – ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the initial calibration.

3.5 **Continuing Calibration Verification Standard (CCV)** - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration. For the LLCCV, see MRL Standard below.

3.6 **Matrix Spike (MS)** - An aliquot of an environmental sample to which known quantities of all of the elements of client interest are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results in a given client matrix.

3.7 **Duplicate (DUP)** - A laboratory duplicate. Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.8 **Laboratory Control Sample (LCS)** – A matrix blank spiked with all of the elements of client interest. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate measurements. LCS-Soil is purchased from a vendor.

3.9 **Method Blank (MB)** - An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.10 **Instrument Blank (ICB/CCB)** - The instrument blank (also called initial or continuing calibration blank) is a volume of reagent water acidified with the same acid matrix as in the calibration standards. This blank is the zero standard and has a reagent composition identical to the digestates. The purpose of the ICB/CCB is to determine the levels of contamination associated with the instrumental analysis.

3.11 **Batch** – a group of no more than 20 samples analyzed together on the same day with the same reagents. See the SOP for Batches and Sequences (ADM-BATCH) for more detail.

3.12 **Calibration Blank** - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

3.13 **Instrument Detection Limit (IDL)** - The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 21 replicate measurements of a low standard's signal at the same wavelength.

3.14 **Internal Standard** - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.15 **Linear Range** - The concentration range over which the instrument response to an analyte is linear.

3.16 **Limit of Detection (LOD) –** An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory – dependent. For DOD, the smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%.

3.17 **Limit of Quantitation (LOQ) –** The minimum levels, concentrations, or quantities of a target that can be reported with a specified degree of confidence. For DOD, the lowest concentration that produces a quantitative result within specified limits of precision and bias. The LOQ shall be set at or above the concentration of the lowest initial calibration standard.

3.18 **Plasma Solution** - A solution that is used to determine the optimum height above the work coil for viewing the plasma.

3.19 **Interference Check Solution (ICS)** - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria.

3.20 **MRL Standard –** Standard prepared with a known concentration of elements to check accuracy at the quantitation limit. This is also known as Low-level calibration check standard (LLCCV or LLICV). This standard is not digested.

3.21 **LOQ Standard – also called LLQC** – Standard prepared at the LOQ that undergoes digestion and preparation procedures.

3.22 **HLCCV1 –** A standard prepared at the bench at a high concentration to encompass the range of the samples being analyzed. This standard is used to assess accuracy at the high end of the calibration curve.

3.23 **HLCCV2 –** A standard prepared slightly higher than the calibration range for metals. This is an "upper range limit" standard used to verify the upper limit of the linear dynamic range of the instrument.

3.24 **Matrix** - the predominant material, component, or substrate (e.g., surface water, drinking water, etc.) of which the sample to be analyzed is composed.

3.25 **Relative Percent Difference (RPD)** – The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.26 **Interelement Correction Factors (IECs)** - factors that the instrument uses to compensate for spectral overlap when analyzing samples with complex spectra.

4) Health and Safety Warnings

4.1 All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personal protective equipment, such as safety glasses, lab coat and the correct gloves.

4.2 Chemicals, reagents and standards must be handled as described in the Company safety policies, approved methods and in MSDSs where available. Refer to the Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

4.3 Hydrochloric and Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

4.4 The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

4.5 Refer to the Safety Manual for further discussion of general safety procedures and information.

4.6 High Voltage - The power unit supplies high voltage to the RF generator which is used to form the plasma. The unit should never be opened. Exposure to high voltage can cause injury or death.

4.7 UV Light - The plasma when lit is a very intense light, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available.

4.8 Waste Management And Pollution Prevention

It is the laboratory's practice to minimize the amount of acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when disposed of properly.

The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the EH&S Manual..

Samples with analyte concentrations exceeding TCLP regulatory limits are disposed of as hazardous waste, see SOP *SMO-SPLDIS*.

5) Cautions

5.1 Typical preventive maintenance measures include, but are not limited to, the following items:

- Changing the pump tubing as needed
- Empty waste container, as needed
- Cleaning the nebulizer, spray chamber, and torch, as needed
- Replace water and vacuum filters, as needed

6) Interferences

6.1 There are several types of interferences by the ICPs: Spectral interferences can be from an overlap of spectral lines, background points or background from line emissions of high concentration elements. Physical interferences are effects associated with the sample introduction process, example high dissolved solids buildup on the nebulizer tip. Chemical interferences caused by the sample matrix itself. IECs aid in eliminating some of these interferences. IECs are interelement correction factors that the instrument uses to compensate for spectral overlap when analyzing samples with complex spectra. The following is the text from Method 6010B Section 3.0. Similar text is found in Method 200.7 and 6010C. Not all of the items may be applicable to this laboratory's instruments or procedures.

6.2 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

6.3 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

6.4 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

6.5 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction **require** the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interfering effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

6.6 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary.

6.7 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

6.8 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

6.9 Users of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm centered on the wavelength of interest for several samples. The range for lead, for example, would be from 220.6 to 220.1 nm. This procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

6.10 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

6.11 When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within the 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

6.12 When interelement corrections are not used, verification of absence of interferences is required.

6.13 One method is to use a computer software routine for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

6.14 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is > 20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

6.15 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers.

6.16 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

6.17 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

6.18 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

6.19 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interfering concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

7) Personnel Qualifications and Responsibilities

It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

Training – see CE-QA003.

8) Sample Collection, Preservation, and Storage

8.1 Solid samples require no preservation prior to digestion other than storage at 0-6°C. Sample containers may be glass or plastic. When the laboratory provides the sample containers, the containers are purchased, certified clean glass soil jars with Teflon-lined lids. Samples are analyzed within 6 months of collection.

8.2 For aqueous samples, glass or plastic sample containers are acceptable. When the laboratory provides the sample containers, the containers are purchased, certified clean 250 or 500 mL plastic bottles. Sample volume should be acid preserved with (1+1) nitric acid to pH <2. Samples are held at room temperature (although refrigeration is acceptable also). Samples are analyzed within 6 months of sample collection.

8.3 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silicon are critical.) Samples should be filtered prior to acidification, because acidification changes the sample (usually by dissolving particulates that would be filtered out). Acidified samples received at the lab that require lab filtration must be noted in the case narrative. See digestion SOPs for filtration procedure.

8.4 Samples received by the ICP lab as digestates contain nitric and hydrochloric acid. Digestates are stored at room temperature in plastic B-cups or Hot Block Digestion cups.

8.5 Following analysis, digestates are stored until all results have been reviewed. Digestates are diluted and disposed of through the sewer system in approximately 90 days after receipt of sample.

8.6 For more information about custody, sample handling, and storage procedures, see SMO-GEN and SMO-ICOC.

9) Equipment and Supplies

Instrument ID	Instrument Configuration	Manufacturer Part	Serial Number	Year Acquired
ICP #3 (R-ICP-AES-03)	Instrument	Perkin Elmer 5300DV	077N6051602	2006
	Computer Workstation	Dell Optiplex GX620		
	Analytical Software	PE ICP WinLab v.3.1		
ICP #4 (R-ICP-AES-04)	Instrument	Perkin Elmer 5300DV	077N6052202	2010
	Computer Workstation	Dell Optiplex GX620		
	Analytical Software	PE ICP WinLab v.3.1		
ICP #5 (R-ICP-AES-05)	Instrument	Perkin Elmer Optima 8000	078N2072408C	2013
	Autosampler	AAS S-10	102S12031301	
	Computer Workstation	Lenova Thinkcentre		
	Analytical Software	PE ICP WinLab 32 v5.2.0.0612		

These instruments are “dual” view – they use axial and radial views simultaneously

9.1 Argon gas supply - high purity

9.2 Volumetric flasks, class A.

9.3 Calibrated adjustable Micropipet with disposable tips. See ADM-PCAL for calibration requirements.

10) Standards and Reagents

10.1 Trace metals grade chemicals shall be used in all tests. Each lot of acid used is to be analyzed to demonstrate that it is free of interference before use (see CE-GEN007). Store all acids at room temperature. Acids expire upon manufacturer's indications or per Expiration Policy if not otherwise indicated.

- Hydrochloric acid (conc.), HCl, and Nitric acid (conc), HNO_3. Purchased commercially.

10.2 Reagent Water. All references to water in this SOP refer to the water produced by the laboratory water system.

10.3 Standards Preparation General Information and Disclaimers

10.3.1 All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 mg/L standard may be made by adding 1 mL of 200 mg/L to 10 mL or may be made by adding 4 mL of 50 mg/L to 10 mL. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used.

10.3.2 Vendors and vendors' products are sometimes listed for the ease of the analyst using this SOP, but products and purchased concentrations are examples only and subject to change at any time. All purchased standards are certified by the vendor. Certificates of Analysis are kept in the department until the standards are no longer being used – at which time they are filed with QA. Certificates of Analysis are available upon request. Purchased standards are routinely checked against an independent source for both analyte identification and analyte concentration.

10.3.3 All Standards must be traceable using the laboratory lot system. See the SOP for Making Entries Onto Analytical Records (CE-QA007) for detail.

10.3.4 All standards are prepared from NIST traceable stock standard solutions. Manufacturer's expiration dates are used to determine viability of standards. Preparatory procedures for standards and QC solutions vary between instruments due to the working ranges. All preparatory information for the standards and QC samples are provided in the Controlled Forms section of the Rochester Intranet in the Metals Standards Logbooks.

10.4 Mixed Calibration Standards are prepared by combining appropriate volumes of the stock solutions in volumetric flasks. Matrix match with the appropriate acid and dilute to 100 mL with water. Calibration standards should be verified using a second source quality control sample (LCS, ICV, or CCV). Calibration standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 7 days.

10.5 Initial and Continuing Calibration Verification (ICV and CCV) Standards are prepared by combining compatible analytes at concentrations equivalent to the midpoint of their respective calibration curves. Matrix match with the appropriate acid. The ICV and CCV standards are prepared from a separate source independent from that used in the calibration standards. ICV / CCV standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 48 hours.

10.6 Internal Standard - An internal standard solution consisting of a 10 mg/L solution of Yttrium and Cesium. The apparent concentration is 1.00 mg/L Yttrium. The Yttrium intensity is used by the instrument to ratio the analyte intensity signals for both calibration and quantitation. Cesium is used only as a stabilizer. Store the prepared solutions at room temperature for up to 6 months.

10.7 HLCCV1- The highest calibration standard with the same storage and expiration as the calibration standards.

10.8 HLCCV2 – A standard prepared to verify the linear dynamic range of the instrument. Store at room temperature for up to 14 days.

10.9 LOQ Standards (low level calibration check standards or MRL Standards) are prepared to contain known concentrations of elements at or near the Reporting Limit. LOQ standards should be stored in plastic containers with a shelf-life of 6 months.

10.10 Interference Check Solutions A and AB are prepared to contain known concentrations of interfering analytes that will provide an adequate test of the correction factors. ICSA / ICSAB standards should be stored in plastic containers with a shelf-life of 6 months.

10.11 Laboratory Control Sample and Matrix Spike – see preparation SOP.

10.12 Blanks

10.12.1 Method Blanks –see preparation SOP.

10.12.2 The Calibration Blank is prepared by acidifying reagent water to the same concentrations of acid found in the standards and samples.

11) Method Calibration

11.1 Follow policies in ADM-ICAL. If these instructions conflict with ADM-ICAL, follow the instructions in this SOP.

11.2 Number of Calibration standards – At least 3 standards and a calibration blank are analyzed for each element at the beginning of the daily sequence. The low standard must be at or below the LOQ. The HLCCV2 standard will define the upper limit of the linear range for the curve.

11.3 Initial Calibration Curve Calculation – Internal Standard Method

11.3.1 Yttrium is added to all samples and QC standards to provide a reference for individual performance of each injection. The software divides the element intensity by the internal standard intensity for each injection and provides a "corrected intensity" for each element on the print-out.

$$\text{Corrected Intensity} = \frac{\text{Intensity}_{\text{sample}}}{\text{Intensity}_{\text{internal standard}}}$$

11.3.2 The "corrected intensity" is plotted against concentration using the linear regression equation of a line and forced through zero intensity and zero concentration. This calibration curve assumes that the relationship between concentration (the X values) and intensity (the Y values) is linear and that the following equation describes this relationship:

Y=MX
Where:
X=concentration
Y= corrected intensity
M=slope of the calibration curve
The intercept is forced to be zero.

Given 2 or more data points, the values for M are calculated using the following equation.

$$M = \frac{\sum_{n}^{i=1} (X_i Y_i)}{\sum_{n}^{i=1} (X_i^2)}$$

Where: n=number of standards (includes the blank)

In this equation, the blank is subtracted from all solutions and included in the calculation of the calibration curve

To avoid bias at the low end of the curve, the curve is forced through zero. Forcing the curve through zero may favor the low end of the curve therefore a MRL Standard (LLCCV) and high level CCV (HLCCV1 and HLCCV2) are analyzed to verify both ends of the curve.

11.4 Acceptance Criteria – the correlation coefficient must be 0.998 or greater for target analytes of interest and the ICV must meet limits (see QC section).

11.5 Corrective Action – if the ICAL does not meet acceptance criteria, correct the problem and recalibrate. The curve must be acceptable before sample analysis begins.

12) Sample Preparation and Analysis

12.1 All samples are digested prior to analysis. Refer to the following Metals Digestion SOPs:

- MET-3010A Metals Digestion, Waters for ICP
- MET-3050B Metals Digestion, Soils, Sediments and Sludges for ICP and GFAA

12.2 Set up the instrument with proper operating parameters established as detailed below. Operating conditions - The analyst should follow the instructions provided in Table 3.

12.3 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data documents the selection criteria of background correction points; linear ranges, and the upper limits of those ranges; the Limits of Detection and Quantitation; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor. The limits and on-going frequency of these performance demonstrations are provided in the QC Section.

12.4 Turn on power supply for the instrument, computer, printer and light the plasma. Allow instrument to warm-up while preparing the run (typically 45-60 minutes before operation, although only ~10 minutes are necessary). The cooling water and the argon are on when the instrument are on.

12.5 Profile the instrument on a daily basis, or when maintenance is done to align it optically for both horizontal and vertical optimization in either mode. The vendor recommends aspirating a 1.0 ppm source of manganese. Choose the Tools menu/Spectrometer Control/Optimize “Axial” or “Radial” The instrument automatically adjusts the torch viewing position for maximum intensity.

12.6 Addition of Internal standard -

12.6.1 Pour 40 mL of the calibration blank, the 3 calibration standards, ICV/CCV standards, LOQ, ICSA, and ICSAB into separate 50 mL centrifuge tubes and add 0.80 mL of the 100 mg/L internal standard solution. All other samples, preparation blanks and laboratory control samples are poured up to 10 mL in a 15 mL centrifuge tube and 0.20 mL of internal standard solution is added. This will give an apparent concentration of 1.00 mg/L Yttrium. Other volumes may be used to result in the same concentration.

12.6.2 Internal standards can be added via pump and mixing block. This technique uses a solution of 10 mg/L Y and 10 mg/L Cs.

12.6.3 Place the tubes on the autosampler and program the software to analyze according to the analytical sequence.

12.7 Analytical Sequence – see the Quality Control Section and ADM-BATCH for frequency and requirements.

12.7.1 Rinse the system with the blank solution before the analysis of each sample. The rinse time will be at least one minute, depending upon the instrument. A reduction in rinse time must be demonstrated to be acceptable.

12.8 Sample Analysis and Evaluation

12.8.1 Sensitivity, LOD, LOQ, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

12.8.2 Samples which exceed the linear range of the instrument (greater than HLCCV2) must be diluted and reanalyzed according to ADM-DIL.

12.8.3 Evaluate QC according to the QC Section. Repeat samples associated with non-compliant QC whenever possible.

13) Troubleshooting

Maintenance log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by ALS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

14) Data Acquisition

Data is electronically transferred from the instrument software to LIMS. The preparation information entered to LIMS is used by LIMS to calculate the final results – see Calculation Section.

15) Calculations and Data Reduction Requirements

15.1 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values.

15.2 The use of the internal standard is found in the Method Calibration Section.

15.3 Sample Calculation (water)

$$\text{Conc. (mg/L)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial volume (L)}}$$

15.4 Sample Calculation (soils)

$$\text{Conc. (mg/g)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial mass (g) x Percent Solids expressed as a decimal}}$$

16) Quality Control, Acceptance Criteria, and Corrective Action

16.1 Instrument values are based on duplicate readings. Precision between the emission readings shall not exceed 20 %RSD. If RSD values exceed 20%, reanalyze the sample. Exception: Analytes <MRL are OK to report with RSD>20%.

16.2 Method Blanks

- Frequency -at least one MB with preparation batch of 20 or fewer samples of the same matrix.
- Limits - MB values must not exceed the LOQ(1/2 LOQ for DOD).
- Corrective Action - Fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable MB values have been obtained. If detections are greater than the LOQ, the batch needs to be redigested if sample concentration is less than 10 times the concentration found in the method blank. If the sample concentration is less than the LOQ the sample does not require redigestion.

16.3 HLCCV1 – High standard used in curve

- Frequency - analyzed once during daily analysis.
- Limits - Should agree within 10% of the true value.
- Corrective Action - If HLCCV1 is > 10% different the analysis is judged to be out of control and the source of the problem should be identified and resolved before continuing analysis.

16.4 HLCCV2 – standard slightly higher than calibration for some metals.

- Frequency - Analyzed once during daily analysis.
- Limits - Should agree within 10% of the true value.
- Corrective Action - If out of control, client data above the HLCCV1 should be re-analyzed.

16.5 ICV –

- Frequency - must immediately follow each calibration.
- Limits - ±5% for Method 200.7 and ±10% for Method 6010C.
- Corrective Action – correct the problem and recalibrate the instrument.

16.6 CCV

- Frequency - after every tenth sample, and at the end of the sample run
- Limits - ±10%
- Corrective Action – correct the problem and analyze another CCV. If second CCV fails, recalibrate. Reanalyze affected samples since the last successful CCV. Non-detect samples associated with a high recovery CCV may be reported.

16.7 ICB/CCB

- Frequency – ICB after every ICV and CCB after every CCV (at the beginning and end of the run and after every 10 samples)
- Limits - The results of the calibration blank must be less than the LOQ (less than LOD for DOD).
- Corrective Action - If the limits are not met, terminate the analysis, correct the problem, recalibrate, and reanalyze the samples affected. Non-detect samples associated with a high blank may be reported.

16.8 MS –

- Frequency - one per matrix batch (max. 20 samples) or one per 10 for Method 200.7.
- Limits - within 70-130% (80-120% for DOD) of the actual value or within the documented historical acceptance limits for each matrix. All elements of client interest are evaluated. Sample concentrations greater than four times the spike concentration are not valid and shall not be evaluated.
- Corrective Action - If the matrix spike does not meet these criteria, analyze a Post Digestion Spike. DOD requires project-specific DQOs be examined or contact the client for additional measures. See Table F-7.

16.9 DUP –

- Frequency - one per matrix batch (max. 20 samples) or one per 10 for Method 200.7
- Limits - A control limit of ± 20% RPD shall be used for original and duplicate samples greater than or equal to 5X the LOQ. A control limit of ± the LOQ shall be used if either the sample or duplicate value is less than 5 times the LOQ.
- Corrective Action – If the DUP does not meet criteria, data will be reported with a qualifier.

16.10 Laboratory Control Sample –

- Frequency – one per matrix batch (max. 20 samples).
- Limits – all elements of client interest are evaluated. Client specific QC recoveries may supercede these limits.
    - Waters - Results should be within ± 15% of the true value for method 200.7 and ± 20% for 6010C.
    - Soils – Results must be within the limits indicated on the Certificate of Analysis for the soil reference.
- Corrective Action - Outlying recoveries may indicate loss of analyte due to digestion procedures or laboratory contamination. If an LCS is found to be out of the specified limits, recalibrate and reanalyze. If the LCS remains out of control with a low bias, redigestion of the entire batch should occur. If the LCS remains out of control with a high bias, redigestion of all positive results (greater than the LOQ) should occur.

16.11 MRL standard (LLICV/LLCCV) - A standard less than or equal to the LOQ is analyzed

- Frequency - at the beginning and end of each daily analytical run but not before the ICV.
- Limits- There are no limits in the 200.7 method. 6010C requires 70-130%. DOD requires 80-120%.
- Corrective Action - If the limits are not met the analysis is stopped and the instrument is recalibrated.

16.12 Interference Check Samples-

16.12.1 ICSA

- Frequency - at the beginning and end of each daily analytical sequence.
- Limits – less than LOQ (less than 2 times LOQ for metals with LOQ < 10mg/L) – DOD requires that the ICSA be less than the LOD unless they are a verified trace impurity from one of the spiked analytes.
- Corrective Action – terminate analysis; locate and correct problem;

reanalyze ICS and any associated samples. Samples less than LOQ will be flagged and reported.

16.12.2 ICSAB –

- Frequency – immediately after ICSA
- Limits - The analyte recoveries for the AB solution must fall within 20% of the true value
- Corrective Action - terminate analysis; locate and correct problem; reanalyze ICS and all associated samples unless analytes are not detected in the associated samples or interfering elements are not present at the ICSA level.

16.13 Serial Dilution Test –

- Frequency – one each prep batch or when a new or unusual matrix is encountered. Only applicable to samples with a concentration greater than 50 times the LOQ. If no samples in the prep batch are >50xLOQ, analyze a post-digestion spike.
- Limits - a 5-fold dilution should agree within ± 10% of the original determination.
- Corrective Action – if the results are not within limits, flag the data with a qualifier. For DOD, if the results are not within limits, perform post-digestion spike addition.

16.14 Post Digestion Spike Addition (for 6010C analyses): The spike addition should produce a minimum level of 10 times and a maximum of 100 times the LOQ.

- Frequency – When a dilution test fails, or when no samples have a concentration 50 times the LOQ or if a matrix spike does not yield acceptable results.
- Limits - should be recovered to within 75% to 125% of the known value.
- Corrective action - If the spike is not recovered within the specified limits, a matrix effect has been confirmed and the data must be flagged.

16.15 Instrument Performance

16.15.1 InterElement Correction Factors (IEC)

- Procedure – A calibration curve is analyzed as per instrument specifications. Once completed, individual standards for Al, Ca, Fe, Mg, and Mo (Mo for Optima 4 only) are analyzed. The instrument software then creates an IEC table.
- Frequency - annually, or as needed.
- Limits and corrective action – The ICSA check standard routinely confirms the IECs. If the ICSA is persistently problematic, re-establish IECs.

16.15.2 Linear Ranges (LR)

- Frequency – Standards (HLCCV1 and HLCCV2) are prepared at the linear range level and analyzed every quarter
- Limits - must be ±5% of true value.
- Corrective Action – If the linear range is too high, lower the linear range and repeat the study.

16.15.3 Instrument Detection Limits (IDL)

- Procedure – Analyze 7 replicates of a low level standard. Repeat twice more for a total of 21 replicates over 3 non-consecutive days.
- Frequency – with initial set-up and after significant change.
- Limits – the calculated IDL must be less than the LOD.
- Corrective Action - If the IDL fails, correct the problem and repeat the study or raise the LOD.

16.15.4 Ongoing verification of detection and quantitation limits is required. See CE-QA011 for requirements.

16.15.5 LOQV (LLQC) – This digested standard spiked at the reporting limit must be analyzed quarterly for DOD (6010C requires "as needed"). The limits are 70-130% for 6010C and LCS limits for DOD. If this QC does not meet these limits, determine the source of the problem. Achieve an acceptable LOQV before continuing.

17) Data Records Management

See CE-GEN003 and ADM-ARCH.

18) Contingencies for Handling Out Of Control Data

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, flag and narrate appropriately.

19) Method Performance

Detection and Quantitation limits are determined for all wavelengths utilized for each type of matrix commonly analyzed. See Table 2 for approximate wavelengths. Determine limits according to the requirements in CE-QA011. The supporting information is filed with the QA office.

Demonstration of Capability is performed according to CE-QA003.

20) Summary of Changes

- Updated to new ALS format
- Incorporated SOP change form for reporting non-detects when MRL standard fails high.
- Added ICP #5
- Removed copies of standards log and referenced Controlled Forms
- Updated MRL for Beryllium

21) References and Related Documents

- Test Methods For Evaluating Solid Waste, Physical/Chemical Methods. USEPA SW-846, Update IV, December 1996.
- Methods For the Determination of Metals in Environmental Samples Supplement I. USEPA/600/R-94/111, May 1994.
- DOD Quality Systems Manual for Environmental Laboratories – Version 4.2, October 2010.

22) Appendix

- DOD Summary
- Table 1 List of Analytes and Practical Quantitation Limits
- Table 2 Potential Interferences
- Table 3 Recommended Wavelengths and Instrument Specifications
- Table F-7 DOD specific Requirements from DOD QSM Version 4.2 October 2010

DOD SUMMARY

For work for the Department of Defense – the DOD Quality Systems Manual must be followed. The DOD Manual is based on the NELAC Standards with some additional requirements. The exact wording is in Table F-7. The following are the requirements which are different or additional to routine analysis and must be followed for DOD work:

- The CCB must be less than the LOD.
- The Method Blank must be less than ½ the reporting limit (<RL for common laboratory contaminants).
- Apply J flag to all hits between LOD and LOQ.
- The limits for LCS and MS are 80-120%. All targets are spiked and evaluated.
- The IDL must be less than or equal to the LOD.
- Low Level Check Standard (MRL standard) must be spiked at or below the reporting limit and it must have a recovery of 80-120% of the true value when analyzed at the beginning of the run.
- ICS-A absolute value of concentration for all non-spiked analytes must be <LOD (unless they are a verified trace impurity from one of the spiked analytes).
- Serial Dilution Test Corrective Action – If the limits are not met, perform a post digestion spike addition.

TABLE 1

	*TypicalMRL/ LOQ***	
Analyte	***Water-Optima***	***Soil***
	ug/L	***ug/g***
Silver	10	1.00
Aluminum	100	10.0
Arsenic	10	1.0
Boron	200	20.0
Barium	20	2.00
Beryllium	3.0	0.300
Calcium	1000	100.0
Cadmium	5.0	0.500
Cobalt	50	5.00
Chromium	10	1.0
Copper	20	2.00
Iron	100	10.0
Potassium	2000	200
Magnesium	1000	100
Manganese	10	1.0
Molybdenum	25	2.50
Sodium	1000	100
Nickel	40	4.00
Lead	50	5.00
Antimony	60	6.00
Selenium	10	1.00
Tin	500	50.0
Titanium	50	5.00
Thallium	10	1.00
Vanadium	50	5.00
Zinc	20	2.00
Lithium	100	10
Silicon	1000	100
Strontium	100	10
Gold	50	
Gallium	200	
Germanium	100	
Hafnium	100	
Indium	100	
Palladium	100	
Platinum	100	
Ruthenium	100	
Rhenium	100	
Tungsten	100	
Tantalum	100	
Zirconium	100	

**See Data Quality Objectives Table for the most current LOQs

TABLE 2

POTENTIAL INTERFERENCES AND ANALYTE CONCENTRATION EQUIVALENTS (mg/L)
ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelenth (nm)	Interferant[a,b]									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al at 1000 mg/L	Cu at 200 mg/L	Mn at 200 mg/L
Ca at 1000 mg/L	Fe at 1000 mg/L	Ti at 200 mg/L
Cr at 200 mg/L	Mg at 1000 mg/L	V at 200 mg/L

[b] The data shown above as analyte concentration equivalents are not the actual observed concentrations. To obtain those data, add the listed concentration to the interferant figure.

[c] Interferences will be affected by background choice and other interferences may be present.

Table 3

Recommended Wavelengths and Instrument Specifications

Suggested wavelengths are listed below:

Analyte	Wavelength
Ag Silver	328.068
Al Aluminum	308.215
B Boron	249.773
Ba Barium	233.527
Be Beryllium	234.861
Ca Calcium	430.253
Cd Cadmium	226.502
Co Cobalt	228.616
Cr Chromium	267.716
Cu Copper	324.754
Fe Iron	238.863
Mg Magnesium	279.079
Mn Manganese	257.610
Mo Molybdenum	202.030
Na Sodium	330.237
Ni Nickel	231.604
Pb Lead	220.353
Sb Antimony	206.833
Sn Tin	189.933
Ti Titanium	334.941
V Vanadium	292.402
Zn Zinc	206.191
Y Yttrium	371.030

Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument operating conditions herein are recommended based upon manufacturer's instrument manuals.

Current Method Operating Conditions are as follows, these conditions may vary to optimize the instrument for different analyses:

Parameter	Radial Plasma	Axial Plasma
Resolution	Fixed	Fixed
Purge Gas Flow	Normal	Normal
Read Time (min/max sec.)	5/20	5/50
Replicates	2	2
Plasma (L/min)	15	15
Aux. (L/min)	0.5	0.3
Nebulizer Flow (L/min)	0.72	0.56
Power (watts)	1300	1450
Viewing Height (mm)	15	15

Table F-7. Inorganic Analysis by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry and Atomic Absorption Spectrophotometry (AA) (Methods 6010 and 7000 Series)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Demonstrate acceptable analytical capability	Prior to using any test method and at any time there is a significant change in instrument type, personnel, test method, or sample matrix.	QC acceptance criteria published by DoD, if available; otherwise, method-specified criteria.	Recalculate results; locate and fix problem, then rerun demonstration for those analytes that did not meet criteria (see Section C.1.f).	NA.	This is a demonstration of analytical ability to generate acceptable precision and bias per the procedure in Appendix C. No analysis shall be allowed by analyst until successful demonstration of capability is complete.
LOD determination and verification (See Box D-13)					
LOQ establishment and verification (See Box D-14)					
Instrument detection limit (IDL) study (ICP only)	At initial set-up and after significant change in instrument type, personnel, test method, or sample matrix.	IDLs shall be ≤ LOD.	NA.	NA.	Samples may not be analyzed without a valid IDL.
Linear dynamic range or high-level check standard (ICP only)	Every 6 months.	Within ± 10% of true value.	NA.	NA.	

Table F-7. Inorganic Analysis by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry and Atomic Absorption Spectrophotometry (AA) (Methods 6010 and 7000 Series) (continued)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Initial calibration (ICAL) for all analytes **ICP: minimum one high standard and a calibration blank;** **GFAA: minimum three standards and a calibration blank;** **CVAA: minimum 5 standards and a calibration blank**	Daily ICAL prior to sample analysis.	If more than one calibration standard is used, r ≥ 0.995.	Correct problem, then repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second source calibration verification (ICV)	Once after each ICAL, prior to beginning a sample run.	Value of second source for all analyte(s) within ± 10% of true value.	Correct problem and verify second source standard. Rerun ICV. If that fails, correct problem and repeat ICAL.	Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until calibration has been verified.
Continuing calibration verification (CCV)	After every 10 field samples and at the end of the analysis sequence.	ICP: within ± 10% of true value; GFAA: within ± 20% of true value; CVAA: within ± 20% of true value.	Correct problem, rerun calibration verification. If that fails, then repeat ICAL. Reanalyze all samples since the last successful calibration verification.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable calibration verification.	Problem must be corrected. Results may not be reported without a valid CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Low-level calibration check standard (ICP only)	Daily, after one-point ICAL.	Within ± 20% of true value.	Correct problem, then reanalyze.	Flagging criteria are not appropriate.	No samples may be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be less than or equal to the reporting limit.

Table F-7. Inorganic Analysis by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry and Atomic Absorption Spectrophotometry (AA) (Methods 6010 and 7000 Series) (continued)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Method blank	One per preparatory batch.	No analytes detected > ½ RL and greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater). Blank result must not otherwise affect sample results. For common laboratory contaminants, no analytes detected > RL (see Box D-1).	Correct problem, then see criteria in Box D-1. If required, reprep and reanalyze method blank and all samples processed with the contaminated blank.	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply B-flag to all results for the specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid method blank. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Calibration blank	Before beginning a sample run, after every 10 samples, and at end of the analysis sequence.	No analytes detected > LOD.	Correct problem. Re-prep and reanalyze calibration blank. All samples following the last acceptable calibration blank must be reanalyzed.	Apply B-flag to all results for specific analyte(s) in all samples associated with the blank.	
Interference check solutions (ICS) (ICP only)	At the beginning of an analytical run.	ICS-A: Absolute value of concentration for all non-spiked analytes < LOD (unless they are a verified trace impurity from one of the spiked analytes); ICS-AB: Within ± 20% of true value.	Terminate analysis; locate and correct problem; reanalyze ICS, reanalyze all samples.	If corrective action fails, apply Q-flag to all results for specific analyte(s) in all samples associated with the ICS.	
LCS containing all analytes to be reported	One per preparatory batch.	QC acceptance criteria specified by DoD, if available; see Box D-3 and Appendix G.	Correct problem, then reprep and reanalyze the LCS and all samples in the associated preparatory batch for failed analytes, if sufficient sample material is available (see full explanation in Appendix G).	If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to specific analyte(s) in all samples in the associated preparatory batch.	Problem must be corrected. Results may not be reported without a valid LCS. Flagging is only appropriate in cases where the samples cannot be reanalyzed.

Table F-7. Inorganic Analysis by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry and Atomic Absorption Spectrophotometry (AA) (Methods 6010 and 7000 Series) (continued)

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria	Comments
Matrix spike (MS)	One per preparatory batch per matrix (see Box D-7).	For matrix evaluation, use QC acceptance criteria specified by DoD for LCS.	Examine the project-specific DQOs. If the matrix spike falls outside of DoD criteria, additional quality control tests are required to evaluate matrix effects.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the LCS limits, the data shall be evaluated to determine the source of difference and to determine if there is a matrix effect or analytical error.
Matrix spike duplicate (MSD) or sample duplicate	One per preparatory batch per matrix (see Box D-7).	MSD: For matrix evaluation use QC acceptance criteria specified by DoD for LCS. MSD or sample duplicate: RPD ≤ 20% (between MS and MSD or sample and sample duplicate).	Examine the project-specific DQOs. Contact the client as to additional measures to be taken.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	The data shall be evaluated to determine the source of difference.
Dilution test (ICP and GFAA only)	One per preparatory batch.	Five-fold dilution must agree within ± 10% of the original measurement.	ICP: Perform post-digestion spike (PDS) addition; GFAA: Perform recovery test.	Flagging criteria are not appropriate.	Only applicable for samples with concentrations > 50 x LOQ.
Post-digestion spike (PDS) addition (ICP only)	When dilution test fails or analyte concentration in all samples < 50 x LOD.	Recovery within 75-125% (see Table B-1).	Run all associated samples in the preparatory batch by method of standard additions (MSA) or see flagging criteria.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	Spike addition should produce a concentration of 10 – 100 x LOQ.
Recovery test (GFAA only)	When dilution test fails or analyte concentration in all samples < 25 x LOD.	Recovery within 85-115%.	Run all associated samples in the preparatory batch by method of standard additions (MSA) or see flagging criteria.	For the specific analyte(s) in the parent sample, apply J-flag if acceptance criteria are not met.	
Method of standard additions (MSA)	When matrix interference is confirmed.	NA.	NA.	NA.	Document use of MSA in the case narrative.
Results reported between DL and LOQ	NA.	NA.	NA.	Apply J-flag to all results between DL and LOQ.	

ALS Standard Operating Procedure

DOCUMENT TITLE:	HEXAVALENT CHROMIUM BY ION CHROMATOGRAPHY FOR WATER AND SOIL EXTRACTS
REFERENCED METHOD:	EPA 218.6, EPA218.7, SW 7199, EPA 0061, NIOSH 7605
SOP ID:	GEN-7199
REV. NUMBER:	6
EFFECTIVE DATE:	10/14/13

ALS Environmental

HEXAVALENT CHROMIUM BY ION CHROMATOGRAPHY FOR WATER AND SOIL EXTRACTS

EPA 218.6, EPA218.7, SW 7199, EPA 0061, NIOSH 7605

SOPID:	GEN-7199	Rev. Number:	6	Effective Date:	10/14/13

Approved By: Department Supervisor - Christine Kutzer   Date: 9/27/13

Approved By: QA Manager - Lisa Reyes   Date: 9/27/2013

Approved By: Laboratory Director - Michael Perry   Date: 9/27/13

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HEXAVALENT CHROMIUM BY ION CHROMATOGRAPHY FOR WATER AND SOIL EXTRACTS

1) Scope And Applicability

1.1 This SOP uses the following methods for the determination of Hexavalent chromium: EPA Method 7199 for water samples and soil extracts; 218.6 for drinking water and other waters; 218.7 for drinking water; NIOSH 7605 for air filter extracts, and 0061 for air impingers.

1.2 Although testing for Hexavalent chromium is not currently regulated in drinking water (except through total chromium limits), the EPA recommended monitoring (Dec 2010) of Hexavalent chromium using 218.6, modified to reach a MDL of 0.02 ug/L (Jan 2011). The EPA released method 218.7 in January of 2012. Method 218.7 has been included in UMCR3 and is to be used for testing of certain public water systems designated by EPA starting January 2013. The UCMR3 MRL is 0.03 ug/L.

1.3 This method may not be useful for the analysis of samples containing high levels of anionic species such as sulfate and chloride, since these species may cause column overload.

1.4 Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III).

1.5 This method should be used by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

1.6 Current reporting limits:

	Drinking Water	Water	Soils
218.7	0.03 ug/L	NA	NA
218.6	0.02 ug/L	0.02 ug/L (LL) 0.01 mg/L (RL)	NA
7199	NA	0.01 mg/L	0.40 mg/kg
NIOSH 7605		see GEN-N7605	

1.7 Current MDLs:

	Drinking Water	Water	Soils
218.7	0.01 ug/L	NA	NA
218.6	0.01 ug/L	0.01 ug/L (LL) 0.001 mg/L (RL)	NA
7199	NA	0.001 mg/L	0.026 mg/kg
NIOSH 7605		see GEN-N7605	

2) Summary of Procedure

- Waters by 218.6 and 218.7 are preserved with a combined buffer/dechlorinating reagent which complexes free chlorine and increases the pH to a specified value (see Preservation Section). Water samples by 7199 are not chemically preserved with the buffer. Soils are digested by EPA 3060A (GEN-3060A). Air filters are digested by NIOSH 7605 (GEN-N7605).
- A measured volume of the sample is introduced into an ion chromatograph. CrO42- is separated from other matrix components on an anion exchange column. CrO42- is derivatized with 1,5-diphenylcarbazide in a post-column reaction and is detected spectrophotometrically at a wavelength of 530 nm. Cr(VI) is qualitatively identified via retention time, and the concentration of CrO42- in the sample is calculated using the integrated peak area and the external standard technique.

3) Definitions

3.1 Initial Calibration - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

3.2 Matrix Spike (MS) - In the matrix spike analysis, a predetermined quantity of standard solution is added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recovery is calculated for the analyte detected. EPA methods 218.6 and 218.7 call the matrix spike a Laboratory Fortified Sample Matrix (LFM or LFSM).

3.3 Soluble Matrix Spike (MS-Sol) - Only applicable to soil preparation batches digested by GEN-3060A. In the soluble matrix spike analysis, a predetermined quantity of a soluble standard solution of the analyte is added to a sample matrix prior to sample digestion and analysis. The purpose of the soluble matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recovery is calculated for the analyte detected

3.4 Insoluble Matrix Spike (MS-Insol) - Only applicable to soil preparation batches digested by GEN-3060A. In the insoluble matrix spike analysis, a predetermined quantity of an insoluble standard of the analyte is added to a sample matrix prior to sample digestion and analysis. The purpose of the insoluble matrix spike is to evaluate the dissolution during the digestion process and effects of the sample matrix on the dissolution. Percent recovery is calculated for the analyte detected.

3.5 Duplicate Sample (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision. EPA methods 218.6 and 218.7 use the abbreviation LD (Laboratory Duplicate)

3.6 Relative Percent Difference (RPD) – The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.7 Method Blank (MB) - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire preparation and analytical procedure. For waters by 218.7, the MB is the Laboratory Reagent Blank (LRB) or CCB and contains the method preservative.

3.8 Laboratory Control Sample (LCS) - In the LCS or blank spike analysis, a predetermined quantity of standard solution is added to a blank prior to sample analysis. Percent recovery is calculated for the analyte detected. This LCS is a check on the calibration only and has not undergone digestion. The LCS-Insol is a check on the preparation batch.

3.9 Blank Spike (LCS-Insol) – Only applicable to soil preparation batches digested by GEN-3060A. In the LCS-Insol analysis, a predetermined quantity of an insoluble standard solution is added to a blank prior to sample digestion and analysis. Percent recoveries are calculated for the analyte detected.

3.10 Post Verification Spike (PVS) – The PVS (sometimes referred to as PDS for Post Digestion Spike by New Jersey) analysis is designed to verify that neither a reducing nor a chemical interference is affecting the analysis. In the PVS analysis, a predetermined quantity of a soluble standard solution is added to a sample after sample digestion and analysis. Percent recoveries are calculated for the analyte detected.

3.11 Independent Calibration Verification/ Continuing Calibration Verification (ICV / CCV) – ICV/CCV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization. This is sometimes referred to by New Jersey as CCS (Calibration Check Standard), or QCS (Quality Control Sample). Method 218.7 calls the ICV a QCS and the CCV a CCC (Continuing Calibration Check).

3.12 Initial Calibration Blank (ICB) - A blank run immediately after calibration to determine if the instrument is adequately zeroed.

3.13 Continuous Calibration Blank (CCB) - A blank run periodically (every 10 samples after the CCV) to ensure the instrument is still zeroed adequately. The CCB may be used for the MB for waters.

3.14 Preparation Batch - Samples digested together as a unit, not to exceed 20 investigative samples. The Digested QC (PB, LCSs, MSs, DUP) are associated with the preparation batch and may be analyzed in separate analytical batches. See ADM-BATCH for further discussion.

3.15 Analytical Batch - Samples analyzed together as a unit, not to exceed 10 injections for 218.7 or 20 injections for 7199 and 218.6. This batch must contain all of the undigested or instrument QC and may not necessarily contain all of the digested QC associated with the samples in the analytical batch. Typically, the preparation batch QC is analyzed prior to the analysis of client samples to verify that the associated samples are valid for use. See ADM-BATCH for further discussion. The analytical sequence for 218.7 is attached.

3.16 Method Detection Limit (MDL): a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero.

3.17 Method Reporting Limit (MRL): The minimum amount of a target analyte that can be measured and reported quantitatively.

3.18 Limit of Detection (LOD): An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix- specific and may be laboratory-dependent. For DOD, the smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%.

3.19 Limit of Quantitation (LOQ)/Reporting Limit: The minimum levels, concentrations, or quantities of a target that can be reported with a specified degree of confidence. For DOD, the lowest concentration that produces a quantitative result within specified limits of precision and bias. The LOQ shall be set at or above the concentration of the lowest calibration standard.

4) Health and Safety Warnings

4.1 All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

4.2 Chemicals, reagents and standards must be handled as described in the company safety policies, approved methods and in MSDSs where available. Refer to the Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

4.3 Refer to the Safety Manual for further discussion of general safety procedures and information.

4.4 Waste Management And Pollution Prevention

Hexavalent chromium solutions should be dumped in the red inorganic carboys which will later be emptied by qualified personnel. All other waste can be flushed down the drain with large amounts of water. See SMO-SPLDIS for further information on sample disposal.

It is the laboratory's practice to minimize the amount of acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the EH&S Manual.

5) Cautions

- See SOP GEN-300.0 for preventive maintenance of the instrument.
- Clean labware according to GEN-GC. NOTE: Chromic acid must not be used for the cleaning of labware.

6) Interferences

6.1 Contamination - A trace amount of Cr is sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, reagent blanks are analyzed to assess for potential Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact or caustic or acidic reagents of samples with stainless steel or pigmented material.

6.2 OXIDATION-REDUCTION (REDOX) CONCERNS – To ensure sample integrity, Cr(VI) must be protected from reduction, and Cr(III), if present, must not oxidize to Cr(VI) during sample storage or processing.

6.2.1 Within the normal pH range in drinking water, Cr(VI), present as a result of pollution or oxidation of Cr(III) in source water during treatment, forms oxyanions, which are typically represented as HCrO4- and CrO42-. The very stable CrO42- anion dominates above pH 8; therefore, the method preservative is designed to buffer samples to at least pH 8. Chromate compounds are quite soluble, mobile and stable, particularly in an oxidizing environment. In contrast, soluble Cr(III) species oxidize to Cr(VI) in the presence of free chlorine, although natural organic matter in surface water sources may complex Cr(III), slowing its oxidation even in a highly oxidizing environment. The rate of Cr(III) oxidation increases with chlorine concentration and is pH-dependent. For these reasons, the preservation includes ammonium ions to complex free chlorine. The resulting formation of chloramines minimizes, but does not completely prevent, the oxidation of Cr(III). EPA experiments have demonstrated the ability of the method preservative to minimize the oxidation of Cr(III) and to prevent the reduction of Cr(VI) for at least 14 days in drinking water from ground and surface water sources.

6.2.2 A reducing tendency of the sample matrix may change Cr (VI) to Cr(III). The reducing/oxidizing tendency of each sample may be characterized using additional analytical parameters, such as pH, ferrous iron, sulfides, and oxidation/reduction potential. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biochemical Oxygen Demand (BOD). Analysis of these additional parameters establishes the tendency of Cr(VI) to exist in the unspiked sample(s) and may be necessary to assist in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria. Reduction of Cr(VI) to Cr(III) can occur in an acidic medium. However, at a pH of 6.5 or greater, CrO42- (which is less reactive than the HCrO4-) is the predominant species.

6.3 Sample ionic strength may enhance or suppress Cr(VI) response; however, the 4-mm column systems used tolerate typical concentrations of common anions in drinking water in combination with method preservative. Acceptable method performance has been demonstrated by EPA for samples with hardness up to 350 mg/L as CaCO3 and total organic carbon content of 3 mg/L.

6.4 Overloading of the analytical column capacity with high concentrations of anionic species, especially chloride and sulfate, will cause a loss of Cr(VI). The column can handle samples containing up to 5% sodium sulfate or 2% sodium chloride. Poor recoveries from fortified samples and tailing peaks are typical manifestations of column overload.

7) Personnel Qualifications and Responsibilities

Personnel must be trained according to CE-QA003.

It is the responsibility of the Project Manager to obtain information from the client before sampling. The laboratory needs to know whether the client will require additional investigation of the sample matrix in the case of matrix spike failures. A reducing condition in the sample matrix will reduce Cr(VI) to Cr(III) causing low bias. Additional parameters – sulfide, pH, REDOX, ferrous irons, BOD, COD, TOC may be used to demonstrate a reducing condition in the sample matrix. If any or all of these parameters are to be analyzed, additional aliquots are to be sampled and the tests are to be scheduled when hexavalent chromium is scheduled due to holding time limitations. If pH and REDOX are to be analyzed, they are to be analyzed from the same DI extract. It is the responsibility of the Project Manager to appropriately flag the data and make notes in the case narrative about the nature of the matrix, if applicable (see the attached flowchart).

It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

8) Sample Containers, Collection, Preservations, and Storage

8.1 Bottleware - If the lab provides the bottleware, waters are sampled in certified clean 250-mL narrow-mouth, high-density polypropylene containers, or equivalent. Soils are sampled in certified clean 4 or 8 oz. glass soil jars. The client must provide additional aliquots of soil sample if further investigation into the reducing/oxidizing nature of the sample is to be done.

8.2 Pretesting – Pre-test each lot of the the preservation solution (buffer). Add 2.5 mL of the buffer to a 250 mL sample bottle and fill with DI. Preservative is acceptable if result is <MDL of the low level analysis.

8.3 Temperature Requirements - Samples are typically shipped and stored at 0-6°C. Drinking water samples for UCMR3 method 218.7 received within 48 hours of collection must be ≤10ºC or they must be rejected. If UCMR3 samples are received after 48 hours of collection they must be ≤6ºC or they must be rejected. The project manager is to notify the client that a new sample must be collected.

8.4 Preservation and Holding Time:

	Drinking Water 218.7	**Drinking Water 218.6**	**Non-Potable Water 218.6**	**Waters 7199**	**Soil 7199**	**Air filters NIOSH 7605**	**Air (impingers) collected by 0061**
Filter	No	Required see 6.4.1	Required see 6.4.1	Optional – Field or Lab	NA	NA	Field
Preservative	NH4OH/ (NH4)2SO4 liquid	NH4OH/ (NH4)2SO4 liquid	NH4OH/ (NH4)2SO4 liquid	None	None	None	None
pH	>8.0	9.0-9.5	9.3-9.7	unpreserved	NA	NA	NA
Residual Chlorine	<0.1 mg/L	NA	NA	NA	NA	NA	NA
Holding Time	14 days	5 days	28 days	24 hours	7 days from extraction	28 days (recommended)	14 days

Sample pH and residual chlorine (if applicable) is measured and recorded upon receipt (see attached preservation sheet and SMO-GEN for procedures). The preservation sheet and associated steps may be completed by SMO or Wetchem personnel. SMO also records the lot number of the bottle and preservative upon receipt.

- For 218.7, the sample is only valid if received pH>8.0 and Residual chlorine <0.1 mg/L. The sample must be rejected if it does not meet receipt requirements. It may not be reported for UCMR3.

- For 218.6, the holding times listed only apply if the sample is properly filtered and buffered within 24 hours of sampling. If the buffering requirements (pH) are not met, and the sample is still within 24 hours of collection, the pH is adjusted with the appropriate buffer or ammonium hydroxide.

8.4.1 For 218.6, samples shall be filtered and preserved with buffer solution within 24-hours of collection (preferably in the field at the time of collection). Procedures are as follows, listed in order of preference

8.4.1.1 Filter and Buffer in the Field during time of collection:

Filter sample aliquot using an in-line filter or plastic syringe filtration unit equipped with a 0.45um membrane filter (mfr. Gelman, Millipore, or equivalent).

- Non-Potable Water - Adjust the pH of the filtered sample to pH 9.3 - 9.7 using buffer solution provided by the laboratory. pH meter should be capable of ±0.03 SU. Holding time is 28-days from collection.
- Drinking Water - Adjust the pH of the filtered sample to pH 9.0 - 9.5 using buffer solution provided by the laboratory. pH meter should be capable of ±0.03 SU. Holding time is 5-days from collection.

The bottle set shall include unpreserved 125 or 250 mL plastic bottles. A minimum of 25 mL filtered sample should be provided for analysis.

8.4.1.2 Filter and Buffer in the Field during time of collection –No pH meter available:

Filter sample aliquot using an in-line filter or plastic syringe filtration unit equipped with a 0.45um membrane filter (mfr. Gelman, Millipore, or equivalent). Filtered sample shall be collected in a pre-preserved sample bottle containing buffer solution. Samples must be received by the laboratory within 24-hr of collection to ensure proper pH has been achieved by the buffer solution. The lab will adjust the pH, if necessary, within 24-hr of collection. Holding time is 28-days.

The bottle set shall include pre-preserved 125-ml plastic bottles with 1 mL buffer solution, or equivalent. A minimum of 25 mL filtered sample should be provided for analysis.

8.4.1.3 Filter and Buffer at the Laboratory –No filtration unit or pH meter available:

Collect sample in an un-preserved plastic bottle. Samples must be received by the laboratory within 24-hr for immediate analysis, or in-lab filtration and pH adjustment with buffer solution. Holding time is 28-days for non-potable water and 5 days for drinking water if properly filtered and buffered.

The bottle set shall include unpreserved 125 or 250-mL plastic bottles.

8.5 Method 7199 water sample: If it is impossible to complete 2 simultaneous injections of all samples within the 24 hour holding time, perform the injections separately in order to meet one injection within holding time of as many samples as possible.

8.6 If investigation is requested, the investigative tests (such as sulfide, pH, REDOX and Fe2+) must be scheduled with the Cr6+ test because some of the investigative test have shorter holding times than hexavalent chromium. These tests must be completed prior to the evaluation of the Cr6+ QC so that the results are available if needed.

8.7 Sample handling, storage, receipt, and custody procedures are discussed in SMO-GEN and SMO-ICOC.

9) Equipment and Supplies

Instrument ID	Instrument Configuration	Manufacturer Part	Serial Number	Year Acquired
IC #8 (R-IC-08)	Ion Chromatograph	Dionex ICS-2100	12030901	2012
	Heated Conductivity Cell	DS6	12030664	
	Reagent Pump	AXP	20045075	
	Variable Wavelength Detector	ICS Series VWD	12031294	
	Autosampler	AS-AP	12031171	
	Loop	1000 uL		
	Analytical Column	Dionex AS-7 2x250mm		
	Computer Workstation	Dell Optiplex 790	15105322945	
	Analytical Software	Chromeleon 7.0	151838	

9.1.1 Reaction Coil: Dionex P/N 042631 750 uL

9.1.2 Column Heater - integrated

9.1.3 Pressurized eluent container, plastic, two liter size.

9.1.4 Nitrogen Tanks

9.2 Labware

9.2.1 Class A volumetric flasks, and graduated cylinders.

9.2.2 Assorted pipettes - of acceptable precision and accuracy – calibrated according to ADM-PCAL.

9.2.3 Disposable syringes - 50-mL, with male luer-lock fittings.

9.2.4 Dionex ONGuard-P sample pretreatment cartridges - p/n 39597

9.2.5 Syringe filters - 0.45-µm, Millipore, p/n SLHV 025 NK.

9.2.6 Storage bottles - high density polypropylene or amber glass, 1-L capacity.

9.2.7 Orion Model 720A pH meter or Orion SA 520 pH meter, or equivalent, calibrated according to ADM-phSupport, with accuracy ± 0.05 pH.

9.2.8 Analytical and TopLoading Balances – calibrated according to ADM-DALYCK.

10) Standards and Reagents

10.1 All standards must be traceable using the laboratory lot system (CE-QA007)

10.2 All purchased standards are certified by the vendor. Certificates of Analysis are kept in the department until the standards are no longer being used – at which time they are filed with QA. Certificates of Analysis are available upon request.

10.3 Purchased Reagents and Standards - store at room temperature and expire per Expiration Policy (CE-QA012) unless otherwise indicated.

10.3.1 Ammonium hydroxide, NH4 OH. EM Science cat. #AX1303-14, or equivalent, sp.gr. 0.902, CAS RN 1336-21-6.

10.3.2 Ammonium sulfate, (NH4)2SO4 . EM Science cat #SX0597-1, or equivalent, CAS RN 7783-20-2

10.3.3 1,5-Diphenylcarbazide. EM Science cat. #DX2205-1, or equivalent, CAS RN 140-22-7.

10.3.4 Methanol, HPLC grade, EM Science cat #MX0475-1, or equivalent

10.3.5 Sulfuric acid, concentrated, EM Science, Omnitrace, cat #SX1247-2 or equivalent.

10.3.6 Cr(VI) Standards Stock Solution (1000 mg/L)

10.3.7 Cr(VI) Reference Stock Solution (1000 mg/L) – the Reference Stock is to be from a separate manufacturer of the Standard Stock.

10.3.8 Chlorine Residual Test Strips capable of reading to 0.1 mg/L. HF Scientific Micro Check Test Strips.

10.4 Prepared Reagents

10.4.1 Buffer Solution. Dissolve 3.3 g of ammonium sulfate in 75 mL of reagent water in a 100 mL volumetric flask. Add 6.5 mL of ammonium hydroxide. Dilute to volume (100 mL) with reagent water. Degas the solution with helium gas for 5-10 minutes prior to use. Store at 0-6°C for up to one year.

10.4.2 Buffered DI (Dilution Water). A batch of reagent grade water must be prepared by adjusting the pH within the range of 9-9.5 using the buffer solution. Use this solution for diluting working standards and high level samples. Prepare fresh before use. pH range of 9.3-9.7 shall be used for Method 218.6 waters as per Footnote 20 of EPA Method Update Rule and FAQ-Cr6.

10.4.3 Eluent.- Dissolve 33 g of ammonium sulfate in 500 mL of DI and add 6.5 mL of ammonium hydroxide. Dilute to one liter with reagent water. Degas the solution with helium gas for 5-10 minutes prior to use. Expires 1 month from preparation.

10.4.4 Post-column reagent. Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 mL of HPLC grade methanol in a 1000 mL volumetric flask. In a separate container, add about 500 mL DI, then add 28 mL of 98% sulfuric acid, mix and degas with helium gas for 5-10 minutes. Carefully combine the degassed acid with the diphenylcarbazide/methanol solution, introducing as little air as possible. This method of preparation reduces the frequency and intensity of air spikes in the chromatography. Dilute to volume with reagent water. Store in amber glass at 0-6°C. This reagent should be made fresh for the low level analysis, and may be kept no longer than 5 days.

10.5 Standards: 7199/218.6 Regular Level. Prepare fresh before use.

10.5.1 Regular Level Intermediate Standards Working Stock (10 mg/L). Do two 1/10 serial dilutions of the 1000 ppm standard stock solution, using buffered DI.

10.5.2 Initial Calibration Standards: Prepare a series of standards and a blank by pipetting suitable volumes of the Intermediate Standards Working Stock and buffered DI into a dispo cup.

The typical calibration for regular level (7199 and 218.6) is as follows:

Standard #	Volume (mL) of 10.0 mg/L Standard	Volume buffered DI (mL)	Final Concentration (mg/L)
6	1.00	9.0	1.00
5	0.70	9.3	0.70
4	0.50	9.5	0.50
3	0.10	9.9	0.10
2	1/10 of #3	-	0.01
1	0.0	10	0.000

10.5.3 Regular Level Intermediate Reference Working Stock (10 mg/L) - Do two 1/10 serial dilutions of the 1000 ppm reference stock solution, using buffered DI (as above).

10.5.4 Regular Level ICV/CCV (0.5 mg/L): In a 10mL dispo cup add 9.5 mL buffered DI (as above) and 0.5 mL Intermediate Reference Working Stock.

10.5.5 ICB / CCB / Method Blank / LRB (waters): DI preserved as a sample.

10.5.6 LCS - Regular Level Waters (0.20 mg/L): Add 0.20 mL of 10 mg/L Intermediate Standards Working Stock to 9.8 mL buffered DI. Analyze as a sample.

10.5.7 MS Regular Level Waters (0.2 mg/L): Add 0.20 mL of 10 mg/L Intermediate Standards Working Stock to 10 mL sample.

10.5.8 MB/LCS/MS Soils:prepared and digested according to GEN-3060A.

10.5.9 Post Verification Spike (PVS) – soil extracts only - after digestion, filtration, pH adjustment to 9.0-9.5, and dilution to 100 mLs (as described in GEN-3060), add 0.45 mL of 100 mg/L Cr(VI) standard stock solution to a 45 mL aliquot (this is equal to 40 mg/Kg) OR a concentration twice the original sample, whichever is higher.

10.6 Standards: 218.7 Prepare fresh before use.

10.6.1 1000 ug/L Standards Working Stock - Add 75 mL of DI to a 100 mL volumetric flask. To this add 1.0 mL Buffer Solution. Add 0.1 mL 1000 mg/L Cr(VI) Standard Stock Solution. Bring to volume with DI. Prepare fresh before use. Mix thoroughly.

10.6.2 100 ug/L Standards Working Stock - Add 75 mL of DI to a 100 mL volumetric flask. To this add 1.0 mL Buffer Solution. Add 10 mL 1000 ug/L Cr(VI) Standard Working Stock Solution. Bring to volume with DI. Prepare fresh before use. Mix thoroughly.

10.6.3 Initial calibration standards: For each standard, add 75 mL DI to a 100 mL volumetric flask. To this add 1/0 mL Buffer Solution. Then follow the recipe below:

Standard #	Volume (mL) of 1000 µg/L Standard	Final Volume with DI (mL)	Final Concentration (µg/L)
8	0.5	100	5.00
7	0.1	100	1.00
6	0.7 mL of 100 ug/L Std	100	0.70
5	0.5 mL of 100 ug/L Std	100	0.50
4	0.3 mL of 100 ug/L Std	100	0.30
3	0.1 mL of 100 ug/L Std	100	0.10
2	10 mL Std#4	100	0.030
1	10 mL Std#3	100	0.010

10.6.4 MS Spiking Stock (10 µg/L). Perform two 1/10 serial dilutions of the 1000 µg/L Standard Stock using DI.

10.6.5 1000 ug/L Reference Working Stock - Add 75 mL of DI to a 100 mL volumetric flask. To this add 1.0 mL Buffer Solution. Add 0.1 mL 1000 mg/L Cr(VI) Reference Stock Solution. Bring to volume with DI. Prepare fresh before use. Mix thoroughly.

10.6.6 ICV/CCVs:

10.6.6.1 Low Level (LL-CCV): 0.03 ug/L –

- o 100 ug/L Reference Working Stock - Add 75 mL of DI to a 100 mL volumetric flask. To this add 1.0 mL Buffer Solution. Add 10 mL 1000 ug/L Reference Stock Solution. Bring to volume with DI. Prepare fresh before use. Mix thoroughly.
- o 0.30 ug/L Reference Working Stock - To a 100 mL volumetric flask add about 75 mL DI. To this add 1.0 mL Buffer Solution and 0.3 mL of the 100 ug/L Reference stock. Bring to volume with DI. Prepare fresh before use. Mix thoroughly.
- o To a separate 100 mL volumetric flask, add about 75 mL DI. To this add 1.0 mL Buffer Solution and 10 mL of the 0.30 ug/L Reference Working Stock. Bring to volume with DI. Prepare fresh before use. Mix thoroughly.

10.6.6.2 Mid Level CCV (ML-CCV) / ICV: 2.5 ug/L – To a 100 mL volumetric flask, add about 50 mL DI. To this add 1.0 mL Buffer Solution and 0.25 mL of 1000 ug/L Reference stock. Bring to volume with DI and mix. Prepare fresh before use.

10.6.6.3 High Level CCV (HL-CCV): 4.0 ug/L - to a 100 mL volumetric flask, add about 50 mL DI. To this add 1.0 mL Buffer Solution and 0.4 mL of 1000 ug/L Reference. Bring to volume with DI and mix. Prepare fresh before use.

10.6.7 ICB / CCB / Method Blank / LRB (waters): In a 250 mL volumetric flask, add 2.5 mL liquid preservative to about 100 mL DI. Bring to volume with DI and transfer to a 250 mL HDPE sample bottle, received from SMO.

10.6.8 MS/LFSM - Add 0.20 mL of 10 µg/L Low Level LCS/MS Spiking Stock to 10 mL pH adjusted sample.

10.7 Standards: 218.6 Low Level –prepare fresh before use

10.7.1 1000 ug/L Standards Working and Reference Stocks – same as 218.7.

10.7.2 100 ug/L Standard Working Stock – make a 1/10 dilution of the 1000 ug/L Standard Working stock.

10.7.3 ICAL standards –

Standard #	Volume (mL) of 1000 µg/L Standard	Final Volume with buffered DI (mL)	Final Concentration (µg/L)
6	0.1	100	1.00
5	0.7 mL of 100 ug/L Std	100	0.70
4	0.5 mL of 100 ug/L Std	100	0.50
3	0.2 mL of 100 ug/L Std	100	0.20
2	10 mL of Std#6	100	0.10
1	10 mL Std#3	100	0.020
0	0	100	0

10.7.4 LCS/MS Spiking Stock (10 µg/L). Perform two 1/10 serial dilutions of the 1000 µg/L Standard Stock.

10.7.5 ICV/CCV (0.5 µg/L): To 5 mL buffered DI (as above) add 5 mL 1.0 µg/L Low Level Intermediate Reference Working Stock.

10.7.6 LCS (0.20 µg/L): Add 0.20 mL of 10 µg/L Low Level LCS/MS Spiking Stock to 9.8 mL buffered DI. Analyze as a sample.

10.7.7 Matrix Spike(0.20 µg/L): Add 0.20 mL of 10 µg/L Low Level LCS/MS Spiking Stock to 10 mL pH adjusted sample.

10.7.8 ICB/CCB/MB – same as 218.7

11) Method Calibration

11.1 Follow policies in ADM-ICAL unless otherwise specified in this SOP.

11.2 Initial Calibration

11.2.1 For New Jersey - Inject a calibration blank. Be sure this calibration blank is less than the MDL before continuing.

11.2.2 Number of Standards - Calibrate the instrument using the standards prepared as per the Standards and Reagents Section. Six or more standards must be used for 218.7. Three or more standards must be used for 218.6. A blank and three or more standards must be used for 7199. If a quadratic fit is to be used, analyze at least 6 standard levels plus blank.

11.2.3 Frequency – Initially and whenever continuing calibration verification criteria cannot be met.

11.2.4 Calibration Fit– Construct a calibration curve of analyte response (peak area) versus analyte concentration. The curve may be first order (y=mx+b), or second order (quadratic). Weighting may be used (1/x).

11.2.5 Limits –

11.2.5.1 For first order polynomial, the coefficient of correlation must be 0.999 or greater. File the printout of the linear regression with the ICAL.

11.2.5.2 For second order, mark the linear regression printout so that it is clear that the linear was for verification only. The accuracy of the quadratic calibration is verified by assessing the recovery of each standard. The recovery of each standard above the LOQ must be within 10% for 218.6 and 7199.

11.2.5.3 The LOQ standard must be within ±50% of the true value.

11.2.5.4 For 218.7, all standards above the LOQ must be within ±15% of the true value (regardless of curve type).

11.2.6 ICV(QCS) - Analyze an ICV immediately after the calibration standards. The ICV must be within limits to use the curve. The limits are 90-110% for 7199, 95-105% for 218.6, and 85-115% for 218.7. If the correctly prepared ICV is not compliant, the second source standard does not verify the curve. Fix the problem and recalibrate. If the ICV was prepared incorrectly, the curve may be used if a correctly prepared ICV verifies the curve.

11.3 Continuing Calibration Verification and Blank

11.3.1 Frequency - run a CCV and CCB set to start a daily run, every ten injections (or 24 hours, whichever is more frequent), and at the close of the run. For water samples, one blank counts as both the CCB and the MB. For 218.7, the CCV concentration varies (see attached Analytical Sequence and Standards and Reagents Section).

11.3.2 Limits –

Method	CCV % Recovery
7199	90-110
218.6	95-105
218.7	85-115
NIOSH 7605	85-115

Method	ICB/CCB/MB Limit
7199 7605	<MRL
7199 NJ	<MDL
218.6	<LOD
218.7	<0.01 ug/L
NIOSH 7605	<MRL

11.3.3 CCV Corrective Action - If a CCV fails, corrective actions must be performed. If routine corrective action fails to produce a second consecutive (immediate) acceptable CCV, then either the lab has to demonstrate acceptable performance after corrective action with two consecutive CCVs or a new ICAL must be performed.

11.3.4 Blank Corrective Action - Sample results greater than 10 times the result of the contaminated blank may be reported without qualification. Samples <10x blank contamination must be reanalyzed with a compliant blank whenever possible. If samples associated with a contaminated blank are not repeated (due to holding time restrictions, etc.), the data must be qualified on the report.

12) Sample Preparation and Analysis

12.1 Sample preparation.

12.1.1 Waters - Allow pH-adjusted samples to equilibrate to ambient temperature prior to analysis. Samples that have not been pH adjusted should be adjusted to pH 9-9.5 by dropwise addition of buffer solution. Record the pH adjustment and the pH meter ID on the benchsheet. If salts are formed as a result of the pH adjustment, the filtrate must be filtered again prior to analysis. pH range for 218.6 non-potable waters shall be 9.3-9.7 due to footnote 20 of EPA method update rule and FAQ-Cr6. All drinking waters are to be pH 9.0-9.5.

12.1.2 Soils – Digest according to GEN-3060A except pH adjust the sample to 9.0-9.5 instead of 7.5±0.5.

12.1.3 Air Filters – Prepare according to GEN-7605.

12.2 Establish Operating Conditions:

	IC #5	IC #8
Warm up	45-60 minutes	45-60 minutes
Eluent flow rate	1.0 mL/min	0.36 mL/min
Post-column flow rate	~0.33 mL/min	~0.12 mL/min
Column heater	30ºC	30ºC
Sample loop	2000 uL (LL) or 100 uL (RL)	1000 uL
Wavelength	530 nm	530 nm

Check flow rate of waste after the flow cell prior to calibration and sample analysis.

12.3 Sample Analysis.

12.3.1 Standards and samples are injected onto the column using an autosampler.

12.3.2 Color Interference - The guard column should be removing any inherent color in samples. If, however, a sample appears colored after elution through the columns, it is possible that not all sample color/organic material was removed and a false positive due to color could occur. At this point, pass a sample aliquot through Dionex ONGuard-P syringe filters and re-analyze. Alternatively, re-analyze a sample aliquot, but replace the post-column reagent with the matrix match reagent and subtract the matrix-match reagent result from the post-column reagent result.

12.3.3 Double Injection – 7199 requires that samples are injected twice (double injections are not required for 218.6 nor 218.7). The RPD between the samples must be less than 20 if the sample concentration is ≥ four times the reporting limit. A control limit of ± the reporting limit is used when the sample concentration is < four times the reporting limit. If it is impossible to meet holding times for both injections, it is best to inject samples once within holding time and make the second injection out of holding time. Report both results. Label the comments field R1, R2, R3, R4, etc.

12.4 Sample Evaluation –

12.4.1 Each chromatogram is reviewed for compliance and initialed by the reviewer. All chromatographic baselines should be examined by a knowledgeable analyst to ensure that proper integrations have been made by the analytical software. Especially for the low level analysis, care must be taken to ensure proper identification and integration of all low level peaks approaching a signal to noise ration of 3:1. When the data system incorrectly quantitates or identifies analytes, manual integration is necessary. Data must be integrated consistently between standards, samples, and QC. See CE-QA002 for integration requirements and manual integration documentation.

12.4.2 Samples or extracts exceeding the highest calibration standard (including PVS) must be diluted using buffered DI and re-analyzed.

12.4.3 Sample must be bound by acceptable analytical QC and from a batch with acceptable batch QC. Double injection must meets limits.

13) Troubleshooting

13.1 See Instrument manual or maintenance log for help with solving specific analytical or instrument problems.

13.2 Maintenance log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by laboratory staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

14) Data Acquisition

Data is uploaded electronically from the instrument to LIMS. As applicable, sample volumes, weights, and dilutions are entered to LIMS and final results are adjusted by LIMS accordingly. Calculations are presented in the following section.

15) Calculation and Data Reduction Requirements

15.1 Determine the concentration of the injected sample from the calibration curve.

15.1.1 For waters, multiply the injected concentration by dilution (use 1 if there is no dilution). Report in mg/L except report in µg/L for low level 218.6 and 218.7.

15.1.2 For digested soils:

$$\text{Concentration (mg/Kg dry wt.)} = \frac{A \times D \times E}{B \times C}$$

where:

A	=	Concentration observed in the digest (mg/L)
B	=	Initial moist sample weight (g)
C	=	% Solids/100
D	=	Dilution factor
E	=	Final digest volume (mL)

15.1.3 For air stips (NIOSH 7605) – see GEN-N7605.

15.2 Report both of the results from the double injection (if applicable).

15.3 For NJ - Data is “R” flagged if the MS is outside of 50-150%, if CCV or LCS is out of control, if calibration CC<0.999, if calibration blank >MDL, if PB >MDL for samples >MDL, if a water sample is run beyond 48 hours from sampling, if required QC is not performed, or if a soil sample is not redigested as required.

15.4 For NJ - Data is “J” flagged if the result is run between 24 and 48 hours from sampling (waters only), if QC is not performed at the correct frequency, if the MS is outside of limits but within 50-150%, if the RPD of a double injection or a DUP is greater than 20, if digested QC fails the initial and the redigestion, or if PDS <85%.

15.5 If samples are redigested, report as replicates. Both original and redigested data is reported.

15.6 All sample data and QC data, including calibration verification must reference the name (date or filename) of the ICAL on the raw data report. The current system lists the ICAL under the heading of "Quantif. Method" and the convention is to use the IC# and date in the name. For Example: "5-121610" is IC#5 on 12/16/10.

15.7 Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

16) Quality Control, Acceptance Limits and Corrective Action

16.1 ICV/CCV and ICB/CCB/MB requirements are in the Calibration Section.

16.2 For Water Samples

16.2.1 Matrix Spike –

16.2.1.1 Frequency - A minimum of one matrix spike sample per sample batch (1/10 for 218.6) must be analyzed to check for matrix interference.

16.2.1.2 Limits - The recovery of the matrix spike must be within limits in the Data Quality Objectives Table. For 218.7 – the MS must be within 15%.

Method	MS Limit
7199	DQO Table
7199 NJ	DQO Table
218.6	90-110
218.7	85-115

16.2.1.3 Corrective Action - If the matrix spike recovery fails these limits, report with appropriate qualifiers.

16.2.2 DUP/MSD

16.2.2.1 Frequency - A minimum of one duplicate sample per sample batch must be analyzed to check for precision. Alternatively, a Matrix Spike Duplicate may be used instead of a Duplicate. The MSD is required for UCMR3.

16.2.2.2 Limits:

	RPD	Other
7199	<20	+/-MRL if <4xMRL
218.6	<20	+/-MRL if <4xMRL
218.7	<15	NA

16.2.2.3 Corrective Action - If the RPD is out of limits, repeat the sample and duplicate unless there is assignable matrix interference, historical failures, or lack of volume. If an out of control duplicate is not repeated, note the reason on the data quality checklist. If, at the time when the problem is discovered, the sample exceeds twice the holding time, discuss with supervisor or Project Manager prior to repeating the samples. Report all of the replicates and explain in the checklist for the case narrative.

16.2.3 LCS -

16.2.3.1 Frequency –An LCS must be analyzed with every batch for 7199 and 218.6. An LCS is not required for 218.7 (performance measured with CCV). See GEN-N7605 for air strips.

16.2.3.2 Limits –

Method	Limits
7199	DQO Table
218.6	90-110%
218.7	NA

16.2.3.3 Corrective Action - If the LCS fails these limits, correct the problem and reanalyze the affected samples or flag the associated data.

16.3 For Samples Digested by GEN-3060A – see also the attached flowchart. Undigested QC (LCS, MB, DUP, MS) is not required to be analyzed with the digested QC in a 7199 run which only has digested samples.

16.3.1 MB - A preparation blank must be prepared and analyzed with each digestion batch. Detected Cr(VI) concentrations must be less than the reporting limit (less than the MDL for New Jersey) or the batch must be redigested and reanalyzed. If the samples are out of holding time, redigest and reanalyze and both sets of data will be reported. If insufficient sample volume necessitate the use the data, flag the data associated with the non-compliant PB (the entire preparation batch – not just those in the analytical batch).

16.3.2 LCS Insoluble – An insoluble LCS must be prepared and analyzed with each digestion batch. Recovery must be within 80-120% or the entire sample batch must be redigested and reanalyzed. If the samples are out of holding time, redigest and reanalyze and both sets of data will be reported. If insufficient sample volume necessitate the use the data, flag the data associated with the non-compliant LCS (the entire preparation batch – not just those in the analytical batch)

16.3.3 DUP - A separately prepared duplicate soil sample must be analyzed at a frequency of one per batch. Duplicate samples must have a Relative Percent Difference (RPD) of ≤ 20%, if the sample concentration is ≥ four times the reporting limit. A control limit of ± the reporting limit is used when the sample concentration is < four times the reporting limit. If the RPD of the duplicates is out of limits, repeat the sample and duplicate unless there is assignable matrix interference, historical failures, or lack of volume. If an out of control duplicate is not repeated, note the reason on the data quality checklist. If, at the time when the problem is discovered, the sample exceeds twice the holding time, discuss with supervisor or Project Manager prior to repeating the samples. Report all of the replicates and explain in the checklist for the case narrative.

16.3.4 MS- Both soluble an insoluble digested matrix spikes must be analyzed at a frequency of one each per batch. Both matrix spike recoveries must be within 75-125% of the true value. If either of the matrix spike recoveries are not within these recovery limits the entire batch must be redigested and reanalyzed. If the reanalysis also fails the 75-125% limit, sample data is flagged. Exception – if the sample concentration is greater than 4 times the spike concentration, the spike is “diluted out” and is not used to evaluate the batch (redigestion is not required). The client should be notified of the possible condition of the sample and further investigation is needed using the oxidation/reduction parameters discussed in 4.1. If the samples are out of holding time for the reanalysis, redigest and reanalyze and both sets of data will be reported. If insufficient sample volume necessitate the use the data, flag the data associated with the non-compliant LCS (the entire preparation batch – not just those in the analytical batch).

16.3.5 A post-digestion Cr(VI) matrix spike must be analyzed per batch, whether or not the MS passed or failed. Use the attached PVS Calculation sheet. The criteria for the post digestion matrix spike recovery is 85-115% recovery. If spike recovery is outside limits, and the matrix spike also failed, no further action is needed apart from the corrective action for the MS. The corrective actions will show whether these digestates may contain soluble reducing agents for Cr(VI). If the PVS fails and the MS passes, reanalyze the PVS.

17) Data Records Management

See CE-GEN003 and ADM-ARCH

18) Contingencies for Handling Out of Control Data

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, data is flagged with the appropriate data qualifiers.

19) Method Performance

19.1 Reporting limits are based upon an MDL study performed according to CE-QA011 and filed in the MDL binders in the QA office.

19.2 Demonstration of Capability is performed according to CE-QA003.

19.3 From the EPA Method 7199:

- Single Laboratory Precision and Accuracy is available in Table 3
- Single Analyst Precision, overall precision and Recovery from Multilaboratory Study is available in Table 4.

20) Summary of Changes

- Added NIOSH 7605 throughout.
- Removed IC-5
- Updated to current ALS format.

21) References and Related Documents

- Test Methods for Evaluating Solid Waste Physical/Chemical Methods, USEPA SW-846.
- NJDEP Standard Operating Procedure (SOP No.5.A.10) Dated August 15, 2005: Standard Operating Procedure for Analytical Data Validation of Hexavalent Chromium.
- Methods for the Determination of Metals in Environmental Samples, Supplement I. EPA/600/R-94/111. May 1994. Method 218.6 revision 3.3.
- Method 218.7: Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatization and UV-Visible Spectroscopic Detection. EPA Document Number EPA 815-R-11-005. Version 1.0, November 2011.
- NIOSH Manual of Analytical Methods, Fourth Edition, Method 7605 Issue 1, March 15, 2003.

22) Attachments

- Table 3 Single Laboratory Precision and Accuracy
- QC Flowchart
- PVS Calculation Sheet
- PH Adjustment Sheet – controlled separately on the Controlled Forms section of the Rochester Intranet.
- eH/pH diagram
- Analytical Sequence

TABLE 3
SINGLE-LABORATORY PRECISION AND ACCURACY

Sample Type	Cr(VI) (μg/L)[a]	Percent Mean Recovery	RPD[b]
Reagent Water	100	100	0.8
	1000	100	0.0
Drinking Water	100	105	6.7
	1000	98	1.5
Ground Water	100	98	0.0
	1000	96	0.8
Primary Sewage	100	100	0.7
Wastewater	1000	104	2.7
Electroplating	100	99	0.4
Wastewater	1000	101	0.4

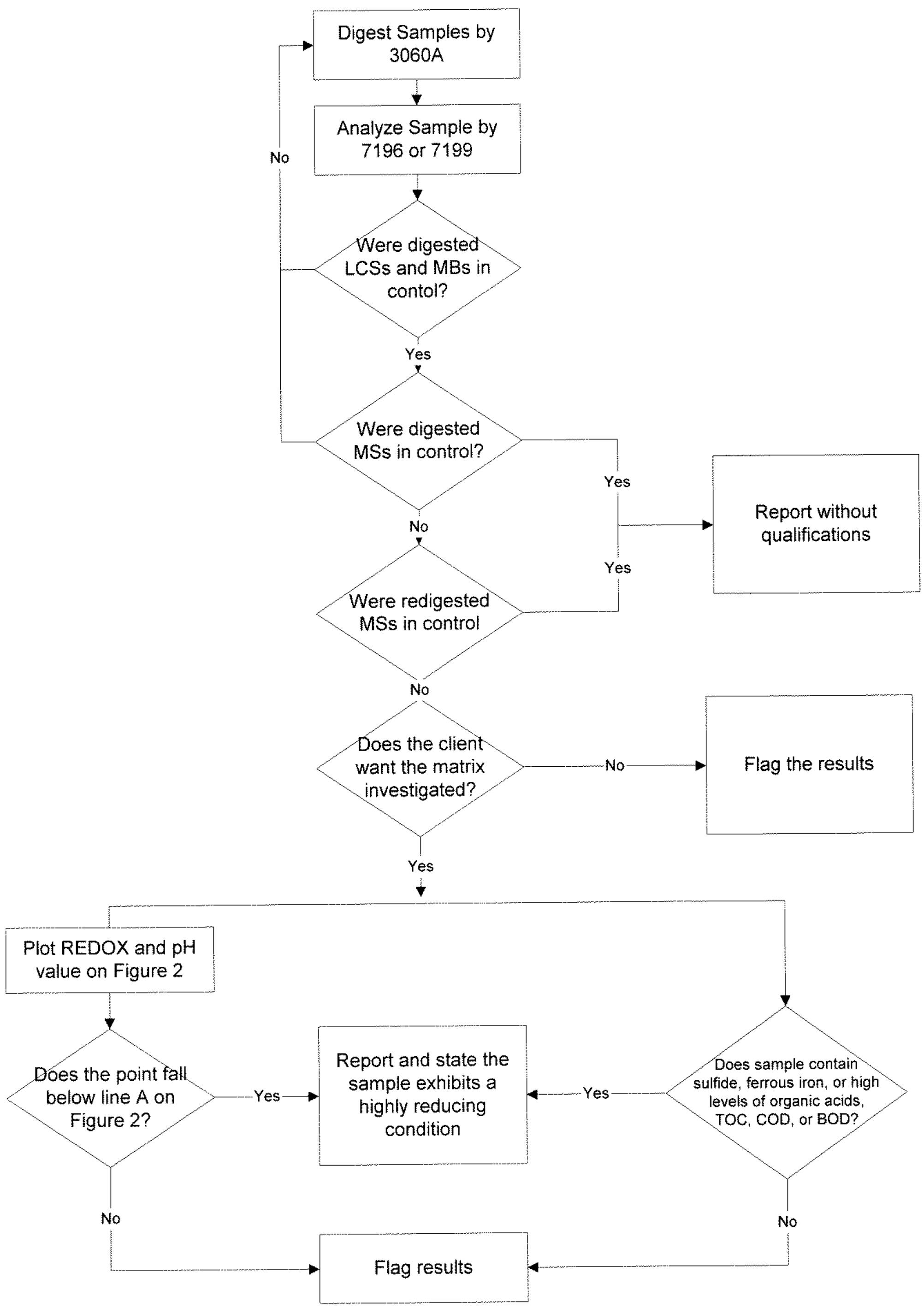
[a] Sample spiked at this concentration level.
[b] RPD - relative percent difference between duplicates.

TABLE 4
SINGLE-ANALYST PRECISION, OVERALL PRECISION AND RECOVERY
FROM MULTILABORATORY STUDY

	Reagent Water (6-960 μg/L)	Matrix Water (6-960 μg/L)
Mean Recovery	X = 1.020C + 0.592	X = 0.989C - 0.411
Overall Standard Deviation	S_R= 0.035X + 0.893	S_R= 0.059X + 1.055
Single-Analyst Standard-Deviation	S_R= 0.021X + 0.375	S_R= 0.041X + 0.393

X = Mean concentration; μg/L, exclusive of outliers.
C = True value, μg/L.
S_R= Overall standard deviation.
S_R= Single-Analyst standard deviation.

HEXAVALENT CHROMIUM QUALITY CONTROL FLOW CHART



Columbia Analytical Services
1 Mustard St., Suite 250
Rochester, NY 14609-0859

Analyst: ____________________
Date: ____________________
Pipet ID: ____________________

Hexavalent Chromium

Method: ________EPA 7196A, Manual Colorimetric
________ 7199, IC
________218.6, IC

Post-Verification Spike (PVS) Calculations

$$\text{True Value} = \frac{A \times B}{C}$$

Note: Calculations based on sample result and PVS expressed in mg/L before dilution or digest factors

Order #	Original Result mg/L on curve	Vol. (mL) of Spk Added (A)	Conc. (mg/L) of Spk Sol'n (B)	Digestate Vol. (mL) spk'd (C)	PVS True Value (mg/L)	Spike Result (mg/L)	Percent Recovery

Date/Time Received	Sample ID	Analysis	Matrix	Date/Time Sampled	Sample Filtered	Filter Lot ID	Chlorine Residual (mg/L) 218.7 only	pH at Receipt	pH Adjustment	Analyst/ Date/ Time pH Adjustment	Solution Used For PH Adjust	Solution Lot ID
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	
		7199 218.6 RL 218.6 LL 218.7	Water Drinking Water		Yes No Field						Buffer 10%H2SO4 10%NH4OH NH4OH(conc)	

	Drinking water 218.7	Drinking water 218.6	Non-Pot Water 218.6	Water 7199
Filter	No	Required	Required	Optional
pH	>8.0	9.0-9.5	9.3-9.7	unpreserved - adjust to 9.0-9.5
Res Chlorine	<0.1 mg/L	NA	NA	NA
Holding Time	14 days	5 days	28 days	24 hours

P:\INTRANET\QAQC\Forms Controlled\SMO Cr6+ preservation log r1
SMO Cr6+ preservation log r1 1/10/13

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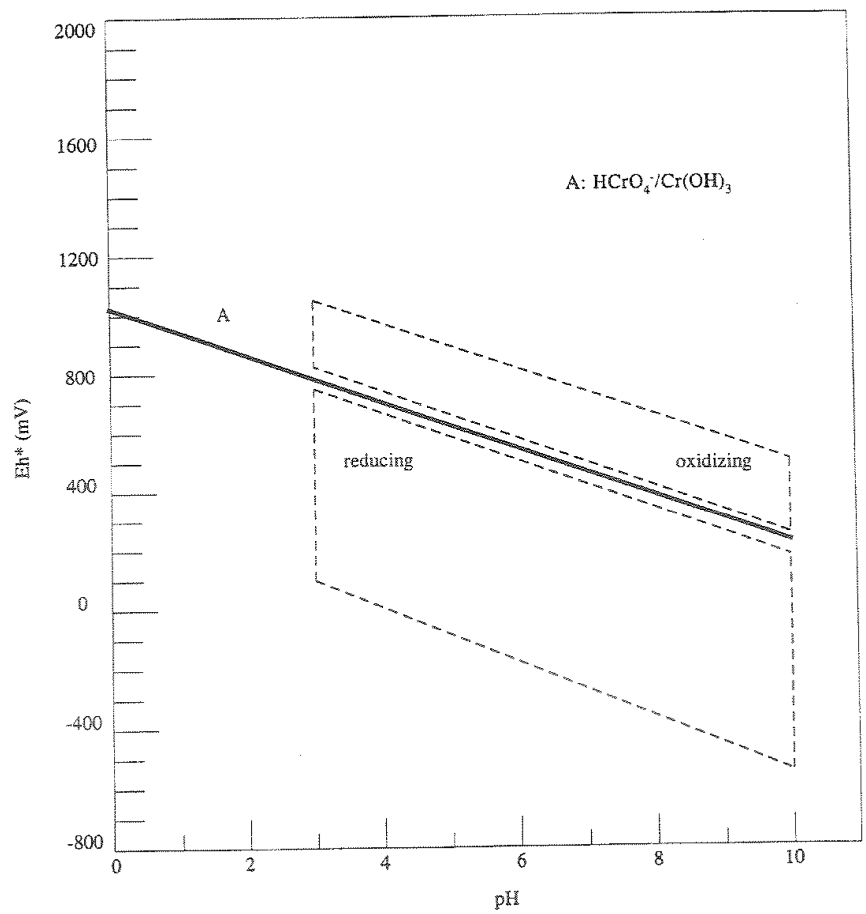
FIGURE 2
Eh/pH PHASE DIAGRAM

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

Analytical Sequence for Method 218.7

Injection Number	Sample ID
1	Calibration Standard 1
2	Calibration Standard 2
3	Calibration Standard 3
4	Calibration Standard 4
5	Calibration Standard 5
6	Calibration Standard 6
7	Calibration Standard 7
8	LL-CCV
9	CCB
10	Analytical Sample 1
11	Analytical Sample 2
12	Analytical Sample 3
13	Analytical Sample 4
14	Analytical Sample 5
15	Analytical Sample 6
16	Analytical Sample 7
17	Analytical Sample 8
18	Analytical Sample 8 Spike
19	Analytical Sample 8 Spike Dup
20	ML-CCV
21	CCB

Injection Number	Sample ID
22	Analytical Sample 9
23	Analytical Sample 10
24	Analytical Sample 11
25	Analytical Sample 12
26	Analytical Sample 13
27	Analytical Sample 14
28	Analytical Sample 15
29	Analytical Sample 16
30	Analytical Sample 16 Spike
31	Analytical Sample 16 Spike Dup
32	HL-CCV
33	CCB
34	Analytical Sample 17
35	Analytical Sample 18
36	Analytical Sample 19
37	Analytical Sample 20
38	Analytical Sample 20 Spike
39	Analytical Sample 20 Spike Dup
40	ML-CCV
41	CCB

ALS Environmental

DOCUMENT TITLE:	ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM IN SOIL
REFERENCED METHOD:	SW846 3060A
SOP ID:	GEN-3060
REV. NUMBER:	3
EFFECTIVE DATE:	3/1/2013

ALS

ALKALINE DIGESTION FOR HEXAVALENT CHROMIUM IN SOIL

SOPID:	GEN-3060	Rev. Number:	3	Effective Date:	3/1/2013

Approved By: [signature] Date: 2/13/13
Department Supervisor – Christine Kutzer

Approved By: [signature] Date: 2/15/2013
QA Manager – Lisa Reyes

Approved By: [signature] Date: 2/15/13
Technical Director – Michael Perry

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1) Scope and Applicability

1.1 This SOP uses USEPA Method 3060A for extracting hexavalent chromium [Cr(VI)] from soluble, adsorbed, and precipitated forms of chromium compounds in soil, sludge, sediment, and some industrial waste materials. To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied: (1) the extracting solution must solubilize all forms of Cr(VI), (2) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III), and (3) the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI).

1.2 The quantification of Cr(VI) in the digestates produced by this SOP is performed using Method 7196A (See GEN-7196A) or Method 7199 (see GEN-7199).

1.3 The reporting limits are listed in the analytical SOPs.

2) Summary of Procedure

2.1 This procedure is an alkaline digestion to solubilize Cr(VI) compounds in solid samples. The pH of the digestate must be carefully adjusted during the digestion procedure. Failure to meet the pH specifications will necessitate redigestion of the samples. The sample is digested using a Na_2CO_3/NaOH solution and heated to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

2.2 Analysis of Cr(VI) solubilized in the alkaline digestate is accomplished by reaction with diphenylcarbohydrazide (Method 7196A or 7199). It is highly selective for Cr(VI), and few interferences are encountered when it is used on alkaline digestates.

3) Definitions

3.1 Soluble Matrix Spike (MS-Sol) - In the soluble matrix spike analysis, a predetermined quantity of a soluble standard solution of the analyte is added to a sample matrix prior to sample digestion and analysis. The purpose of the soluble matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recovery is calculated for the analyte detected.

3.2 Insoluble Matrix Spike (MS-Insol) - In the insoluble matrix spike analysis, a predetermined quantity of an insoluble standard of the analyte is added to a sample matrix prior to sample digestion and analysis. The purpose of the insoluble matrix spike is to evaluate the dissolution during the digestion process and effects of the sample matrix on the dissolution. Percent recovery is calculated for the analyte detected.

3.3 Duplicate Sample (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4 Method Blank (MB) - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

3.5 Insoluble Laboratory Control Sample (LCS-Insol) – In the LCS-Insol analysis, a predetermined quantity of an insoluble standard solution is added to a blank prior to sample digestion and analysis. Percent recovery is calculated for the analyte detected.

3.6 Post Verification Spike (PVS) – A predetermined quantity of standard solution is added to a sample matrix after digestion and after the sample is pH adjusted and brought up to 100 mLs. Percent recoveries are calculated for the analyte added. This is described in the analytical procedures.

3.7 Preparation Batch - Samples digested together as a unit, not to exceed 20 samples. The Digested QC samples are associated with the preparation batch and may be analyzed in separate analytical batches. See ADM-BATCH for further discussion.

4) Responsibilities

4.1 It is the responsibility of the Project Manager to obtain information from the client before sampling. The laboratory needs to know whether the client will require additional investigation of the sample matrix in the case of matrix spike failures. A reducing condition in the sample matrix will reduce Cr(VI) to Cr(III) causing low bias. Additional parameters – sulfide, pH, REDOX, ferrous irons, BOD, COD, TOC may be used to demonstrate a reducing condition in the sample matrix. If any or all of these parameters are to be analyzed, additional aliquots are to be sampled and the tests are to be scheduled when hexavalent chromium is scheduled due to holding time limitations. It is the responsibility of the Project Manager to appropriately flag the data and make notes in the case narrative about the nature of the matrix, if applicable (see the attached flowchart).

4.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

5) Interferences

5.1 A reducing tendency of the sample matrix may change Cr (VI) to Cr(III). The reducing/oxidizing tendency of each sample may be characterized using additional analytical parameters, such as pH, ferrous iron, sulfides, and oxidation/reduction potential. Other indirect indicators of reducing/oxidizing tendency include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), and Biochemical Oxygen Demand (BOD). Analysis of these additional parameters establishes the tendency of Cr(VI) to exist in the unspiked sample(s) and may be necessary to assist in the interpretation of QC data for matrix spike recoveries outside conventionally accepted criteria.

5.2 Substances not typically found in the alkaline digests of soils may interfere in the analytical techniques for Cr(VI) following alkaline extraction if the concentration of these interferences are high relative to the Cr(VI) concentration. Refer to EPA methods 7196A and 7199 for a discussion of the specific agents that interfere with Cr(VI) quantification.

5.3 For materials suspected of containing high concentrations (greater than four times the laboratory Cr(VI) reporting limit) of soluble Cr(III), Cr(VI) results obtained using Method 3060A may be biased high due to method induced oxidation. The addition of Mg^{2+}, and a phosphate buffer, to the alkaline extraction solution has been shown to suppress oxidation.

5.4 One of the most insoluble forms of chromate in alkaline solution, barium chromate, may require additional heating time to affect complete dissolution in some soil matrices.

5.5 Reduction of Cr(VI) to Cr(III) can occur in an acidic medium. However, at a pH of 6.5 or greater, CrO42- (which is less reactive than the HCrO4-) is the predominant species.

6) Safety

- All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.
- Chemicals, reagents and standards must be handled as described in the company safety policies, approved methods and in MSDSs where available. Refer to the Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.
- Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.
- Nitric and sulfuric acids are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.
- Refer to the Safety Manual for further discussion of general safety procedures and information.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Samples should be collected using devices that do not contain stainless steel. Sample containers provide by the lab are purchased, pre-cleaned, certified 8 oz. wide mouth clear glass jars with Teflon lined lids. The client must provide additional aliquots of sample if further investigation into the reducing/oxidizing nature of the sample is to be done.

7.2 Samples should be stored at 0-6˚C until analysis.

7.3 If investigation is requested, the investigative tests (such as sulfide, pH, REDOX and Fe2+) must be scheduled with the Cr6+ test because some of the investigative test have shorter holding times than hexavalent chromium. These tests must be completed prior to the evaluation of the Cr6+ QC so that the results are available if needed.

7.4 Holding Times

7.4.1 Samples may be held for 30 days from collection to digestion.

7.4.2 7199: Once the samples have been digested, they may be held overnight in tightly capped B-cups in the cooler at 0-6 °C. Holding the samples overnight facilitates settling and subsequent filtering. Samples must be filtered, pH adjusted, and analyzed within 7 days of digestion.

7.4.3 7196A - Once the extracts are pH adjusted to 7.5 ± 0.5, samples are required to be analyzed within 1-hour. Samples must be filtered, pH adjusted, and analyzed within 7 days of digestion.

7.5 For further sample handling, storage and custody procedures, see SMO-GEN and SMO-ICOC.

8) Apparatus and Equipment

8.1 Glassware: Beakers (150 mL), watch glass covers, graduated cylinders (50 mL), volumetric flasks (Class A, 1000 mL), rinsed with 50/50 Nitric Acid.

8.2 Filtration apparatus and filter membranes (0.45, μm), preferably cellulosic or polycarbonate membranes.

8.3 Hot block – Environmental Express SC154 (SN7021CECW3005) – with Stirbase and controller. Capable of maintaining the digesting samples at 90-95°C, and Teflon coated stir bars. The temperature of the sample is monitored as described in the procedure. This is the primary equipment used.

8.4 Stirring hot plates, capable of maintaining the digesting samples at 90-95°C, and Teflon coated stir bars. The hot plates currently in use are all single - place stirring. Plates are to be studied and the position marked on the temperature control dial where the dial should be adjusted to maintain 90-95 °C. The temperature of the sample is monitored as described in the procedure. The manufacturers of the hot plates are VWR, Thermolyne and Corning.

8.5 pH meter: Orion Model 720A and/or Orion Model SA520 with Thermo-Orion combination pH electrodes. Meters are to be calibrated and used according to ADM-pHSupport.

8.6 Balances: Top-Loading – American Scientific products Model DTL 2500g; Analytical – Mettler AE240. Calibrated according to ADM-DALYCK.

8.7 Thermometers – calibrated according to ADM-DALYCK.

8.8 B-cups - 130 mL plastic beakers.

8.9 Micropipettes – Eppendorf 100-1000 uL and 10-100 uL. Calibrated according to ADM-PCAL. IDs of pipettes used during analysis are documented on the digestion and analysis benchsheets so that pipettes can be traced back to pipette calibration logs.

8.10 Computer Hardware and Software – Any computer in the lab which is connected to the LAN and has access to the LIMS and the Excel benchsheet.

9) Standards, Reagents, and Consumable Materials

9.1 All Standards must be traceable using the laboratory lot system (CE-QA007). All purchased standards are certified by the vendor. Certificates of Analysis are kept in the department until the standards are no longer being used – at which time they are filed with QA. Certificates of Analysis are available upon request. Purchased standards are routinely checked against an independent source for analyte concentration.

9.2 Purchased Reagents and Standards – Store at room temperature and expire per the Expiration Policy unless otherwise indicated.

9.2.1 Nitric acid: HNO_3, concentrated, analytical reagent grade or spectrograde quality. Store in the dark. Expires sooner than assigned date if the solution develops a yellow color.

9.2.2 Sodium carbonate: Na_2CO_3, anhydrous, analytical reagent grade.

9.2.3 Sodium hydroxide pellets: NaOH, analytical reagent grade.

9.2.4 Magnesium Chloride: $MgCl_2$ (anhydrous), analytical reagent grade. 392.18 mg $MgCl_2$ is equivalent to 100 mg Mg^{2+}.

9.2.5 K_2HPO_4: Analytical reagent grade.

9.2.6 KH_2PO_4: analytical reagent grade.

9.2.7 Sulfuric acid (H_2SO_4), concentrated, reagent grade.

9.2.8 Cr (VI) standard solution (1000 mg/L): purchased commercially - certified primary standard solution.

9.2.9 Cr (VI) reference solution (1000 mg/L): purchased commercially - certified primary standard solution from a separate source as the standard solution.

9.2.10 Lead Chromate, ($PbCrO_4$), powder

9.3 Prepared Reagents – Store at 0-6 °C and expire per the Expiration Policy unless otherwise indicated.

9.3.1 Phosphate Buffer - 0.5M K_2HPO_4/0.5M KH_2PO_4 buffer at pH 7 (also called 1M Phosphate buffer): Dissolve 87.09 g K_2HPO_4 and 68.04 g KH_2PO_4 into 700 mL of DI. Transfer to a 1L volumetric flask and dilute to volume.

9.3.2 Digestion solution: Dissolve 20.0 ± 0.05 g NaOH pellets and 30.0 ± 0.05 g Na_2CO_3 in DI in a one-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle. The pH of the digestion solution must be checked before using. Expires in 1 month or if the pH is not 11.5 or greater.

9.3.3 10% Sulfuric acid (v/v) (1.8M): Add 10 mL of concentrated H_2SO_4 to approximately 70 mL of DI. Mix well and let cool. Dilute to a final volume of 100 mL with DI.

9.3.4 50/50 Nitric acid wash solution: Slowly and carefully combine 1 part concentrated Nitric Acid with 1 part DI.

9.4 Prepared Standards – Prepare fresh daily.

9.4.1 Cr (VI) intermediate standard solution (100 mg/L): dilute 1.00 mL of 1000 mg/L standard solution to 10.0 mL with DI.

9.4.2 Cr (VI) intermediate reference solution (100 mg/L): dilute 1.00 mL of 1000 mg/L reference solution to 10.0 mL with DI.

9.4.3 Calibration Standards for 7196A:

Conc. (mg/L)	Vol. 100 mg/L stock (mLs)	Volume of digest solution	Final Volume (mL)
2.0	2.00	50	100
1.5	1.50	50	100
1.0	1.00	50	100
0.5	0.50	50	100
0.1	0.10	50	100
0.0	0.00	50	100

7196A standards are adjusted to a pH of 7.5 +/- 0.5 with concentrated nitric acid before they are brought to a final volume of 100 mLs with DI. Must be analyzed within 1 hour after pH adjustment.

9.4.4 Calibration Standards for 7199 – as described in the 7199 SOP. These standards do not undergo these procedures. They are made with buffered DI (pH 9.0-9.5).

9.4.5 ICV/CCV for 7196A (1.0 mg/L): add 1.0 mL 100 mg/L reference solution to 50 mL digest solution. Adjust pH to 7.0 - 8.0 with concentrated nitric acid. Bring to 100 mL with DI. Must be analyzed within 1 hour after pH adjustment.

9.4.6 ICV/CCV for 7199- as described in the 7199 SOP. This standard does not undergo these procedures. It is made with buffered DI (pH 9.0-9.5).

9.5 Soluble MS (1.0 mg/L or 40 mg/Kg): add 1.0 mL 100 mg/L standard solution to sample or blank (Ottawa sand) and 50 mL digest solution. Sample is digested, filtered, and completed as a sample including pH and volume adjustment.

9.6 Insoluble LCS – Add approximately 10 mg PbCrO4 to 50 mLs digest solution. Digest and analyze as a sample. The true value will depend on the amount used. Lead chromate is 0.161% chrome. The 0.0025 is as if it was spiked into 2.5 g sample weight.

$$TrueValue(mg/kg) = \frac{mgPbCrO_4}{0.0025} \times 0.161\%$$

9.7 Insoluble MS - Add 10 mg PbCrO4 to sample. Digest and analyze. Calculate true value as above.

9.8 PVS – described in the analytical SOPs since it is not done during digestion.

9.9 Method Blank – Analyze Ottawa Sand as a sample.

10) Preventive Maintenance

10.1 Inspect thermometers before use. Be sure the liquid column is not separated.

10.2 Be sure glassware is scrupulously cleaned according to GEN-GC.

10.3 Inspect the pH probe for cracks or scratches. Replace the filling solution weekly.

10.4 Troubleshooting – see the manual of the pH meter for specific problems regarding the pH meter.

11) Procedure

11.1 Be sure the analyst has a current Demonstration of Capability and the system has current detection and quantitation studies.

11.2 Print a Responsibility Report from LIMS to determine what samples are available to be run. Prioritize samples to be run based on holding time and due dates. Scan the samples to be analyzed out of storage according to SMO-ICOC. Plan the digestion batch according to ADM-BATCH and the frequency requirements in section 12 of this SOP.

11.3 Heated Digestion

11.3.1 Homogenize and subsample according to ADM-SPLPREP. Place 2.5 ± 0.10 g of the sample into a clean and labeled beaker (for digestion using hot plates) or a labeled digestion vessel (for digestion using stirring hot block). Record the actual weight. Document the ID of the balance used to weigh the sample.

11.3.2 Spike LCSs and MSs (soluble and insoluble) at this time as described in Section 9 and at the frequency in Section 12. Document the spikes added on the benchsheet. Record the ID of the pipette used for spiking.

11.3.3 Measure the pH of the digestion solution with a pH meter. It must be 11.5 or greater to be used. If it is not, discard the solution and make fresh. Record the pH of the solution and the ID of the pH meter on the benchsheet. Add 50 mL of digestion solution to each sample, blank, MS and LCS.

11.3.4 Add approximately 400 mg magnesium chloride and 0.5 mL of phosphate buffer to each sample.

11.3.5 Add the appropriate stir bar to each sample.

11.3.6 Mix each sample thoroughly before placing the beaker on the hotplate.

11.3.6.1 For digestion using hot plates - Turn on the heat to the previously calibrated setting. Place the beakers on the hotplates. Turn on the stirrer. Maintain a temperature range of 90 - 95˚C for 60-65 minutes with constant stirring. Record the start time of the digestion. Check the digestion solution temperature of each sample at 0, 30 and 60 minutes using a calibrated alcohol thermometer placed directly in the digestion beaker so that the thermometer is in the beaker spout and the watch glass is placed over the entire beaker. Record the temperature on the benchsheet. Record the end time of the digestion.

11.3.6.2 For digestion using stirring hot block - Turn on the heat to the previously calibrated setting. For this Environmental Express brand hot block it has been determined that a set point temperature of 112˚C provides the proper temperature for samples to be between 90 - 95˚C. Place the digestion vessels in the hot block. Turn on the stirrer. Maintain a temperature range of 90 - 95˚C for 60-65 minutes with constant stirring. Record the start time of the digestion. Check the digestion solution temperature of each sample at 0, 30 and 60 minutes using a calibrated alcohol thermometer placed directly in the digestion vessel. Plastic thermometer holders (purchased from Environmental Express) can be used to suspend the thermometer in the solution. Record the temperature on the benchsheet. Record the end time of the digestion.

11.3.7 Gradually cool each solution to room temperature. Transfer to b-cups (if digested in beakers), cap, and place in the cooler overnight to allow settling and aid filtration.

11.4 Filtration

11.4.1 Using a 0.45 µm membrane filter, follow the assembly and use procedure for the vacuum filter funnels in GEN-FILTER. Document the filter brand, type, and pore size on the benchsheet. Transfer the digested sample quantitatively to the vacuum filtration apparatus with DI rinses. Rinse the inside of the filter flask and filter pad with DI. Transfer the filtrate and the rinses to a clean, labeled 130-mL B-cup. Record the color of the filtrate on the benchsheet. Cap the cup.

11.4.2 If analysis is not to immediately follow, place the filtered samples in the cooler (0-6°C) and store for up to 7 days (from day of digestion) unless the client has other requirements. On the day of analysis remove the samples from the cooler and allow to warm to room temperature. Continue.

11.5 Standards Preparation

11.5.1 For 7196A - Prepare the standards and references in B-cups. Record the pipettes used. Standards must be prepared and analyzed with each daily run. They do not need to be digested, but they do need the next 2 steps (pH adjustment and dilution).

11.5.2 For 7199 - standards will be prepared by the 7199 analyst with buffered DI and will not need to be pH adjusted and diluted.

11.6 PH adjustment – record the ID of the pH meter on the benchsheet

11.6.1 For analysis by 7199 - With constant stirring, slowly add concentrated sulfuric acid solution to the beaker dropwise. Adjust the pH of the solution to 9.0-9.5 and monitor the pH with a calibrated pH meter. The buffering capacity of the digestion solution is high, so the first 50 drops of acid will bring the pH down to only about 9.5 to 10.0. Record the pH and the date of adjustment on the bench sheet.

11.6.2 For analysis by 7196A - With constant stirring, slowly add concentrated nitric acid solution to the beaker dropwise. Adjust the pH of the solution to 7.5 ± 0.5 and monitor the pH with a calibrated pH meter. The buffering capacity of the digestion solution is high, so the first 50 drops of acid will bring the pH down to only about 9.5 to 10.0. Go very slowly once the pH reaches about 8.5; at that point it will require only a few drops to go to a pH of 7.5 ± 0.5 - the analyst may wish to switch to 1:1 nitric acid at this point to complete adjustment. If the pH of the digest should drop below 7.0, discard the solution and redigest, and adjust the pH with a dilute nitric acid solution. Record the pH and the date of adjustment on the bench sheet.

Note: The pH adjustment and subsequent steps is time consuming. A single analyst should only adjust about 10 digested samples and complete the colorimetry before adjusting more digested samples. This ensures the samples are analyzed within 1 hour of adjustment. Additional analysts speeds the process and production can be adjusted accordingly.

CAUTION: CO2 will be evolved. This step should be performed in a fume hood.

11.7 Volume Adjustment – Transfer the sample to a graduated cylinder. Adjust the sample volume to 100 mL with DI. Transfer back to the same b-cup. Cap and mix well. This applies to 7196A and 7199 samples and digested QC samples.

11.8 Quantitative Analysis - The sample digestates are now ready to be analyzed. Determine the Cr(VI) concentration in mg/kg by Method 7196A (GEN-7196A) or Method 7199 (GEN-7199). For 7196A, be sure to analyze samples within 1 hour of the time that they are adjusted to a pH of 7.5 + 0.5.

12) Quality Assurance/Quality Control Requirements

12.1 Frequency – One of each of the following are required to be digested with each preparatory batch: MB, LCS (insoluble), DUP, MS (soluble), MS (insoluble).

12.2 Acceptance and corrective action are given in the analytical SOPs.

12.3 As per EPA Method 3060A, if there are QC failures, the entire batch may need re-extracted and reanalyzed. See the analytical SOPs for further details.

13) Data Reduction and Reporting

13.1 A Copy of the digestion bench sheet is attached.

13.2 Calculations are given in the analytical SOPs.

13.3 Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

14) Method Performance

Single Laboratory Method Evaluation Data from the EPA Method is available in Table 1.

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

Demonstration of Capability is performed upon instrument set-up , whenever a new analyst begins independent analysis, and annually thereafter according to Section 18 below. The documentation of this method performance is retained by the Quality Assurance office.

15) Waste Management and Pollution Prevention

- Hexavalent chromium solutions should be dumped in the red inorganic carboys which will later be emptied by qualified personnel. All other waste can be flushed down the drain with large amounts of water. See SMO-SPLDIS for further information.
- It is the laboratory's practice to minimize the amount of acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when disposed of properly.
- The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the EH&S Manual.

16) Corrective Action for Out-of-Control Data

Failure to meet established analytical controls, such as the quality control objectives, prompts corrective action. A QC Flowchart provided in the analytical SOPs describes the corrective actions for out of control QC.

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

If a quality control measure is found to be out of control, and the data is to be reported, all samples associated with the failed quality control measure shall be reported with the appropriate data qualifier(s).

18) Training

18.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow Training Policies in the SOP for Training (CE-QA003).

18.2 Observe Sample Preparation and Analysis. Follow Training Plan Form.

18.3 Participate in the methodology, documentation, and data reduction with guidance.

18.4 Perform the analysis independently and show Initial Demonstration of Capability (IDC) by analyzing 4 replicates of a known mid-range standard in succession before client samples are analyzed. If recovery is within acceptable limits, complete IDC certificate and Training Plan Form and file with QA. Continuing Demonstration of Capability (CDC) will be demonstrated annually using a PE sample, single blind, or a new 4 replicate study. Demonstrate Competency by performing the analysis independently.

19) Method Modifications

The method says to mix the sample 5 minutes on the hotplate before turning on the heat. Instead, the lab mixes the sample thoroughly with the reagents before placing the sample beaker on the pre-heated hotplate. This modification reduces the amount of time spent with samples on the hotplates and increases the number of samples which may be analyzed in a day without affecting the quality of the analysis.

20) Summary of Changes

- Updated to ALS format – removed CAS throughout.
- Added information for stirring Hotblock.

21) References

- Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, USEPA SW-846, 3060A, December 1996.

22) Attachments

- Digestion Benchsheets
- Table 1 – Single Laboratory Method Evaluation Data
- 3060 Flowchart

Hexavalent Chromium Soils

Method: EPA 3060A FOR ANALYSIS BY 7196A - INITIAL DIGESTION (Page 1)

Columbia Analytical Services
-Now Part of the ALS Group-
Rochester, NY 14623

Analyst: ____________________ Date: __________ Pipet ID: ______________

A) Digest Time Start: ________ Stop: ________ B) Digest Time Start: ________ Stop: ________

Filters: Brand: __________ Type: ____________________ Pore Size: ________ um. Digest Solution: pH: __________

pH Meter ID: ______________ Balance ID: ____________________

#	Method	Order #	Sample Amt. (g.)	Digest Sol. (mLs.)	Final Vol. (mLs.)	pH Adjust	pH Adjust Date	Filtered Digestate Color/Comments	Digest Temp. Check (deg. C) @ 0 min.	@ 30 min.	@ 60 min.	Thermometer ID
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												

Cr^{6+} Stocks: Standard: ____________________

Reference: ____________________

Insoluble LCS: added _____ mgs of PbCrO4 per ______ kg sample = _______ mg/kg x 0.161 (%Cr) = ______mg/Kg Cr6+

Spike Witness: __________ $PbCrO_4$ Log = ____________________

J:\ACQUDATA\WetChem\Cr6-soils\TEMPLATE-cr6Digest-r0 Template-Cr6Digest-r0 1/3/13

Hexavalent Chromium Soils **Method: EPA 3060A**

Columbia Analytical Services
-Now Part of the ALS Group-
1565 Jefferson Road.
Rochester, NY 14623

Analyst: ________________________ Date: ___________ Pipet ID: __________________

THESE STANDARDS ARE NOT DIGESTED

Filters: Brand: ____________ Type: __________________ Pore Size: ________ um.

Digest Solution: pH: _____________

pH Meter ID:________________

#		Digest Sol. (mLs.)	Final Vol. (mLs.)	pH Adjust	pH Adjust Date
1	2.00	50	100		
2	1.50	50	100		
3	1.00	50	100		
4	0.50	50	100		
5	0.10	50	100		
6	0.00	50	100		
7	I/CCV	50	100		
8	I/CCB	50	100		
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					

Cr^{6+} Stocks: Standard: ________________________

Reference: ________________________

J:\ACQUDATA\WetChem\Cr6-soils\TEMPLATE-cr6Digest-r0 Template-Cr6Digest-r0 1/3/13

TABLE 1

SINGLE LABORATORY METHOD EVALUATION DATA

Sample Type	Eh (mV)[b]	pH[d]	S^{2-} (ppm)[c]	Mean Native Cr(VI) Conc. (mg/kg)	Mean Cr(VI) Spike Conc. (mg/kg)	Matrix Spike Recovery Range,%
COPR[a]/Soil Blends	550	7.4	<10.0	4.1	42.0	89.8-116
Loam	620	6.4	<10.0	ND	62.5	65.0-70.3
Clay	840	3.0	<10.0	ND	63.1	37.8-71.1
COPR[a]	460	7.4	<10.0	759	813	85.5-94.8
Anoxic Sediment	-189	7.2	25.0	ND	381	0
Quartz Sand	710	5.3	<10.0	ND	9.8	75.5-86.3

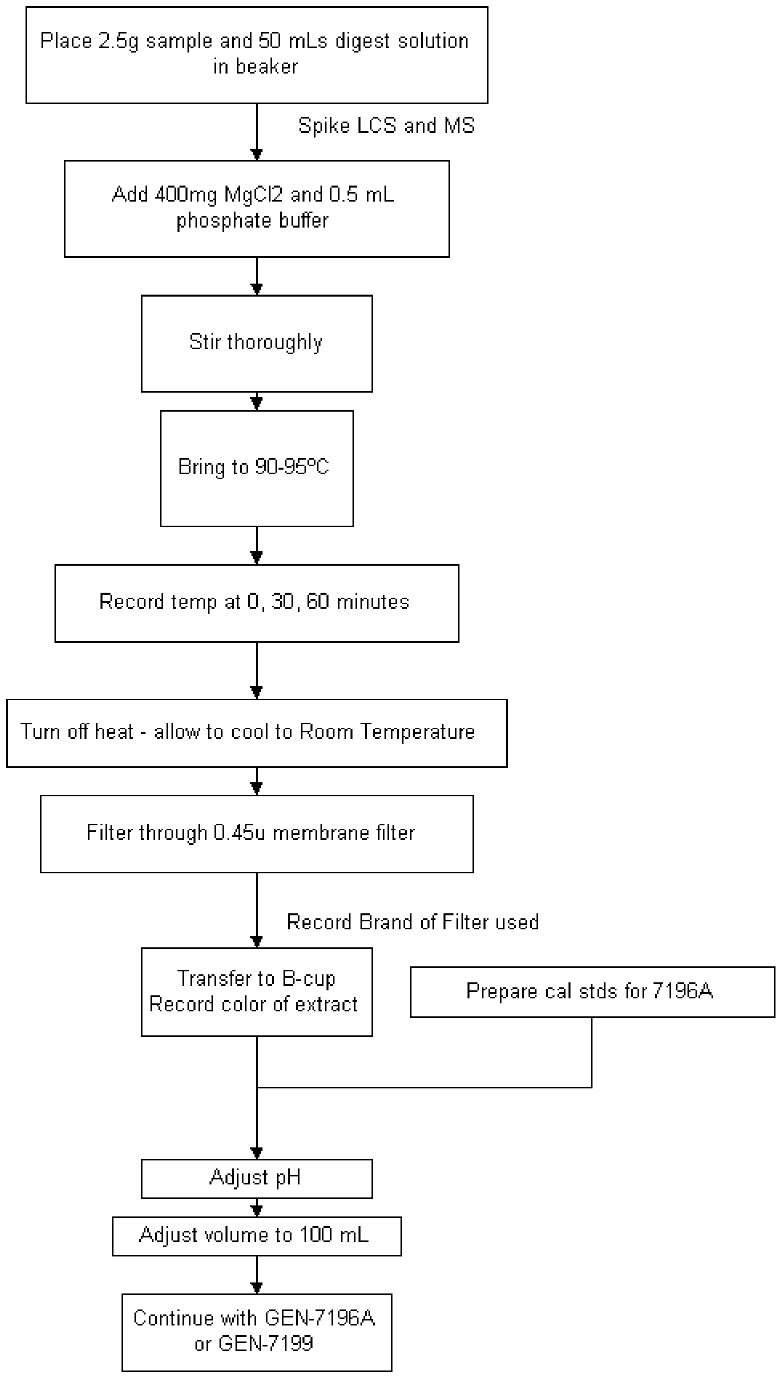
Source: Reference 10.3

Notes:

ND	-	Not detected
a	-	COPR - chromite ore processing residue
b	-	Corrected for the reference electrode, laboratory field moist measurement
c	-	Field measurement
d	-	Laboratory field moist measurement

METHOD 3060 (EPA)

HEXAVALENT CHROMIUM DIGESTION



P:Intranet/QAQC/ControlledForms/3060EPArev1 2/7/13

30-Sep-2013

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

SOIL SAMPLE PREPARATION FOR THE DETERMINATION OF RADIONUCLIDES

(GL-RAD-A-021 REVISION 20)

30-Sep-2013

TABLE OF CONTENTS

1.0 STANDARD OPERATING PROCEDURE FOR THE SOIL SAMPLE PREPARATION FOR THE DETERMINATION OF RADIONUCLIDES

2.0 METHOD OBJECTIVE AND APPLICABILITY

This standard operating procedure provides the necessary instructions to conduct the preparation of soil samples for radionuclide determination.

3.0 SUMMARY

This procedure involves drying the soil at a temperature between 103 and 105 ºC. If that temperature would volatilize any components for which an analysis has yet to be run, a separate aliquot must be set aside for such analyses.

4.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

4.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health, and Chemical Hygiene Plan, GL-LB-N-001.

4.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

4.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

4.4 If there is any question regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

5.0 APPARATUS AND MATERIALS

5.1 Apparatus and Equipment

5.1.1 Metal cans, approximately quart and pint size

5.1.2 Steel balls, approximately 1" and 3/4" diameter

5.1.3 Sieve screens, 28 mesh

5.1.4 Paper funnels

5.1.5 100 cc aluminum cans

5.1.6 Aluminum loaf pans

5.1.7 SPEX steel grinding containers (various sizes)

5.1.8 Assorted tools and labware

5.2 Reagents, Chemicals, and Standards

5.2.1 Sand, clean

5.2.2 Deionized water (DI water)

5.3 Instrumentation

5.3.1 Paint can shaker, heavy duty

5.3.2 Analytical balance

5.3.3 SPEX Model 8515-115 Shatterbox

5.3.4 Drying oven

5.3.5 Hydraulic press

5.3.6 Retsch, Model BB-51, Jaw Crusher

5.3.7 Automatic or manual can sealer

6.0 SAMPLE COLLECTION AND PRESERVATION

A representative sample must be collected from a source of soil and should be large enough (50 to 100 g) so that adequate aliquots can be taken to obtain the required sensitivity. The container of choice should be plastic over glass to prevent loss due to breakage during handling. No preservation is required for solid samples.

7.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

7.1 Refer to the technical manual provided with the paint shaker for information regarding equipment maintenance.

7.2 Refer to Instruction Manual for SPEX Shatterbox and Retsch Jaw Crusher operating instructions.

7.3 The analytical balance should be cleaned after use.

7.4 Refer to operating instructions for automatic or manual can sealer for information regarding equipment maintenance.

7.4.1 After receipt of new can sealer or when maintenance is performed on canner that could affect the proper sealing of the 100 cc gamma cans, perform a leak test on a can as follows:

7.4.1.1 Fill gamma can with water and seal.

7.4.1.2 Apply pressure on top and bottom of can and inspect for any visible signs of leakage.

8.0 SAMPLE PREPARATION PROCEDURES

8.1 Label a clean metal container with the laboratory sample number.

8.2 Weigh container. Record weight into the computerized soil prep balance log.

8.3 Transfer a representative aliquot from the sample to the labeled container.

8.3.1 When the amount of sample to be dried is not the entire contents of the sample container, refer to section 6.6 of SOP GL-LB-E-029 to ensure a representative sample aliquot is taken. This also ensures that the sample remaining is representative of the whole sample.

8.3.2 If the sample contains extraneous materials (i.e. rocks, twigs, vegetation) this shall be documented in the batch case narrative.

NOTE: Sample is dried at 103 to 105 °C. If this temperature will volatilize any component for an analysis that has yet to be run, a separate aliquot must be set aside for such analysis.

8.4 Enter the pre-oven sample weight into the computerized soil prep balance log. This weight represents the wet sample weight and container weight.

8.5 Place the container in a drying oven at a temperature between 103 and 105 °C for a minimum of four hours. (Normally overnight.)

NOTE: The time required to obtain a dry sample will vary depending on the type of material, size of sample, oven type and capacity, and other factors. The influence of these factors generally can be established by good judgment, experience with the materials being tested, and the apparatus being used.

8.6 Using heat resistant gloves, remove the sample from the oven and allow to cool.

8.7 Record weight into the computerized soil prep balance log. Replace sample in drying oven for a minimum of one hour.

8.8 Repeat step 8.7 until a constant weight is obtained. A constant weight is defined as a weight difference of less than about 0.1% (i.e. for a 20 g aliquot, the change in weight shuld be less than 0.02 g).

8.9 Homogenize the sample. This is normally accomplished by placing a lid on the container and placing the container in the industrial paint shaker. Depending on the matrix of the soil, it may be necessary to add several stainless steel balls inside the container to assist in homogenizing the sample. The length of time the sample remains on the shaker is dependent on the matrix of the sample, and normally ranges from 5 to 10 minutes. For solid samples that are composed of large particles, it may be necessary to reduce the particle size before homogenizing. This can be accomplished by placing the larger particles in the hydraulic press and applying enough pressure to break the particles into smaller pieces.

8.10 Remove the metal container from the shaker and allow to settle for several minutes.

8.11 Place the container in the sample preparation hood and remove the lid. If stainless steel balls were added to the container, they should now be removed. The stainless steel balls are discarded.

8.12 Determine an appropriate aliquot based on the analysis required. Normally, depending upon the required analysis, the sample will be passed through a 28 mesh sieve screen. For clients that require a smaller particle size, continue homogenizing samples per section 8.15.

8.13 Discard the unused portion of sample into the appropriate waste container (i.e. rocks or organic material). The soil sample is now ready for radiochemical analysis.

8.14 Place sample in appropriate containers (i.e. plastic bottle or vial, gamma can).

NOTE: If preparing a 100 cc gamma can, it is important that the can is properly sealed to ensure Ra-226 is quantified correctly. Ra-226 in soil samples is quantified by one of its daughter products (Bi-214). Ra-226 decays to Bi-214 through Rn-222, which is a gas, and must be isolated inside the can in order for equilibrium to be re-established.

8.14.1 For proper sealing of gamma can:

8.14.1.1 Place lid on 100 cc can and place can on base plate of the automatic or manual can sealer.

8.14.1.2 Raise the can until it is clamped firmly between the base plate and chuck by turning the can lifter handle as far as possible to the right until the handle locks itself against the frame.

8.14.1.2.1 If using the automatic can sealer push the on button. The flywheel will turn until the can sealing is complete.

8.14.1.2.2 If using the manual can sealer, turn the flywheel 21 turns until the second operational roll returns to its normal position, away from the chuck.

8.14.1.3 Lower the can by turning the can lifter handle to the left. Remove the sealed can from the base plate.

8.14.1.4 Visually inspect can after sealing for any defects. If defects are noticed that may affect the proper sealing of the can, remove contents from can and start over with a new can.

8.15 **Shatter Box (200 mesh sample)**

8.15.1 Take a portion of remaining sample (more than enough to complete the requested analysis) and further homogenize sample to approximately 200 mesh. This is accomplished by pulverizing sample in the shatterbox.

NOTE: The approximately 200 mesh is determined based on particle size study in shatterbox instruction manual.

8.15.2 Pulverize sample for a minimum of 5 minutes.

NOTE: Refer to Shatterbox Instruction Manual for operating procedure.

8.15.3 To prevent cross-contamination the dish and puck must be decontaminated prior to pulverizing the next sample.

8.15.3.1 Decontaminate the dish and puck by filling with approximately50 g of sand. Replace the lid.

8.15.3.2 Place the shatterbox in operation for approximately 1 to 2 minutes. Empty the sand from the container.

8.15.3.3 Dampen a clean paper towel with DI water and wipe the dish, puck and lid to ensure that all traces of sand are removed.

8.15.3.4 To check for contamination, perform a smear survey of dish and puck after each dish and puck decontamination with sand, and submit to Radiation Safety for counting.

8.15.3.5 A decontamination blank is analyzed monthly for gross alpha, beta, and gamma activity. The results of these analyses will be compared to historical data. When a decontamination blank is analyzed, it is pulverized post cleaning.

NOTE: To prevent corrosion, keep the entire container assembly dry.

8.15.4 Record all samples and decontamination blanks in the shatterbox logbook.

8.16 **Pulverizer**

8.16.1 Use the sample jaw crusher to prepare medium to extremely hard substances having a maximum input grain size of 35 mm.

NOTE: Refer to Retsch Jaw Crusher Type BB-51 Operating Instructions manual for operating procedure.

8.16.2 To prevent cross-contamination, the jaw crusher must be decontaminated prior to processing the next sample. Decontaminate the jaw crusher by processing approximately 200 g of pre-dried lava rock having a maximum input grain size of 35 mm. A decontamination blank is analyzed monthly for gross alpha, beta, and gamma activity. The results of these analyses will be compared to historical data.

9.0 CALCULATIONS AND DATA REDUCTION METHODS

The electronic balance program provides documentation of all necessary raw data.

Weights in AlphaLIMS are recorded to three places past the decimal point (Ex: 6.738, 314.197…).

9.1 If client requests results to be reported "as received" (based on wet weight), analysts will correct the "dry" aliquots back to wet weights using the "weight/loss aliquot correction report" link in AlphaLIMS. This report will be included, if necessary, in each analytical batch's raw data.

10.0 QUALITY CONTROL REQUIREMENTS

10.1 Method Specific Quality Control Requirements

10.1.1 When possible (i.e., there is sufficient sample available) for gamma analysis, a separate container will be prepared for counting to meet the duplicate sample requirement.

10.1.2 Refer to the specific isotope operating procedure for instructions concerning method quality control requirements.

10.2 Actions Required if the Quality Control Requirements Are Not Met

If any of the quality criteria cannot be satisfied, the analyst should inform the group leader and initiate a Data Exception Report as outlined in GL-QS-E-004 for Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items.

11.0 CALIBRATION

11.1 Balances are calibrated annually and verified daily in accordance with GL-LB-E-002.

11.2 Temperature monitoring devices are verified in accordance with GL-QS-E-007.

12.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

All data are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

13.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is handled and disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

14.0 REFERENCES

14.1 ASTM C999-05, "Standard Practice for Soil Sample Preparation for Determination of Radionuclides," 1993 Annual Book of ASTM Standards, Vol 12.01, 2005.

14.2 Laboratory Sub-Sampling Procedure, GL-LB-E-029.

14.3 ASTM D6323-98 (2003) "Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities."

14.4 EPA's "Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples", EPA/600/r-03/027, November 2003.

15.0 HISTORY

Revision 20: Section 9.1 revised for clarification to comply with DOECAP audit finding.

Revision 19:Added client specific prep procedure as an appendix.

Revision 18: Changed 8.14-8.17 to 8.15-18.17 in section 8.12.

APPENDIX I: HGEO GROSS SAMPLE PRE-TREATMENT

This proposed procedure is for the preparation of SSFL soil samples for Hydrogeologic, Inc.

1.) Cover an area of bench top, within a HEPA filtered enclosure, with clean paper. Transfer the total raw sample to the paper and spread sample evenly across the surface. Samples may be contained in more than one sample container.

2.) Remove cultural/man-made materials from the sample if applicable, photograph, and place in a labeled container for storage. If no cultural/man/made materials are found, no photograph is required, provided that the laboratory documentation clearly notes that no such objects were found. Notify Project Manager if cultural/man-made materials are found in the samples.

3.) Label a clean metal container with the laboratory sample number. When large amounts of soil are being processed, samples may be dried in aluminum pans to improve effectiveness of complete drying. Note: Samples may be split into more than one drying vessel. Record weights separately until the sample is recombined.

4.) Weigh the containers and record weights into the soil prep balance log.

5.) Transfer the entire sample to the labeled container. When the amount of sample to be dried is not the entire contents of the sample container, document via a Data Exception Report. Any sample removed in this manner shall be done by taking a grab sample to minimize any loss of potentially volatile radionuclides.

6.) Enter the pre-oven sample weight into the soil prep balance log. This weight represents the wet sample weight and container weight.

7.) Place the container(s) in a drying oven at a temperature between 103 and 105 °C for a minimum of four hours. Record the time the sample was placed in the oven.

8.) Using protective heat resistant gloves remove the sample from the oven and allow cooling. Record the time the sample was removed from the oven.

9.) Record the weight in the soil prep balance log and place the sample back in the drying oven for a minimum of one hour. Record the time the sample was returned to the oven. Record the time the sample was removed from the oven for each interval.

10.) Repeat steps 8 and 9 until a constant weight is obtained. A constant weight is achieved when two subsequent weights agree within 1%.

11.) Break up the sample in preparation for passing through the sieves with the process. Transfer sample to an appropriate number of 1 gallon paint cans. Add 6- 1" stainless steel balls to each paint can to aid in the breakup of the samples. NOTE: Paint cans should not be filled above approximately 3/4 full. Overfilling will reduce the effectiveness of sample blending. Place the paint cans on the industrial paint can shaker for 5-10 minutes.

12.) Remove the container(s) from the paint can shaker and allow settling for several minutes.

13.) Place the container(s) in the sample in a ventilated preparation hood and remove the lid. If stainless steel balls were added to the container(s), they should now be removed and discarded.

14.) Pass entire dried sample through a 4-mesh sieve. Transfer material that will not pass through into a labeled container for storage. The analyst will evaluate the material to determine if they may be further broken up in order to be passed through the 4-mesh sieve.

15.) Pass the entire dried sample through a 28-mesh sieve. Any sample not passing through the 28-mesh sieve must be processed until it passes through the 28-mesh sieve. Contact the Group leader if these criteria cannot be met.

16.) Place sample back into the paint cans and mix on the paint can shaker for 5-10 minutes.

17.) From the <28-mesh sample, use the *'Cone and Quartering*' method described below to remove a representative sample fraction for gamma analysis (~2000 grams).

18.) ***Cone and Quartering***' method - Sample is emptied out onto a non-contaminating smooth surface. Material is piled into a cone with a flattened top surface. Two top-to-bottom cuts are made through the cone at perpendicular angles to form four equal portions, or quarters. Two opposite quarters are compiled into a new cone, and the process is repeated until the proper sample mass is obtained. When sub-sampling using this method it is important to remove the entire quarters to be used. Process enough sample to prepare a new 1-Liter Marinelli beaker (~1600-1700 grams) and 100cc gamma can (~160-180 grams) geometries for gamma analysis.

19.) Record the weight of the gamma aliquots in the soil prep balance log. Some samples may need an equal portion of sample for archiving as noted by the project manager.

20.) Take a portion of remaining sample using the 'Cone and Quartering' method(more than enough to complete the requested analysis) and further homogenize sample to approximately 200 mesh. This is accomplished by pulverizing sample in the shatterbox (puck mill).[i]

Note: Some samples may be designated to prepare an equal portion of sample for archiving.

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[i] The approximately 200 mesh is determined based on particle size study in shatterbox instruction manual. The number of replicates included in the study was determined based on guidance provided in chapter 6 of the MARLAP manual (Level B validation).

21.) Pulverize sample for 5 minutes. Refer to Shatterbox Instruction Manual for operating procedure.

22.) To prevent cross-contamination the dish and puck must be decontaminated prior to running the next sample. Decontaminate the dish and puck by filling with approximately 50 g of sand. Replace the lid and operate the shatterbox for 2 minutes. Empty the sand from the container.

23.) Dampen a clean paper towel with DI water and wipe the dish, puck and lid to ensure that all traces of the sand are removed. To check for gross contamination, perform a smear survey of dish and puck and submit to radiation safety office for counting.

24.) To monitor for low level contamination, process blanks will be analyzed. The process blanks will consist of an ICP/MS analysis for U-238 on DI water rinses of the grinding containers (500 mLs). Acceptable results of the blanks shall be less than MDL. Should a blank indicate the presence of U-238 at a level >MDL, it shall be documented and a review conducted to determine the impact on any data produced using the container in question.

Record all samples and decontamination blanks in the shatterbox logbook.

30-Sep-2013

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF GAMMA ISOTOPES

(GL-RAD-A-013 REVISION 25)

APPLICABLE TO METHODS:
EPA 600/4-80-032 Method 901.1
DOE EML HASL-300 Section 4.5.2.3
DOE EML HASL-300 Ga-01-R

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF GAMMA ISOTOPES

2.0 METHOD OBJECTIVE, PURPOSE, AND SUMMARY

2.1 This standard operating procedure (SOP) provides the necessary instructions to conduct the analysis for gamma isotopes in water, soil, urine, filters, drinking water and miscellaneous matrices.

2.2 Water samples are typically counted in Marinelli beakers. Soil samples are typically sealed in aluminum cans, which can be counted immediately if Ra-226 is not desired. If Ra-226 is desired, the sealed can is set aside for minimum of 20 days to allow equilibrium between Rn-222 and Bi-214 to become re-established. Ra-226 is then quantified using the 609 keV line of Bi-214.

2.3 This method is based on the source method EPA 600/4-80-032 "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," August 1980, Method 901.1, and the Department of Energy (DOE) EML Procedures Manual source method for Gamma PHA in environmental samples, HASL-300 Section 4.5.2.3 and Ga-01-R, Gamma Radioassay.

2.4 This SOP is applicable for analyzing samples that contain radionuclides emitting gamma photons with energies ranging from about 5 to 2000 keV (including I-131).

3.0 METHOD SCOPE, APPLICABILITY, AND DETECTION LIMIT

3.1 Minimum Detectable Activity (MDA): The MDA is based upon sample volume, Compton background, instrument efficiency, count time, and other statistical factors, as well as specific isotopic values such as abundance and half-life. A typical detection limit is 10 pCi/L or 0.1 pCi/g (based on Cs-137). The MDA for drinking water samples is 10 pCi/L (based on Cs-137).

3.2 Method Precision: Typical Relative Percent Difference (RPD) is 20% or less or 100% or less if the activity is less than five times the MDA.

3.3 Method Bias (Accuracy): The method accuracy requirement for gamma, measured by running a Laboratory Control Sample (LCS) with each batch, is 25% of the true value. For drinking water samples, laboratory fortified blanks (LFB, equivalent to LCS) recoveries should be between 90-110% of the known value.

3.4 Procedures contained in this SOP may be used to analyze REMP samples.

3.5 Analysts training records are maintained as quality records as outlined in GL-QS-E-008. Analysts training and proficiency in the method is outlined in the Employee Training SOP GL-HR-E-002.

3.6 For drinking water samples, analyst initial and ongoing demonstrations of proficiency will follow critical elements for radiochemisrtry, chapter VI, section 1.5, of The Manual for the Certification of Laboratories Analyzing Drinking Water (reference 20.5).

3.7 Sensitivity studies will follow critical elements for radiochemistry, chapter VI, section 7.3 of The Manual for the Certification of Laboratories Analyzing Drinking Water (reference 20.5).

4.0 METHOD VARIATIONS

4.1 Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

4.2 Filter samples can either be counted directly, or digested prior to counting. If filters are digested, they are digested in accordance with GL-RAD-A-026.

4.3 No method modifications are permitted for drinking water samples.

5.0 DEFINITIONS

5.1 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

5.2 Deionized (DI) water: Type I water.Refer to GL-LB-E-016.

5.3 AlphaLIMS: GEL's Laboratory Information Management System.

5.4 Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

5.5 Method Blank (MB): A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.6 Laboratory Duplicate (DUP): For soils, when sufficient sample is available, a separate duplicate will be prepared. For liquid samples and when sufficient sample is not available for solids, an independent count of the sample container will be performed to show precision.

5.7 Laboratory Control Sample (LCS): A sample matrix, similar to the batch of associated samples (when available) that is free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. The LCS is equivalent to a Fortified Blank in the EPA drinking water compliance manual (See to section 20.5).

6.0 INTERFERENCES

6.1 Some gamma isotopes emit gamma lines that may overlap with other isotopes. If the energies of the two isotopes are within the energy tolerance setting, the peaks may not be resolvable and may give a positive bias to the result. This problem is minimized by careful review of the peak search.

6.2 Soil samples may vary in density from the standard used for calibration. A density correction is applied to the "CAN" geometry. This correction was determined using solids with weights varying between 54 g and 192 g.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Keep hands free from moving parts of canning device and gamma shields.

7.2 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.3 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.4 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for The Handling of Biological Materials.

7.5 If there is any question regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT, AND INSTRUMENTATION

8.1 Ancillary Equipment

8.1.1 100 cc aluminum cans with lids for soil and miscellaneous samples

8.1.2 10 cc Gelman Sciences Petri dish for soil, filters and miscellaneous samples

8.1.3 2 L and 500 mL Marinelli beakers for water samples

8.1.4 Air displacement pipettes

8.1.5 Can sealing tool

8.1.6 Graduated cylinder

8.1.7 25 cc VWR Petri for soil and miscellaneous samples

8.1.8 250 mL plastic jar for filters, soil, and miscellaneous samples

8.1.9 Hot plate

8.1.10 Teflon beakers and lids

8.1.11 1 L Marinelli beaker for soil samples

8.2 Instrumentation

8.2.1 High purity germanium detector, with associated electronics and data reduction software

8.2.2 NaI Detector with associated electronics and data reduction software

8.2.3 Top loader balance

9.0 REAGENTS, CHEMICALS, AND STANDARDS

9.1 NIST traceable mixed gamma standard in 100 cc aluminum can

9.2 NIST traceable mixed gamma standard in 2.0 L Marinelli beaker

9.3 NIST traceable mixed gamma standard in 0.5 L Marinelli beaker

9.4 NIST traceable mixed gamma standard in Gelman Sciences 10 cc Petri dish

9.5 NIST traceable mixed gamma standard in 13, 47 mm glass fiber filter composites in Gelman Sciences Petri dish.

9.6 NIST traceable mixed gamma standard in 0.4 L jar

9.7 NIST traceable mixed gamma standard in 0.25 L jar

9.8 NIST traceable mixed gamma standard in 1, 47 mm glass fiber filter

9.9 NIST traceable mixed gamma standard in Impregnated Charcoal Sample Cartridge.

9.10 NIST traceable mixed gamma standard in VWR (53 mm x 15 mm) Petri dish (approximately 25 cc)

9.11 NIST traceable mixed gamma standard in aqueous solution

9.12 NIST traceable mixed gamma standard in 1.0 L Marinelli beaker

9.13 NIST traceable mixed gamma standard in 20 mL liquid scintillation vial

9.14 16 M Nitric acid, reagent grade (HNO_3)

9.15 49% Hydrofluoric acid (HF)

9.16 12 M Hydrochloric acid, reagent grade (HCl)

9.17 5% Boric acid: Dissolve 50 g of H_3BO_3 per liter of DI water.

9.18 Nitric acid (8 M HNO_3): Prepare by cautiously adding a measured volume of concentrated nitric acid to an equal volume of DI water.

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 For soil samples, 500 g of sample should be collected, preferably in a plastic container to avoid breakage.

10.2 For water samples, 2 L of sample should be collected in a plastic container and preserved to a pH < 2 with nitric acid.

10.2.1 Before beginning an analysis, the analyst should check the sample pH by removing a minimal amount of sample with a transfer pipette and placing it on a pH strip. DO NOT insert pH strip into sample container. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader.

NOTE: If the analysis is requesting I-131 (or any other iodine isotopes) Analysis without preserving is acceptable. If a sample is preserved with acid without stabilizing the iodine, Iodine may volatilize and escape the solution as a gas.

10.2.2 If approved by the client, the analyst should adjust the pH with nitric acid to a pH < 2. If the sample pH is adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis. This acidification should be documented on a batch history sheet and attached to the batch paperwork.

10.3 For filters no preservation is necessary.

11.0 SAMPLE PREPARATION

11.1 Solid Sample Preparation.

11.1.1 Prepare the sample for gamma counting in accordance with SOP GL-RAD-A-021, Soil Sample Preparation for the Determination of Radionuclides.

11.1.2 Fill the appropriate container with sample prepared from step 11.1.1 using the following steps as a guideline:

11.1.2.1 If Ra-226 analysis is required, the sample is placed in a 100 cc can for in-growth.

NOTE: It is recommended that in-growth be allowed 20 days to quantify Ra-226. Shorter ingrowth periods can be used at the request of the client. However, shorter in-growth periods may decrease the accuracy of the data. If there is insufficient mass of sample to fill the 100 cc can, contact the Team or Group Leader.

11.1.2.2 If sufficient mass is available, homogenized samples should be placed in the 100 cc can. Determine the net weight of the sample. If the net weight is less than 54 g or greater than 192 g, contact the Team or Group Leader to determine the appropriate counting container. Record sample weight and date in AlphaLIMS and on sample container.

11.1.2.3 If there is insufficient sample to fill the 100 cc can, place sample in the 10 cc or 25 cc Petri dish, cap and seal. Record sample weight and date in AlphaLIMS and on sample container.

11.1.2.4 If there is insufficient sample to fill the 10 cc Petri dish, perform the following digestion process:

11.1.2.4.1 Weigh out an appropriate aliquot into a labeled Teflon beaker. Record this weight on the Queue sheet.

11.1.2.4.2 Add 10 mL of concentrated nitric acid to each sample.

11.1.2.4.3 Place samples on medium heat (approximately 300 °F) and cover each sample with a Teflon lid. Reflux all samples for 30 minutes.

11.1.2.4.4 Remove Teflon lids and add 5 mL concentrated hydrochloric acid and 10 mL hydrofluoric acid to each sample. Cover samples and reflux for 120 minutes.

11.1.2.4.5 Remove Teflon lids and allow samples to evaporate to dryness.

11.1.2.4.6 Add 5 mL of concentrated nitric acid and evaporate to dryness.

11.1.2.4.7 Repeat Step 11.1.2.4.6.

11.1.2.4.8 Add 5 mL of concentrated nitric acid to the dry samples. Add 1 mL of 5% boric acid. Place the samples back on the hot plate long enough so that the dried sample dissolves into solution.

11.1.2.4.9 Transfer solution to a 250 mL gamma container and dilute to 200 mL. Record the original sample mass and diluted volume on sample container.

Record the original sample mass on batch Queue sheet.

11.2 Water Sample Preparation

11.2.1 Place the appropriate labeled Marinelli beaker (typically 500 mL or 2 L) on a balance and tare the balance.

11.2.2 If less than approximately 1.1 L is available, sample should be poured into a 500 mL Marinelli beaker.

11.2.3 Transfer the appropriate volume to the tared container and record the volume of the sample on the Queue sheet.

NOTE: If there is insufficient sample to fill the Marinelli, record the exact amount of sample volume on the container and on the Queue sheet. Dilute the sample to the appropriate volume to maintain the calibration geometry. Record the volume the sample was diluted to on the sample container, also.

11.2.4 The MB should be recorded on the Queue sheet to be the same aliquot as the largest sample in the batch. An empty Marinelli beaker should be labeled as the MB and submitted with each batch of samples.

11.2.5 Submit the Marinellis and completed paperwork to the count room for gamma counting analysis.

11.3 Urine Sample Preparation

11.3.1 Refer to GL-RAD-B-030.

11.4 Preparation of Miscellaneous Matrices

11.4.1 Prepare the sample in accordance with GL-RAD-A-026 for The Preparation of Special Matrices for the Determination of Radionuclides.

11.4.2 If sample(s) was (were) received from the client in a container that matches a calibrated geometry, a direct count of the sample can be performed.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

Refer to GL-RAD-D-003.

13.0 INSTRUMENT CALIBRATION, STANDARDIZATION, AND PERFORMANCE

Refer to GL-RAD-I-001.

14.0 ANALYSIS AND INSTRUMENT OPERATION

Refer to GL-RAD-I-001.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-010.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

Data recording, calculation and reduction take place in accordance with SOP GL-RAD-D-003 and GL-RAD-D-006.

17.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

Data are reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation, and Data Package Assembly.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as Quality Documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Radioactive samples and material shall be handled and disposed of as outlined in the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 USEPA. Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Method 901.1, August 1980.

20.2 Canberra Nuclear Genie System Spectroscopy, Applications and Display User's Guide, Vol. I and II, May 1991.

20.3 DOE EML Procedures Manual, HASL-300, 27th Edition.

20.4 DOE EML Procedures Manual, HASL-300, 28th Edition.

20.5 Manual for the Certification of Laboratories Analyzing Drinking Water. Criteria and Procedures Quality Assurance. Fifth Edition EPA 815-R-05-004 January 2005.

21.0 HISTORY

Revision 25: Type II to type I water.

Revision 24: Changed recovery limit for laboratory fortified blank from 90-100% to 90-110% in section 3.3.

Revision 23:Procedure updated to include requirements for drinking water samples.

Revision 22: Updated ingrowth period for Ra-226 to 20 days.

Revision 21: SOP revised to add Ra-226, NIST traceable gamma standards, and other clarifications.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

DETERMINATION OF METALS BY ICP-MS

APPLICABLE TO METHODS:
EPA Method 200.8
EPA SW-846 Method 6020 and 6020A

(GL-MA-E-014 REVISION 25)

GEL

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1.0 STANDARD OPERATING PROCEDURE FOR DETERMINATION OF METALS BY ICP-MS

2.0 METHOD CODES

2.1 EPA SW-846 Method 6020

2.2 EPA SW-846 Method 6020A

2.3 EPA Method 200.8

2.4 ASTM D4698-92 Total Dissolution

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure (SOP) describes the determination of metals using a Perkin Elmer ELAN ICP-MS Model 6100 Spectrometer or a Perkin Elmer ICP-MS Model 9000 Spectrometer. Prior to analysis, samples must be digested using appropriate sample preparation methods (such as Methods 3005, 3010, 3050, or 200.2) and other applicable requests.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 Refer to Appendix 3 for analyte lists and masses.

4.2 Applicable Matrices: These methods are applicable to the determinations of any of the analytes listed above for various matrices including waters, oils, soils, sludges, biological tissues, Toxicity Characteristic Leaching Procedure (TCLP) extracts and other more unusual types of sample which are generally classified as a miscellaneous matrix.

4.3 General Method Summary: After the samples are prepared in accordance with the sample preparation SOP, they are analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) as follows:

4.3.1 The instrument is calibrated with a minimum of two calibration points for each element to be analyzed. The points consist of a calibration blank solution to define the lower calibration point and at least one standard calibration solution at the analyte concentrations to define the higher calibration point(s). A correlation coefficient of 0.995 or better (0.998 or better for SW-846 Method 6020A) is required for each analyte if multiple standards are used or the instrument is recalibrated for the analyte of interest.

4.3.2 Prepared client samples and numerous check standards and quality control samples, identified in Section 22.1 are then analyzed. The check standards and quality control samples are used to determine the quality and acceptability of the analytical data.

4.3.3 Continuing Calibration Verification standards (CCV) and Continuing Calibration Blanks (CCB) are analyzed a minimum of every 10 samples to ensure that the instrument is continuing to perform correctly. For 6020A, low level continuing calibration verification standards are analyzed in conjunction with the CCVs and CCBs.

4.4 Method Codes: Analyses must conform to SW-846 Method 6020, SW-846 Method 6020A, EPA Method 200.8, and/or customer contract specifications.

4.5 Radiochemistry conversion calculations for the uranium isotopes are included in Appendix 4.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 Calibration Range: The range of concentrations between the calibration blank, typically 0, and that of the highest calibration standard for each analyte. Calibration standards vary according to method and equipment. A minimum of two, a blank and value standard, are required.

5.2 Linear Dynamic Range standards (LRS) are analyzed with each calibration. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from the resulting data. The instrument is calibrated. The target linear range should be prepared and analyzed. The LRS results must fall within ± 10% of the target value. This LRS value is entered into the instrument's software. Any hits below this value will be valid. Hits at or above this value will be flagged by the system and must be diluted to fall within the linear dynamic range. If a linear range standard is not used for a specific calibration, the highest calibration standard becomes the upper limit of reporting.

5.3 Instrument Detection Limits (IDLs) in µg/L are determined by calculating the average of the standard deviation of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months.

5.4 Method Detection Limit (MDL) studies for each analyte are performed and/or verified at least annually. These studies are conducted and calculated in accordance with SW-846, Chapter 1, paragraph 5.0, and GL-LB-E-001 for the Determination of Method Detection Limits. The relevant quantitation limits are established based on the most current MDL study. The current MDLs are maintained and can be found in the AlphaLIMS database.

5.5 Method Precision: To assure analytical precision of methods used, Laboratory Control Samples (LCS) are analyzed with each batch. LCS duplicates are analyzed with each batch when requested.

5.6 Method Bias (Accuracy) is determined by calculating recoveries of LCS of a similar matrix.

5.7 If uncertainty and total propagated uncertainty measurements are needed, they may be determined using GL-QS-E-014 for Quality Assurance Measurement Calculations and Processes.

6.0 DEFINITIONS

6.1 AlphaLIMS: The Laboratory Information Management System used at GEL Laboratories, LLC.

6.2 Analysis Date/Time: The date and military time (24-hour clock) of the introduction of the sample, standard, or blank into the analysis system.

6.3 Analytical Sample: Any solution of media introduced into an instrument on which an analysis is performed excluding instrument calibration, initial calibration verification (ICV), initial calibration blank (ICB), continuing calibration verification (CCV), and continuing calibration blank (CCB).

6.4 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6.5 Continuing Calibration Blank (CCB): An aliquot of reagent water or other blank matrix that is analyzed after each CCV. The CCB is used to determine whether the analytical sequence is in control during sample analysis.

6.6 Continuing Calibration Verification (CCV) Standard: An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The CCV is analyzed exactly like a sample, periodically throughout the run sequence. Its purpose is to determine whether the analytical sequence is in control during the sample analysis. It may be prepared from the same source as the calibration standards, and is usually of varied concentrations.

6.7 Contract Required Detection Limit (CRDL): Minimum level of detection acceptable under the client project requirements.

6.8 Control Limits: A range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

6.9 Correlation Coefficient: A number (r) that indicates the degree of dependence between two variables (concentration-absorbance). The more dependent they are, the closer the value to one. Determined on the basis of the least squares line.

6.10 Data Qualifiers: The following qualifiers should be used in order to identify analytical situations that might need additional information stated in narrative before the release of the data.

U - Non-Detect. Below the Instrument or Method Detection Limit (depending upon specific project requirements)

B - Sample concentration value is between the MDL (or IDL) and the CRDL or analyte was detected in the Method Blank (Client Specific)

J - Sample concentration is between the MDL (or IDL) and the CRDL-client specific qualifier.

Blank - Concentration value is above the CRDL

* - An RPD value in the duplicate sample is out of criteria

N - A percent recovery value in the spike sample is out of criteria

E - A percent difference in the serial dilution sample is out of criteria because of the presence interference.

6.11 Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

6.12 Initial Calibration Blank (ICB): An aliquot of reagent water or other blank matrix that is analyzed after each ICV. The ICB is used to determine whether there is carryover contamination.

6.13 Initial Calibration Verification (ICV): A solution of method analytes of known concentrations. The ICV is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

6.14 Instrument Performance Check Solution (IPC): A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

6.15 Interferants: Substances that affect the analysis for the element of interest.

6.16 Internal Standard: Pure analyte(s) added to a sample, extract, or standard solution in known amounts and used to measure the relative responses of other method analytes.

6.17 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

6.18 Linear Calibration Range (LCR): The concentration range over which the instrument response is linear.

6.19 Method Blank (MB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

6.20 Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified measured and reported with 99% confidence that the analyte concentration is greater than zero.

6.21 Serial Dilution: The dilution of a sample by a known factor. When corrected by the dilution factor, the diluted sample should agree with the original undiluted sample within the specified limits. Serial dilution may reflect the influence of interferants.

6.22 Spike (Matrix Spike or Post Spike): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS or PS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS or PS corrected for background concentrations.

6.23 Limit of Detection (LOD): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reliably detected.GEL has established LOD = 2 x MDL.

6.24 Limit of Quantitation (LOQ): An analyte, method and matrix specific estimate of the minimum amount of a substance that can be reported with a specific level of confidence. The LOQ is set at or above the concentration of the lowest initial calibration standard. The laboratory must empirically demonstrate precision and bias at the LOQ. The LOQ and associated precision and bias must meet client requirements and must be reported. GEL uses the following guidance (LOD < LOQ):

When LOD < PQL, PQL = LOQ

When LOD > PQL, LOQ is raised to next lowest calibration standard.

6.25 Practical Quantitation Limit (PQL): The PQL is typically at or above the lowest point on an acceptable initial calibration curve. It may also be determined by multiplying the MDL by approximately 2 to 10. Concentrations of a target analyte determined to be greater than its PQL are defined as quantitative results. This limit is not used in DoD ELAP reporting.

6.26 Statistical Process Control (SPC) Limits: Statistically derived limits that establish acceptable ranges for recoveries of analytes of interest, including LCS, MS, MSD, PS and PSD.

6.27 Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using certified reference materials or purchased from a reputable commercial source.

6.28 10% Frequency: A frequency specification during an analytical sequence allowing for not more than 10 analytical samples between required calibration verification measurement, as specified by the EPA methodology.

7.0 INTERFERENCES TO THE METHOD

7.1 Chemical interferences are minimal in ICP-MS Spectroscopy because the extremely high energy of the plasma breaks nearly all the chemical bonds. However, ICP-MS analysis is subject to the following three types of interferences:

7.1.1 Physical interferences are those physical properties of a sample solution that prevent their introduction to the plasma with efficiency equal to that of the calibration standards. This type of interference can be corrected via the bias correction calculation in SW-846, Chapter 1, paragraph 5.0, through the use of an internal standard in accordance with the instrument operating manual or by diluting the sample in reagent blank solution until the percent recovery falls with method guidelines.

7.1.2 Isobaric elemental interferences are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio and that cannot be resolved by the mass spectrometer. If analytical isotopes are selected that may have an isobaric interference, then all data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest.

7.1.3 Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest, and that cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified and are listed in Method 200.8, Table 2 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes or sample prep procedures, appropriate corrections must be made to the data.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

8.1 PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

8.2 WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

8.3 Sample digestates are not extremely volatile or spontaneously combustible, but they are normally acidic and should be handled with care. Small spills may generally be wiped up with paper towels that can be disposed of in the trash. Larger spills may require the use of a mop, and the mop head may have to be disposed of as potentially hazardous waste in accordance with the Laboratory Waste Management Plan (GL-LB-G-001). If the spilled digestates begin any obvious fuming or reacting, pour a generous amount of the acid neutralizer, which is located in each lab, onto the spill before attempting to clean it up.

8.3.1 Gloves should be worn to avoid skin contact with digestate during clean-up.

8.3.2 Eye protection is required when handling samples and an eyewash station is located in each analysis lab.

8.3.3 Do not persist in cleaning up a spill in the presence of strong fumes. Move out of the area, try to isolate the area and notify your supervisor immediately.

8.4 Handling radioactive samples requires the use of gloves, a lab coat or an apron in addition to eye protection. Refer to GL-RAD-S-004 for Radioactive Material Handling

8.5 These instruments use high voltage electricity and therefore, should be shut completely down any time electronic components may be exposed to personnel or any liquids.

8.6 Wear eye protection with side shields while performing procedures in the lab.

8.7 All chemicals and samples should be treated as potential health hazards, and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents are maintained in the laboratory. Individual sample MSDS forms provided by the clients are kept in Login.

8.8 Personal protective equipment

8.8.1 Gloves are required when handling the chemicals in this procedure.

8.8.2 Work under a hood when using concentrated acids.

8.9 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

8.9.1 Wear a lab coat when working with radioactive samples.

8.9.2 Prohibit admittance to immediate work area.

8.9.3 Protect counter tops with counter paper or work from radioactive sample handling trays.

8.9.4 Post signs indicating radioactive samples are in the area.

8.9.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the nearest swipe count box.

8.9.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

8.10 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.10.1 Segregate solid wastes from liquid wastes in the satellite area containers.

8.10.2 Segregate oil wastes from water-soluble wastes in the satellite area containers

8.11 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

8.12 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

8.13 Fire escape routes are posted in the lab; all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

9.0 CAUTION WARNINGS

9.1 Because they can be health hazards, the exhaust gases from the plasma and vacuum systems must be eliminated through the laboratory's ventilation duct, which is attached to the instrument's exhaust vent. If inadequate ventilation occurs, pump-fluid vapor, ozone, and other toxic products of combustion can accumulate in the laboratory and cause bodily harm. Hydrofluoric acid (HF) fumes, if inhaled, extensively burn lung tissue. Ensure that the exhaust system established at installation continues to operate effectively.

9.2 Prepare sample and transfer acids using a hood to avoid fumes.

9.3 Store and prepare sample away from the instrument to minimize corrosion.

9.4 Clean up any spills quickly.

9.5 The drain vessel contains the spray chamber's effluent, which can be toxic. Corrosion of the vessel and connecting tube can result in leaks that damage the instrument or cause bodily harm.

9.5.1 Use the capped plastic drain vessel that was provided with the instrument. Never use glass.

9.5.2 Place the drain vessel on the instrument table below the peristaltic pump where the container is easy to check.

9.5.3 Check the drain vessel frequently. Empty it before it is three-fourths full.

9.5.4 Check the tubing and vessel for deterioration. If the tubing becomes brittle or cracked, replace it. Organic solvents cause more rapid deterioration than aqueous solutions.

9.6 The torch and interface remain hot after the plasma is turned off. Do not touch the torch box or interface cones for 10 minutes after the plasma has been shut off.

9.7 High voltages and radio frequencies are potential hazards of the ICP-MS. Shut the instrument down completely before removing any of the outside panels (to clean air filters, replace a fuse, etc.).

9.8 When changing the rotary pump oil, remember that the pump oil may be hot. The oil can cause a burn if allowed to contact the skin.

10.0 APPARATUS, MATERIALS, REAGENTS, EQUIPMENT, AND INSTRUMENTS

10.1 Apparatus and Equipment

10.1.1 Replacement special glass parts for the ICP-MS such as quartz torch bodies, injector tips and spray chambers may be ordered from a qualified vendor through the GEL Purchasing Agent.

10.1.2 Replacement ICP-MS interface parts such as sampling cones, skimmer cones and ion-optics can be purchased from a qualified vendor through the GEL Purchasing Agent.

10.1.3 Consumable materials such as tubing are often attainable from various scientific product companies. The GEL Purchasing Agent can help to find the best prices. These items may also be ordered from the instrument manufacturer if necessary. All orders must be placed through the GEL Purchasing Agent.

10.2 Reagents, Chemicals, and Standards

10.2.1 Reagents: Refer to Reagent Logbook

10.2.2 Standards: Refer to GL-LB-E-007 for Laboratory Standards Documentation and GL-LB-E-015 for Control of Laboratory Standards.

10.2.3 Other Chemicals: Additional compounds, surfactants, oils, cleaning agents, etc., may be routinely ordered through the GEL Purchasing Agent.

10.3 Instrumentation

10.3.1 Perkin Elmer ICPMS ELAN Model 6100 with IBM compatible PC, Monitor, Printer.

10.3.2 Perkin Elmer ICP-MS ELAN Model 9000 with IBM compatible PC Monitor, Printer.

10.3.3 CETAC Model ASX-500 Autosampler (PE 6100)

10.3.4 CETAC Model ASX-510 Autosampler with accessory autodiluter (PE 9000)

10.3.5 Neslab CFT75 recirculating bath provides cooling to the ICP-MS (PE 6100/ PE 9000)

10.3.6 CETAC ASXpress Rapid Sample Introduction System

11.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

11.1 Aqueous samples should be preserved with nitric acid to a pH of < 2 prior to receipt by the analyst. Solid samples should be kept at 0° ≤ 6° C prior to digestion.

11.2 Refer to GL-SR-E-001 for Sample Receipt, Login and Storage.

12.0 SAMPLE PREPARATION TECHNIQUES

12.1 All samples except drinking water with Turbidity < 1 NTU and samples specifically exempted by contract, are prepared in accordance with the following SOPs:

12.1.1 GL-MA-E-016 for Sample Preparation for Total Recoverable Elements by EPA Method 200.2 (USEPA Method 200.2)

12.1.2 GL-MA-E-006 for Acid Digestion of Total Recoverable or Dissolved Metals in Surface and Groundwater Samples for Analysis by ICP or ICP-MS (USEPA SW-846 Method 3005A)

12.1.3 GL-MA-E-008 for Acid Digestion of Total Metals in Aqueous Samples and Extracts for Analysis by ICP or ICP-MS (USEPA SW-846 Method 3010A)

12.1.4 GL-MA-E-009 for Acid Digestion of Sediments, Sludges and Soils (USEPA SW-846 Method 3050B)

12.1.5 GL-MA-E-021 for Total Digestion of Sediment Samples for Analysis by ICP or ICP-MS (ASTM D4698-92)

12.2 Additional filtration may be required to prevent clogging of sample introduction system.

12.3 All sample preparation records are stored in AlphaLIMS.

12.4 Sample spills should be handled as stated in Section 8.3.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

13.1 Routine Preventative and Special Operational (Failure)

13.2 Routine Preventative Maintenance (PM) Procedures are done as follows:

Frequency	Procedure
When Needed	Clean nebulizer tip after use. Replace peripump sample introduction tubing. Change pump hoses on drain systems. Check drain waste collection containers, and empty as necessary. Check Neslab water level and add water if required. Clean/replace interface cones. Clean/replace nebulizer. Clean/replace torch. Check/replace water filter.
Quarterly	Change oil in interface rotary pump (or as needed). Clean ion lenses 4-6 months (or as needed).
6 Months	Clean air filters.
12 months	Change pump oil in backing rotary pump. Evaluate/replace EM (electron multiplier)

13.3 Non-Routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

13.3.1 If the instrument will not function properly see the trouble shooting section in the appropriate Maintenance Manual.

13.3.2 If the analyst is unable to determine cause/fix instrument, the GEL Service Engineer is called, and if needed, the manufacturer's customer support number may be found in the owner's maintenance manuals.

13.4 Refer to ICP-MS Maintenance Logbook for routine records. Service call records are also available.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

14.1 Source standards records are recorded in AlphaLIMS.

14.2 Recommended Suppliers: Refer to source log and use Approved Vendors List maintained in Procurement.

14.3 Standards are receipted, labeled, prepared and stored in accordance with the GL-LB-E-007 for Laboratory Standards Documentation.

15.0 INSTRUMENT CALIBRATION

15.1 Samples may be analyzed manually or automatically.

15.1.1 Tuning for each instrument is performed daily according to the following directions and criteria.

15.1.2 PE 6100/ 9000: Aspirate a tuning solution consisting of 10 µg/L each of ^{9}Be, ^{24}Mg, ^{59}Co, ^{115}In and ^{208}Pb. Perform 5 replicates. Manufacturer's recommended tune criteria are as follows:

Parameter	Starting Point
^{9}Be	± 0.10 amu
^{24}Mg	± 0.10 amu
^{59}Co	± 0.10 amu
^{115}In	± 0.10 amu
^{208}Pb	± 0.10 amu
Ba^{++} net intensity mean	< 0.05 or 5%
CeO net intensity mean	< 0.03 or 3%
Be, Mg, Co, In, Pb net intensity RSD	< 5%
Resolution at 10% peak height	< 0.9 amu

15.1.3 Conduct additional tuning procedures as specified by client contract or other methodology.

15.1.4 If any of the preceding tune criteria does not meet the recommended requirements, investigate the problem, correct the situation, and reanalyze the tune sequence.

15.1.5 Standardization: Standardization is required on a daily basis.

15.2 Internal standards are used as appropriate for the analytes of interest. The internal standards are made in the appropriate acid and contain varying concentrations of such elements as ^{45}Sc, ^{74}Ge, ^{115}In, ^{175}Lu, and/or ^{181}Ta. The internal standard solution is mixed in-line with the sample stream using a dedicated channel of the peristaltic pump. Internal standards may be added at the time of analysis as an alternative to in-line mixing. Alternate internal standards may be used to meet client needs.

15.3 Calculations are described in the instrument manual.

15.4 Calibration standards vary according to method and equipment. A minimum of two, a blank and value standard, is required.

15.5 For required quality control standards refer to Section 21.0.

15.6 For continuing calibration requirements refer to Section 21.0.

15.7 For what to do when initial or continuing calibrations fail to meet requirements, refer to Section 21.0.

16.0 INSTRUMENT PERFORMANCE REQUIREMENTS

16.1 Before samples may be analyzed to generate reportable data, the instrument must have been tuned and calibrated. Also, the Initial Calibration Verification (ICV), which is prepared from an independent source, Initial Calibration Blank (ICB), the Reportable Detection Limit (CRDL), the Interference Check Standards (ICS-A, ICS-AB), and the Linear Range Standards (LRS) must meet the requirements stated in Section 21.2 for each analyte being reported, unless otherwise required by methodology, clients or contracts.

16.2 The instrument calibration and all continuing verification data is maintained in the printed hard copy file. The printouts are kept in chronological order by instrument. Recent files are in the metals laboratory; older records are archived in short or long-term storage.

17.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

17.1 Analyst training is conducted and certified in accordance with the GL-HR-E-002 for Employee Training.

17.2 Method performance is verified by the conductance of MDL studies in accordance with GL-LB-E-001 for The Determination of Method Detection Limits, and by the evaluation of LCS and LCS duplicates for each batch of samples.

18.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

18.1 All samples are introduced in a set measured quantity, via a peristaltic pump, through a nebulizer into a spray chamber and carried with argon gas through the Radio Frequency (RF) field to generate analyte ions that are selected and measured by the quadruple mass spectrometer.

18.2 Run Sequence

18.2.1 Instrument Calibration executed in accordance with Section 16.

18.2.2 Initial Calibration Verification steps include:

18.2.2.1 ICV

18.2.2.2 ICB

18.2.2.3 CRDL (low level ICV for 6020A)

18.2.2.4 ICS-A

18.2.2.5 ICS-AB

18.2.2.6 CCV

18.2.2.7 CCB

18.2.2.8 LRS

18.2.2.9 CCV

18.2.2.10 CCB

18.2.3 Sample Run (10 samples or less)

18.2.4 Continuing Calibration Verification:

18.2.4.1 CCV

18.2.4.2 CRDL (for SW-846 Method 6020A only and analyzed at end of batch).

18.2.4.3 CCB

18.2.5 Repeat steps 18.2.3 and 18.2.4 until end of run or verification is out of specification. When the latter occurs, repeat step 18.2.1 and continue with steps 18.2.2 and 18.2.3.

18.2.6 Repeat steps 18.2.3 through 18.2.5 until the end of the run or verification is out of specification. When latter condition occurs, repeat 18.2.1 and continue sequentially through 18.2.7.

18.2.7 Final Verification Steps

18.2.7.1 ICS-A (if required)

18.2.7.2 ICS-AB (if required)

18.2.7.3 CCV

18.2.7.4 CRDL (for SW-846 Method 6020A only)

18.2.7.5 CCB

NOTE: Method 6020A only requires there to be a closing low level continuing calibration standard (CRDL). For ease of analysis, the CRDL standard can be analyzed every 10 samples.

18.3 For data storage refer to Section 24.1.

18.4 General operation of the instrument.

18.4.1 The Perkin Elmer Model 6100 and Perkin-Elmer Model 9000 are inductively-coupled argon plasma mass spectrometers. The ICP-MS is capable of determining analytes from m/z = 6 (Li) through m/z = 238 (U). The operating software of the system is based on Microsoft Windows.

18.4.2 Set-up

18.4.2.1 Attach the nebulizer argon line to the quick-connect on the nebulizer's argon tube and ensure that it is tightly in place.

18.4.2.2 Attach the nebulizer and endcap to the spray chamber.

18.4.2.3 Attach sample pump tubing to the front peristaltic pump (various sizes may be used depending on need), and attach feed end to endcap.

18.4.2.4 If running manually, place the suction end of the sample tubing in acidified rinse water; otherwise attach it to the autosampler.

18.4.2.5 Ensure that drain hose is connected to the spray chamber and properly plumbed through the drain peristaltic pump.

18.4.3 Run Procedure

18.4.3.1 Refer to the respective owner's manuals for specific instructions for tuning, sequence loading, and method development on each instrument; ELAN 6000/6100 software guide; ELAN 9000 software guide.

18.4.3.2 The owner's manual for each instrument is located in the ICP-MS laboratory.

18.4.4 Typical Analysis Problems

18.4.4.1 Sample Overrange: If a requested element is overrange for a sample, it is necessary to dilute the sample and rerun. Dilution factors must be taken into account when reporting final values.

18.4.4.2 Interferences: Although the ICP-MS can compensate for many interferences with appropriate correction factors, unpredicted interferences may still occur. If the analyst suspects this, then the sample should be diluted and rerun. Dilution factors must be taken into account when reporting final values.

18.4.4.3 Torch/Sample Introduction Drift: Various changes in torch plasma conditions or sample introduction can have a great effect on the detector counts. They must be corrected or the instrument must be re-standardized.

18.4.4.3.1 If oils or solid samples have been run, and the CCV is not acceptable, allow the instrument to rinse 15 to 20 minutes. If CCV is then acceptable, reanalyze the samples and continue. If the CCV again fails its requirements, re-standardize as necessary.

18.4.4.3.2 If sample introduction drift is suspected, check peristaltic pump tubing for collapse and replace as needed.

18.4.4.3.3 Tubing connections may become loose allowing air to bubble into the sample path. Tighten or replace tubing. If necessary, seal with Parafilm.

18.4.4.4 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 100 times above the IDL for non-DOE Clients, 100 x the MDL for DOE-Alb Clients, and 50 times the LOQ for DoD QSM in the original sample), an analysis of a five fold (1 + 4) dilution should agree within 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

18.5 Power switches and auxiliaries

18.5.1 Each instrument has one main power switch. Refer to the respective maintenance manuals for the location (ELAN 6100 and ELAN 9000 Hardware Guide). This switch remains on except while servicing the instrument.

18.5.2 The computer system has 3 power cords all connected to a switchable power strip: the computer main, the monitor and the printer power cords. The power to these is left on while the instrument is not in use for short times (e.g. overnight).

18.5.2.1 The main computer switch is on the front of the CPU.

18.5.2.2 The ***monitor switch*** is on the front of the monitor itself.

NOTE: If the computer is left in use without an analyst present for an extended period of time, turn the monitor off to prevent screen burn-in.

18.5.2.3 The ***printer switch*** is on the lower front of the printer. Refer to printer manual for operating instructions.

18.5.3 Argon gas is provided through a manifold from the storage tank. Under normal conditions a constant argon flow is available.

18.5.4 Start-up

18.5.4.1 Before starting, ensure that the power is on and the vacuum system is switched on.

18.5.4.2 The owner's manual for each instrument provides specific instructions for ignition of the plasma (refer to Section 18.5.1 for software manuals).

18.5.4.3 The plasma should be steady and should not flicker.

18.5.4.4 Once ignition has occurred, levels may be adjusted; it is best to set levels appropriate to the method by loading or editing an appropriate tune file and allow 30 minutes for warm-up.

18.5.5 Shutdown

18.5.5.1 When the plasma is off, the instrument is either in Standby or Shutdown mode. The ICP-MS should be completely shut down only in case of major maintenance, relocation of the instrument, or when the lab is closed for an extended time.

18.5.5.2 Daily shutdown (if required): Refer to the respective owner's manual shutdown procedures (Refer to Section 18.5.1 for software manuals.)

18.6 Sample quantity requirements are approximately 5 mL for each run with the nebulizer. If out of specification or range, further sample may be necessary for reruns.

18.7 The autosampler can be used by attaching introduction tube to sample introduction system, and rinsing tubing to peristaltic pump and following autosampler table set-up and procedures. To define a sequence, refer to the appropriate software manual (refer to Section 18.5.1).

19.0 CALCULATIONS AND DATA REDUCTION METHODS

19.1 Any dilutions, concentrations, or preparation factors must be taken into account prior to reporting data to a client.

$$\text{Relative Percent Difference} = \frac{100 * |\text{Sample 1 Value - Sample 2 Value}|}{\frac{(\text{Sample 1 Value + Sample 2 Value}}{2}}$$

$$\text{Matrix Spike Recovery} = \frac{100 * (\text{Spike Value} * DF * PF - \text{Sample Value} * DF * PF)}{\text{Spike Nominal Concentration} * DF * PF}$$

$$\text{Post Spike Recovery} = \frac{100 * (\text{Spike Value - Sample Value})}{\text{Spike Nominal Concentration}}$$

$$\text{LCS Recovery} = \frac{100 * (\text{Sample Value} * DF * PF)}{\text{Nominal Concentration} * DF * PF}$$

Where: Sample Value = instrument reading for the sample
Spike Value = instrument reading for the spiked sample
DF = Dilution Factor
PF = Preparation Factor

Relative Error Ratio (RER) 2 sigma equation:

$$RER = \frac{|\text{Sample Activity} - \text{Duplicate Activity}|}{\sqrt{(\text{Sample 2 sigma TPU}/1.96)^2 + (\text{Duplicate 2 sigma TPU}/1.96)^2)}} = \leq 3$$

NOTE: Activity calculations can be found in Appendix 4 of this SOP. Two sigma TPU calculations can be found in SOP GL-QS-E-014.

19.2 Care must be taken that the correct units are being employed.

20.0 DATA RECORDING

20.1 ICP-MS data are generally stored to the hard disk drive of the ICP-MS computer system and printed at the instrument as each sample is analyzed.

20.2 ICP-MS samples are generally analyzed in three replicates (minimum of 2) and the reported value is the average of the replicates. The data for individual replicates is stored in the computer.

20.3 Data are processed locally by manual or programmable procedures to eliminate unused data, to enter dilution factors, and to enter relevant conversion factors prior to uploading to AlphaLIMS.

21.0 QUALITY CONTROL REQUIREMENTS

21.1 Frequency of Quality Control Activities (also refer to Appendix 1)

21.1.1 Initial Calibration Verification (ICV) is performed immediately following each calibration and Continuing Calibration Verification (CCV) is performed after at least every 10 samples.

21.1.2 Initial Calibration Blank (ICB) is performed immediately following the ICV and Continuing Calibration Blanks (CCB) must run with each CCV.

21.1.3 An Interference Check Standard (ICS) is analyzed at the beginning of each analytical run and at least once every twelve hours (if required). Additional requirements may be specified by client contract or methodology.

21.1.4 The PQL standard is analyzed after each calibration and recommended at least every 10 samples between the CCV and CCB analyses for SW-846 Method 6020A. Method 6020A requires analysis at the end of every batch and only recommends analysis every 10 samples. This standard may also be labeled as a CRDL standard.

21.1.5 A method blank (MB) is performed for each batch of 20 or fewer samples or per client requirement.

21.1.6 A matrix spike (MS) and a duplicate (DUP), or matrix spike (MS) and matrix spike duplicate (MSD) are analyzed for each batch of 20 or fewer samples or per client requirements (5% frequency). For EPA 200.8, the same QC are analyzed for each batch of 10 or fewer samples (10% frequency).

21.1.7 A laboratory control sample (LCS) is analyzed with each batch of 20 or fewer samples. An LCS duplicate (LCS DUP) may be added if required by the client.

21.1.8 Serial dilutions or analytical spikes are analyzed to confirm the presence or absence of interferences when analyzing a new matrix type. The serial dilution is generally performed at a 5x of the test sample.

21.1.9 A post spike (PS) is required for DoD-QSM or SW 846 6020A if the matrix spike (MS) or matrix spike duplicate (MSD) recoveries fall outside of the limits in section 21.2.8. Post spikes can also be performed at client request.

21.2 Acceptance Limits (also refer to Appendix 2)

21.2.1 ICV results must be between 90% and 110% of the true values for work under EPA SW-846 Method 6020A or EPA Method 200.8. CCV results must be between 90% and 110% of the true values for work under EPA Method 200.8 or SW846 Method 6020A.

NOTE: The ICV is the second source standard and may be used as the CCV as it also will show calibration verification.

21.2.2 ICB and CCB results must have an absolute value less than the Reporting Limit (RL). For DoD QSM analysis, the absolute value must be less than the LOD. If this is not the case, the reason for the out-of-control condition must be found and corrected, or any data reported must be 10 times greater than the absolute value for the element or less than the RL.

21.2.3 Interference Check Sample results must be monitored at the beginning of an analytical run or once every 12 hours, whichever is more frequent, for work under SW-846. The ISCA and ICSAB must recover 80-120% the reporting level for the spiked analysis and must have an absolute value less that 2x the reporting level for the non-spiked analyte. For DoD QSM, the ICSA must have an absolute value of less than the absolute value of the LOD analytes.

21.2.4 The Linear Range Standard (LRS) is analyzed within the calibration verification read back and must fall between 90% and 110% of the true values. Meeting these criteria allows target analyte concentration to be reported up to the LRS concentration thus extending the calibration range of the instrument. Any sample concentrations above the LRS concentration will be diluted to fall below the concentration of the linear calibration range standard.

21.2.5 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between

30% and 120% (or 70% and 130% for SW-846 Method 6020A) of the intensity of that internal standard in the initial calibration then the sample must be diluted five fold (1 + 4) and reanalyzed with the addition of appropriate amounts of internal standards. The intensity levels of the internal standards for the calibration blanks (ICB and CCB) and instrument check standards (ICV and CCV) must agree within ± 20% of the intensity level of the internal standard of the original calibration solution. For work done under EPA Method 200.8, the internal standard responses of any one internal standard must not deviate more than 60% to 125% of the original response in the calibration blank. Five internal standards (^{45}Sc, ^{74}Ge, ^{115}In, ^{175}Lu, and/or ^{181}Ta) are used to cover the mass ranges reported. Refer to Appendix 3 for list of internal standard/ analyte associations. Other exotic analytes may be used as needed. Refer to Section 15.2.

21.2.6 Method blank results must be lower than the PQL or less than 10% of the determined value of all samples in the batch. When performing work under EPA Method 200.8, if LRB (laboratory reagent blank) values are 10% or more of the analyte level determined for a sample or are 2.2 times the analyte MDL, then fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained. For DoD QSM work, the absolute value must be less than ½ RL or less than 10% of the determined value of all samples in the batch. Al, Fe, Mg, Ca, Na, and K must be less than the RL.

21.2.7 LCS results, and LCS duplicate (if performed), must be within process control limits as established by Statistical Process Control, manufacturer's certification, or method requirements.

21.2.8 Matrix spikes with recoveries between 75% and 125% suggest the absence of interference for work under EPA Method 200.8. Matrix spikes with recoveries between 75% and 125% suggest the absence of interference for work under SW-846 Method 6020 and SW-846 Method 6020A. Matrix spikes with recoveries between 80% and 120% suggest the absence of inteferences for work under DoD QSM.

21.2.9 The relative percent difference (RPD) between a sample and a sample duplicate should be within ± 20% if the analyte concentration in the sample or duplicate is greater than 5 times the RL. If either the sample or duplicate concentration is less than 5 times the RL, the results should agree within the absolute value of the RL. Results less than the MDL or IDL are not evaluated. The relative error ratio (RER) between a sample and a sample duplicate should be ≤ 3%.

21.2.10 Serial dilution results that agree within 10% of the original analytical results, if the original results are greater than 100 times the instrument detection limit or greater than 50 times the LOQ, suggest the absence of interference.

21.2.11 Post spikes with recoveries between 75% and 125% under EPA Method 200.8 and SW-846 Method 6020, and between 80% and 120% under SW-846 6020A suggest the absence of interference.

21.3 Out-of-Control Situations

21.3.1 ICV and/or CCV failure requires recalibration of the instrument and/or preparation of new standard solutions. Samples analyzed prior to or after calibration verifications that are not acceptable for required analytes must be reanalyzed. An ICV or CCV that has failed may be rerun once only if there is an attributable cause known to have affected the CCV only and not the previous samples. Examples of an acceptable cause may be a sample tip out of solution during analysis, an incorrectly prepared CCV, or obvious carryover in the CCV from a very high sample immediately prior to the CCV. If a CCV is reanalyzed, the data must be lined through, initialed and dated, and the reason for the rerun must be documented on the raw data. In addition, corrective action should be taken to eliminate the cause of the initial CCV failure to prevent future occurrence.

21.3.2 ICB and CCB failure requires recalibration of the instrument and/or calibration blank solution to be remade. The CCB is acceptable if the level of analyte in the corresponding sample(s) is 10 times greater or less than the PQL for the failing element. For DoD QSM work, the absolute values must be less than the LOD or less than 10% of the determined value of all samples in the batch.

21.3.3 ICS failure requires that the instrument be re-calibrated or the interferences be corrected, via recalculation, of Interelement Correction Factors so that the ICS can be read within the required limits before samples are analyzed. ICS failure at the end of an analysis period will require that the samples' ICSA run for the affected analyte(s) during that period to be reanalyzed. The ICSA and ICSAB must recover 80-120% for the spiked analytes and must have an absolute value less than 2x the reporting level for the non-spiked analytes. For DoD QSM, the ICSA must have an absolute value of less than the LOD for the non-spiked analytes.

21.3.4 LRS failures limit the reportable calibration range to the high standard in the calibration curve. Any sample concentration that falls above the high calibration standard will be diluted to fall within the calibration range.

21.3.5 Internal Standard failure requires one or more of the following: five-fold dilution of the sample, correction of the problem, termination of analysis, recalibration of the instrument, and/or reanalysis of the affected samples depending on whether the failure is due to the samples or the instrumental drift.

21.3.6 Method blank results higher than the PQL and greater than 10% of any sample value in that batch that has concentrations above the PQL require that batch be redigested and reanalyzed. If the method blank results are less than -2x PQL there may be significant interference, calibration, or contamination problems with the sample, instrument, or calibration standards that must be resolved before the batch can be analyzed. For DoD QSM work, the absolute value must be less than ½ RL or less than 10% of the determined value of all samples in the batch. Al, Fe, Ca, Mg, Na, and K must be less than RL.

21.3.7 Matrix spikes, duplicates and spike duplicates are used only as indicators of method effectiveness on that sample and will not be used as acceptability criteria for the process, unless a special requirement of the client.

21.3.8 LCS and/or LCS duplicate results outside of established acceptance limits require the batch to be redigested and reanalyzed.

21.3.9 When analytical results suggest the presence of interference, one of the methods listed in Section 18.4.4.2 should be employed.

21.3.10 The CRDL standard should be evaluated, but no action is required if the results fall outside of the 70-130% advisory window. For DoD QSM, the CRDL standard must be 80-120% of the true value or recalibration is required. For SW-846 Method 6020A, the CRDL standard must be 70-130% of the true value or recalibration is required. This also includes the low level continuing calibration verification standard analyzed every 10 samples. Sample results can be evaluated for reporting if they are at least 2x the CRDL for a given analyte.

21.4 Corrective actions taken for data not conforming to the requirements in Section 21.2 are stated in Section 21.3. If these corrective actions can be taken by the analyst prior to the acceptance of the data, then no nonconformance documentation is required. However, if these corrective actions include redigestion of the batch or sample, if the data have already been accepted, or if the corrective action requires an instrument service call, then a nonconformance and/or corrective action report should be completed. This report includes the date, person requesting the action, sample(s) or batch(s) affected, and action requested, all provided by the requester. The person taking the action will provide any pertinent comments, their signature, and the date the action is completed. The disposition of the nonconformance will then be verified by the Quality Systems specialist. These reports will be kept on file. Refer to GL-QS-E-002 for Documentation of Nonconformance Reporting and Dispositioning and Control of Nonconforming Items.

21.5 Analytical data are evaluated for conformance with the requirements stated in Section 21.2 by the analyst during and/or after the analysis, but before the data are entered into AlphaLIMS. Data may be accepted or rejected by the analyst at this point or by the data reviewer(s) as stated in Section 22.0.

22.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

22.1 After samples are analyzed, the data must go through the review process before it can be reported out of the lab. The analyst who performed the analysis will review the raw data prior to uploading it into AlphaLIMS. The upload process may be handled by the analyst or by a data entry clerk.

22.2 After the upload is complete, an AlphaLIMS data report is generated that will be passed (along with the batch sheet, data review checklist, and the raw data) to another analyst for a peer review. Discrepancies found in this review will be resolved before the batch data are passed and the status updated.

22.3 When this peer review is completed and all of the data are found to be acceptable, the reviewer signs and dates the batch data report and updates the status of the batch to done. If the reviewer determines that the reviewed data are not acceptable and requires additional work or correction, data are returned to the analyst or representative with an appropriate explanation.

22.4 Listed below are the data review responsibilities of the Analyst and Peer Reviewer:

22.4.1 Analyst Review is performed by the analyst who generated the data before the data are submitted for entry into AlphaLIMS. Analyst completes and attaches the run data cover sheet to the printout.

22.4.2 Peer Analyst Review is performed by an individual who did not perform the analysis but is familiar with the analytical method used and the reporting requirements. This person will review the complete data report after all data are entered, will ensure that any data entry corrections are made before data are approved, and will complete the reviewer portion of the data review check list. If the data do not meet the necessary quality requirements and need further analysis, they are returned to the analyst or representative.

22.5 A Third Review is performed for Data Packages (level 3 to level 6 CLP-Like) and/or by client requirement. This review is by the Metals Team Validator or other qualified person.

22.6 Specific items that are reviewed at each level include the following:

22.6.1 Analyst Review: Before data is submitted for entry into AlphaLIMS.

22.6.1.1 All analyses in the batch are completed.

22.6.1.2 Any corrections and comments on the data are properly initialed and dated.

22.6.1.3 Proper standard identification numbers appear on the runlog to ensure traceability from the data to original source standards.

22.6.1.4 All data are complete and accurate in the AlphaLIMS data report.

22.6.1.5 Data acceptance limit criteria identified in Section 21.2 are met or an explanation given.

22.6.2 Peer Analyst Review: Before data are submitted for further review or update:

22.6.2.1 All data are complete and accurate in the AlphaLIMS Data Report.

22.6.2.2 Any exceptions or shortcomings have been sufficiently explained or corrected.

22.6.2.3 Data are reported in the proper units or an explanation is given.

22.6.2.4 Prep factor and dilution calculations by AlphaLIMS are present in the data report and AlphaLIMS calculations are correct.

22.6.2.5 LCS and Spike Recoveries and RPD calculations by AlphaLIMS are correct, and the values are within control limits.

22.7 When the data review is completed and the data have been reported out of the lab, they are bound with the batching sheet and kept on file in the lab.

22.8 The complete data review process requires the use of the Prep Log Book, Prep data report, batch sheet, AlphaLIMS data report, raw instrument data, and runlog.

23.0 DATA REPORTING

23.1 To report data after the review process has been completed:

23.1.1 Enter the AlphaLIMS program through an available terminal and select DATA MENU, BATCH ITEMS, CHANGE BATCH STATUS.

23.1.2 Enter the Batch Number and "Submit."

23.1.3 Use the down arrow key to move the cursor down the new status column to the end. Change status from REVW to DONE and "Save."

24.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

24.1 Records of the instrumental analysis, operation, and maintenance are maintained as follows:

24.1.1 Run logs are an accurate chronology of what the instrument did during a specified period of time. The logs detail the standard name or sample number for each standardization or analysis, the analyst identification, and the date and time of each analysis or standardization. This information is periodically retrieved from the instrument data files, printed in chronological sequence, and maintained as documentation of the sequence of events and as a reference for the raw data.

24.1.2 Extraction/Digestion Logs are maintained in accordance with the established procedures in the areas where these processes are performed.

24.1.3 Instrument Maintenance Logs are chronological representations of all maintenance activities involving the instrument operation. This record is kept in bound composition books and consists of the details of the action, who performed it, when it was performed, and when instrument was returned to operation.

24.1.4 Batch Sheets accompany the batch of samples through digestion and analysis and then accompany the raw analytical data through data entry and data review until the batch status is changed to "DONE" in the laboratory. This record is maintained in the Metals group files.

24.1.5 Batch Data Reports are generated to be used in the peer data review. After the batch is reviewed, corrected if necessary, and updated to "DONE," the batch data report is stored with the Batch sheet.

24.1.6 Raw Instrument Data are generated as the analyses are performed and from AlphaLIMS after the data are entered and attached to the batch sheet to be used in the data review process and kept in the Metals group files.

25.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES, AND REAGENTS

25.1 Standard solutions that must be disposed are taken to the Waste Disposal coordinator for disposal in accordance with Laboratory Waste Management Plan, GL-LB-G-001.

25.2 Sample digestates are stored in the lab for a specified period of time following analysis. At this time, they are composited into a waste container that is picked up by the Waste Management Technician for proper disposal.

25.3 Radioactive Waste:

25.3.1 Samples returned to sample storage

25.3.2 Drain waste collected in the radioactive waste carboy is dumped when full into the appropriate 55 gallon drum sitting outside the ICPMS laboratory. Ultimate disposal of liquid radioactive waste done by waste management department.

25.3.3 Implements, vials, gloves, etc., are wrapped and labeled with radioactive tape and placed in the radioactive waste container in high bay area.

25.3.4 Expired Standard Solutions: Refer to Section 25.1.

26.0 REFERENCES

26.1 Perkin Elmer ELAN 9000 Hardware Guide

26.2 Perkin Elmer ELAN 6100 Hardware Guide

26.3 Perkin Elmer ELAN 9000 Software Guide

26.4 Perkin Elmer ELAN 6000/6100 Software Guide

26.5 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods. Volume 1A, USEPA SW-846, Third Edition, Revision 2, September 1994.

26.5.1 Method 6020A, "Inductively Coupled Plasma – Mass Spectrometry," Revision 1, February 2007.

26.5.2 Method 6020, "Inductively Coupled Plasma – Mass Spectrometry," Revision 0, September 1994.

26.5.3 Method 3005A, "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy", Revision 1, July 1992.

26.5.4 Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy," Revision 1, July 1992.

26.5.5 Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils", Revision 2, December 1996.

26.6 USEPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry," Revision 5.4, May 1994.

26.7 2001 Annual Book of ASTM Standard, D4698-92 "Standard Practice for Total Digestion of Sediment Sampler for Chemical Analysis of Various Metals."

26.8 Conversion Constants for Uranium Isotopes, Dr. Robert Litman, April 2009.

26.9 Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2, October 25, 2010.

26.10 U.S. Department of Energy, Quality Systems for Analytical Services (DOE QSAS). Rev 2.6, November 2010.

27.0 HISTORY

Revision 25: Clarifications on analyte lists, internal standards, and method requirements.

Revision 24: Updated section on sample preparation techniques to include procedure GL-MA-E-016

Revision 23: Updated sections 15.2, 21.2.5 and Appendix 3 to four internal standards. Removed outdated SOP references.

Revision 22: Editorial corrections only.

APPENDIX 1: FREQUENCY OF QUALITY CONTROL ACTIVITIES

(For illustrative purposes only)

Frequency of Quality Control Activities

Method/ Frequency	SW-846 6020	EPA 200.8	SW-846 6020A
Calibration Std readbacks	Not required	Not required	Not required
ICV	Per calibration	Per calibration	Per calibration
ICB	Per calibration	Per calibration	Per calibration
PQL	Per calibration	Per calibration	Per calibration and at end of each analytical batch.
ICSA	Per calibration	Per calibration	Per calibration
ICSAB	Per calibration; every 12 hours after	Per calibration	Per calibration; every 12 hours after
Linear Range Standard (LRS)	Per calibration, if applicable	Per calibration, if applicable	Per calibration, if applicable
CCV	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
CCB	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
Method Blank	5% or per batch	5% or per batch	5% or per batch
LCS – liquid LCS – soil	5% or per batch	5% or per batch	5% or per batch
Matrix Spikes	5% or per request	10% or per request	5% or per request
Sample Duplicates	5% or per request	5% or per request	5% or per request
Serial Dilutions	5% or per request	5% or per request	5% or per request
Matrix Spike Duplicates	5% or per request	10% or per request	5% or per request
Post-Digestion Spikes	5% or per request	10% or per request	5% or per request

APPENDIX 2: ACCEPTANCE LIMITS

Method/ Acceptance Criteria	SW-846 6020	EPA 200.8	DoD QSM	SW-846 6020A
Calibration Std readbacks	Not required	Not required	Not required	Not required
ICV	90% - 110%	90% - 110%	90%-110%	90% - 110%
ICB	< absolute value of RL	< absolute value of RL	< LOD	< absolute value of RL
PQL/CRI (CLP)	70% - 130% advisory limits only	70% - 130% advisory limits only	80%-120% or investigate and recalibrate	70% - 130% or investigate and recalibrate
ICSA	80-120% for major components; ± 2x RL for non-spiked	80-120% for major components; ± 2x RL for non-spiked	80%-120% for major compounds; ± LOD for non-spiked	80-120% for major components; ± 2x RL for non-spiked
ICSAB	80%-120%	80%-120% (may be requested)	80%-120%	80%-120%
Linear Range Standard (LRS)	90%-110%, or up to the high calibration standard	90%-110%, or up to the high calibration standard	90%-110%, or up to the high calibration standard	90%-110%, or up to the high calibration standard
CCV	90% - 110%	90% - 110%	90%-110%	90% - 110%
CCB	± RDL	± RDL	< LOD	± RDL
Method Blank	± RDL	± RDL	± ½ RL except for Al, Fe, Mg, Ca, Na, and K	± RDL
LCS - liquid LCS - soil	80% - 120% current SPC limits	85% - 115% current SPC limits	80%-120%	80% - 120% current SPC limits
Matrix Spikes	75% - 125%, when applicable	75% - 125%, when applicable	80%-120%	75% - 125%, when applicable
Sample Duplicates	0% - 20% when greater than 5X RL, ± RL when less than 5X RL	0% - 20% when greater than 5X RL, ± RL when less than 5X RL	0% - 20% when greater than 5X RL, ± RL when less than 5X RL	0% - 20% when greater than 5X RL, ± RL when less than 5X RL
Serial Dilutions	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when applicable (> 50x LOQ)	0% - 10% of initial raw value, when applicable
Post-digestion spikes	75%-125%, when applicable	75%-125%, when applicable	75%-125%	80%-120%, when applicable
Internal Standards	30%-120%, samples 80%-120% for ICB, ICV, CCV, CCB	60%-125% for all	30%-120%	70%-130%, for all
Matrix Spike Duplicate	0% - 20% when greater than 5X RL, ± RL when less than 5X RL	0% - 20% when greater than 5X RL, ± RL when less than 5X RL	0% - 20% when greater than 5X RL, ± RL when less than 5X RL	0% - 20% when greater than 5X RL, ± RL when less than 5X RL

APPENDIX 2-Cont'd

Method/ Acceptance Criteria	SW-846 6020	EPA 200.8	DoD QSM	SW-846 6020A
Sample Duplicates RER activity	≤ 3%	≤ 3%	≤ 3%	≤ 3%

APPENDIX 3: INTERNAL STANDARDS WITH ASSOCIATED ANALYTES/ISOTOPES

IS ^{45}Sc	IS ^{74}Ge	IS ^{115}In	IS ^{175}Lu ^{181}Ta
^{7}Li	^{66}Zn	^{88}Sr	^{133}Cs
^{9}Be	^{67}Zn (calc)	^{90}Zr	^{135}Ba (calc)
^{11}B	^{68}Zn (calc)	^{98}Mo	^{137}Ba
^{23}Na	^{75}As	^{105}Pd	^{139}La
^{24}Mg	^{77}Se (calc)	^{107}Ag	^{140}Ce
^{27}Al	^{82}Se	^{111}Cd	^{141}Pr
^{31}P	^{83}Kr (calc)	^{114}Cd (calc)	^{142}Nd
^{39}K		^{120}Sn	^{152}Sm
^{43}Ca		^{121}Sb	^{153}Eu
^{47}Ti		^{123}Sb (calc)	^{158}Gd
^{52}Cr			^{159}Tb
^{53}Cr (calc)			^{178}Hf
^{55}Mn			^{187}Re
^{57}Fe			^{195}Pt
^{59}Co			^{197}Au
^{60}Ni			^{205}Tl
^{63}Cu (calc)			^{208}Pb
^{65}Cu			^{209}Bi
			^{232}Th
			^{233}U
			^{234}U
			^{235}U
			^{236}U
			^{238}U

*(calc) – isotope used in calculations

APPENDIX 4: RADIOCHEMISTRY CONVERSION CALCULATIONS FOR URANIUM ISOTOPES

Conversion for liquids (µg/L x CF = pCi/L)
^{233}U (µg/L to pCi/L) = 9640.6
^{234}U (µg/L to pCi/L) = 6224.9
^{235}U (µg/L to pCi/L) = 2.1615
^{236}U (µg/L to pCi/L) = 64.698
^{238}U (µg/L to pCi/L) = 0.33627

Conversion for solids (mg/kg x CF = pCi/g)
^{233}U (mg/kg to pCi/g) = 9640.6
^{234}U (mg/kg to pCi/g) = 6224.9
^{235}U (mg/kg to pCi/g) = 2.1615
^{236}U (mg/kg to pCi/g) = 64.698
^{238}U (mg/kg to pCi/g) = 0.33627

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ACID DIGESTION OF

SEDIMENTS, SLUDGES, AND SOILS

(GL-MA-E-009 REVISION 22)

APPLICABLE TO METHODS:
EPA SW-846 3050B Modified

PROPRIETARY INFORMATION

TABLE OF CONTENTS

1.0 STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

2.0 METHOD CODE

2.1 EPA SW-846 3050B Modified

3.0 METHOD OBJECTIVE/PURPOSE

To describe the manner in which sediments, sludges, and soils for Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis are digested by EPA SW-846 Method 3050B Modified. Samples digested by this procedure are applicable for analysis by SW-846 methods 6010B and 6020. Included in this standard operating procedure is guidance for paint and jewelry preparation.

4.0 METHOD SUMMARY

A representative portion of sample is digested with nitric acid and hydrogen peroxide. This digestate is then refluxed with hydrochloric acid for ICP analysis only. Samples prepared by this method may be analyzed for all the listed metals. Other metals may be analyzed if they pass control standard criteria:

Aluminum	Copper	Palladium	Terbium
Antimony	Europium	Phosphorus	Tin
Arsenic	Gold	Platinum	Thorium
Barium	Hafnium	Praseodymium	Titanium
Beryllium	Iron	Rhenium	Thallium
Bismuth	Lanthanum	Ruthenium	Tungsten
Boron	Lead	Samarium	Uranium
Boron-10	Lithium	Selenium	Uranium-233
Cadmium	Magnesium	Silica	Uranium-234
Calcium	Manganese	Silicon	Uranium-235
Cerium	Molybdenum	Sulfur	Uranium-236
Cesium	Neodynium	Sodium	Uranium-238
Chromium	Potassium	Silver	Vanadium
Cobalt	Nickel	Strontium	Zinc
			Zirconium

This method is not a "total" digestion technique for most samples. It is a very strong acid digestion that will dissolve all elements that could become "environmentally available" by design; elements bound in silicate structures (boron, silicon, silica) are not normally dissolved by this procedure as they are not usually mobile in the environment.

5.0 APPLICABLE MATRICES

5.1 Soils

5.2 Sludges

5.3 Sediments

5.4 Solid debris/powders

5.5 Heavy oils

5.6 Filters

5.7 Paints

5.8 Metal jewelry

6.0 HOLD TIME

Holding time is 180 days from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

Solid samples are not preserved but should be stored at 0°- 6°C.

8.0 INTERFERENCES

There are rarely any interferences with this digestion. If any are encountered, consult the group leader or quality officer before continuing.

9.0 PERFORMANCE CHARACTERISTICS

Method detection limits (MDLs) are performed annually and method detection limit verification (MDLVs) are performed quarterly.

10.0 DEFINITIONS

10.1 Blank: Type I water that has been taken through the digestion process. The blank is used to determine the amount of background contamination.

10.2 Laboratory Control Sample (LCS): A certified reference material that has been taken through the digestion process. The LCS is used to determine digestion accuracy and to determine if the digestion process is in control.

10.3 Laboratory Control Sample Duplicate (LCS DUP): A duplicate of the LCS. The LCS DUP is used to determine reproducibility and to indicate precision.

10.4 Matrix Spike (MS): A sample that has added to it a known amount of solution containing known concentrations of analytes. The MS is used to determine the presence or absence of interferences and matrix effects in the digested sample.

10.5 Matrix Spike Duplicate (MSD): A duplicate of the MS. The MSD indicates reproducibility.

10.6 Sample Duplicate (DUP): A duplicate of a sample. The DUP indicates reproducibility.

10.7 AlphaLIMS: The Laboratory Information Management System used at GEL.

10.8 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

11.0 ANALYST VERIFICATION

Before a technician/analyst is allowed to analyze samples without supervision, he or she is trained by qualified personnel and is required to successfully analyze a proficiency sample. Training records are maintained as quality records (Refer to GL-QS-E-008).

12.0 DOCUMENTATION OF DATA

Sample preparation data are recorded in AlphaLIMS.

13.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

CONCENTRATED HYDROCHLORIC ACID AND NITRIC ACID ARE EXTREMELY CORROSIVE AND CAN CAUSE SEVERE BURNS TO THE SKIN.

CONCENTRATED 30% HYDROGEN PEROXIDE IS A VIOLENT OXIDIZER. KEEP AWAY FROM OPEN FLAMES, AND RINSE WITH WATER IF SKIN CONTACT OCCURS.

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as potential health hazards, and reduce exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

13.3 Personal protective equipment

13.3.1 Disposable gloves are worn and changed frequently when working with acids, glassware, or samples. Dirty gloves pose a contamination hazard to the samples. Gloves that have holes can be dangerous to the wearer by allowing acids and toxic metals to come in contact with skin.

13.3.2 Hood doors are pulled down partially while digesting samples. Acidified samples can splash and pop as they are being heated.

13.3.3 To protect clothes and skin from exposure to corrosive material, wear a lab jacket.

13.4 Prior to handling radioactive samples, analysts must have had radiation safety training and must understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Wear plastic apron over lab coat when working with radioactive samples.

13.4.2 Protect counter tops with counter paper, or work from radioactive sample handling trays.

13.4.3 Prohibit admittance to immediate work area.

13.4.4 Post signs indicating radioactive samples are in the area.

13.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from the Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.7 Fire escape routes are posted in the lab, and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician submits the list of samples needed to the sample custodian group. The sample custodian removes the appropriate sample from the cooler and scans it using the barcode scanner to the appropriate area of the lab. The analyst then takes custody of the samples and scans them to the sample batch. The samples are now ready to be prepared or analyzed.

14.2 Analysts/technicians are responsible for retrieving their own samples when the sample custodian is unavailable.

15.0 INSTRUMENT/EQUIPMENT/GLASSWARE

15.1 Equipment

15.1.1 Air displacement pipettes

15.1.1.1 5-10 mL with disposable tips

15.1.1.2 0.5-5 mL with disposable tips

15.1.1.3 100-1000 µL with disposable tips

15.1.1.4 10-100 µL with disposable tips

15.1.2 Environmental Express hot blocks or equivalent

15.1.3 Analytical balance capable of reading to three decimal places

15.1.4 Certified disposable 50 mL digestion tubes (polypropylene)

15.1.5 Ribbed disposable watch glasses (polypropylene)

15.1.6 Water resistant lab markers

15.1.7 Styrofoam trays to handle up to 25 digestion tubes

15.1.8 500 mL Nalgene squirt bottle

15.1.9 Teflon chips

15.1.10 1-inch white laboratory tape

15.1.11 Borosilicate beakers (various sizes)

15.1.12 Borosilicate watch glasses (various sizes)

16.0 REAGENTS

16.1 Nitric acid (HNO_3), concentrated high purity grade 70% nitric acid

16.2 Hydrochloric acid (HCl), concentrated high purity grade 37% hydrochloric acid

16.3 Hydrogen peroxide (H_2O_2), concentrated 30% hydrogen peroxide

16.4 Type I deionized (DI) water.

16.5 Multi-element spiking solutions are purchased from NIST-traceable vendors.

17.0 PREPARATION OF SAMPLES

A batch consists of samples of the same matrix and quality control (QC) samples that are digested together. Each of the quality control samples listed in steps 10.1 through 10.6 must be included in each batch at the frequency listed or as per client request. The blank, LCS, and/or LCS DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent. The MS, MSD, and/or DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent, or per specified client/program requirements.

17.1 Glassware preparation:

17.1.1 Glassware that has been cleaned according to GL-LB-E-003 for Glassware Preparation is soaked in a water and acid mixture for at least 30 minutes.

17.1.2 After soaking, the glassware is rinsed with copious quantities of Type I water and then inverted over clean, absorbent paper or onto a rack for drying.

17.2 Label the Teflon beakers or centrifuge tube with the sample numbers in the batch. If centrifuge tube is to be used for measuring initial and final volumes it must be calibrated before usage. Refer to GL-LB-E-026 for centrifuge tube testing procedure.

17.3 Refer to GL-LB-E-029 for subsampling instructions. Mix the sample to achieve homogeneity. Weigh approximately 0.5 g of sample. Transfer the weighed sample to the appropriately labeled Teflon beaker or centrifuge tube.

17.3.1 Sample aliquots should not be taken from the top of an unmixed sample because large particles tend to rise in solid matrixes and heavy materials tend to sink in liquid matrixes.

17.3.2 Powdered samples may be homogenized by gently rocking the sample side to side. Then a representative aliquot may be taken from the center of the powder.

17.3.3 Other matrixes must be stirred, turned or mixed before sampling.

17.4 Quality control samples are prepared prior to digestion.

17.4.1 The beaker or tube to be used for the blank, MS, MSD, and/or DUP, LCS, and/or LCS DUP is labeled.

17.4.2 Weigh approximately 0.5 g of sample and transfer to the MS, MSD, and/or DUP beaker or tube.

The MS, MSD, LCS, and/or LCS DUP are spiked with known amounts of spiking solution.

17.4.3 Select a LCS. The LCS is purchased for an outside vendor and comes with a certificate of certified values and recovery ranges. The LCS is logged into the AlphaLIMS system for traceability and for the use of nominal calculations. For analytes not certified in the Solid Reference Material (SRM), a series of 20 preparations and analyses are conducted and an average concentration is determined. A value of 3 times the standard deviation is used as control limits for the LCS recovery for these analytes. Mix the LCS to achieve homogeneity. Weigh approximately 0.5 g of the sample and transfer to the LCS and/or LCS DUP Teflon beaker or centrifuge tube. For non-soil solid samples, a liquid LCS is used in combination with approximately 0.5 g of Teflon chips.

17.4.4 The blank beaker or tube is labeled and no water, spike, or sample is added to it. Approximately 0.5 g of Teflon chips is used.

17.5 If the samples are being prepared for ICP-MS analysis:

17.5.1 Add 2.5 mL nitric acid and Type I DI water to the samples and quality control samples.

17.5.2 Gently swirl the sample and acid mixture.

17.5.3 Cover the sample with a watch glass and heat the sample on a hot plate/block to 95° ± 5° C. Reflux the sample for 10 to 15 minutes.

17.5.4 Remove the sample from the hot plate or block and allow the sample to cool.

17.5.5 Add 2.5 mL of concentrated nitric acid, replace the watch glass, and reflux for 30 minutes. If brown fumes are generated indicating oxidation of the sample by nitric acid, repeat step 17.5.5 over and over until no brown fumes are given off by the sample.

17.5.6 Using a ribbed watch glass or vapor recovery system, allow the solution to evaporate to approximately 0.5 mL without boiling, or heat for 2 hours.

17.5.6.1 Remove the sample from the hot plate or block and allow the sample to cool.

17.5.6.2 Add 1.5 mL of hydrogen peroxide and 1.0 mL of Type I water. Return the sample to the hot plate or block and allow the peroxide reaction to occur. Continue to add hydrogen peroxide to the sample until the effervescence subsides. Do not add more than 5 mL hydrogen peroxide.

17.5.6.3 Cover the sample with a ribbed watchglass, heating the acid-peroxide digestate until the volume is reduced to approximately 2.5 mL, or heat at 95° ± 5° C without boiling for 2 hours.

17.5.6.4 Do not allow the sample to evaporate to dryness.

17.5.6.5 Remove the sample from step 17.5.6.3 from the hot plate or block.

17.5.6.6 Allow the sample to cool.

17.5.6.7 Dilute the sample to 50 mL with Type I water.

17.5.6.8 Cap and shake the sample.

17.5.6.9 Filter each sample with a 2.0 µm pore size plunger type filter (PTF grade) or allow to settle overnight.

17.5.6.10 Organize the samples in a storage container, and label the container with the batch number of the sample group.

17.6 If the samples are being prepared ICP analysis:

17.6.1 Add 1.25 mL nitric acid and 10 mL hydrochloric acid to the samples and quality control samples.

17.6.2 Gently swirl to mix.

17.6.3 Cover the sample with a watch glass and heat the sample on a hotplate/block to 95° ± 5° C. Reflux the sample for 30 minutes.

17.6.4 Remove the sample from the hotplate/block and allow to cool.

17.6.5 Dilute the sample to 50 mL with Type I water.

17.6.6 Cap and shake the sample.

17.6.7 Filter each sample with 2.0 µm pore size plunger type filter (PTF grade) or allow to sit overnight.

17.6.8 Organize the samples in a storage container, and label the container with the batch number of the sample group.

17.7 If the sample contains particulate material that could clog the nebulizer, you may filter or centrifuge the sample if necessary.

17.8 Be advised that filtration is a common cause of contamination. If a sample is filtered, any QC associated with the sample must also be filtered. Additionally, if any sample in the batch is filtered the method blank and laboratory control sample must also be filtered.

17.9 Filters may be prepared via this method. If the filters are small enough to fit inside the 50 mL digestion tubes, they can be treated as any solid prep materials. If the filters are too big to undergo adequate digestion using the 50 mL digestion tube, a borosilicate beaker will need to be used. All reagents and standards will need to be adjusted for any extra volumes needed. All filter analyses should be discussed and the process verified with the group/team leader prior to digestion. The group leader or project manager may have to contact the client to get the full description of what is required.

18.0 PREPARATION OF STANDARDS

Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with GL-LB-E-007 for Laboratory Standards Documentation.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Hot plates/blocks are allowed to come to the proper temperature before digestions are started. The temperatures are monitored before and after a daily digestion session.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC

20.1.1 A matrix spike (MS) and a matrix spike duplicate (MSD) or a sample duplicate (DUP) and a matrix spike are prepped for every batch of ≤ 20 samples

20.1.2 A method blank (MB) and a laboratory control standard (LCS) are prepped for every batch of ≤ 20 samples. A laboratory control standard duplicate (LCSD) is prepared if matrix QC is unavailable or upon client request.

20.2 Makeup of QC Samples

20.2.1 Sample duplicate (DUP) is a separate aliquot taken through the prep process exactly the same as the original sample.

20.2.2 Matrix spike and/or matrix spike duplicate is a separate aliquot of the sample to which appropriate spike volumes and solutions are added. The ID numbers and volumes of the spikes are recorded in the prep logbook.

20.2.3 The method blank (MB) is a reagent blank taken through the same prep process as the samples. Teflon chips are used to approximate matrix weights of 0.5 g.

20.2.4 The laboratory control standard (LCS) is a standard performed two different ways. For DOE-ALB clients, a purchased SRM is used at approximately 0.5 g and is taken through the same process as the samples. For all other clients, Teflon chips weighted to approximately 0.5 g are used. The chips and acid solution is spiked with the appropriate spike volumes and solutions. The ID number and volumes of the spikes are recorded in the prep logbook.

20.3 Handling Out-Of-Control Situations

If sample reactions cause popping or splattering of the digestate, discontinue the prep and contact team leader or group leader.

21.0 RUN SEQUENCE

Not applicable

22.0 PROCEDURE

Refer to section 17.0, Preparation of Samples

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Before turning off the hotplate/blocks at the end of the day, a final monitoring temperature is recorded for each plate/block that was utilized.

24.0 METHOD VARIATION

24.1 This procedure deviates from method 3050B in that sample volumes are half the method recommendations.

24.2 The ICP procedure references a modified 3050B section 7.5 procedure. The modification eliminates the use of the Whatman 41 filters, thus eliminating contamination of common minerals.

25.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

25.1 Upon completion of batch preparation, digestion data shall be entered into the AlphaLIMS Prep Logbook (refer to Appendix 1) following the guidelines in GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Recordkeeping Devices.

25.2 Data to be entered into the electronic logbook include analyst name, prep data and time, initial volume or weight with units, and final volume with units.

25.3 Standards and reagents may also be entered into the logbook and fall under the guidelines of GL-LB-E-015 for Control of Laboratory Standards and GL-LB-E-007 for Laboratory Standards Documentation.

25.4 Upon entry of prep data, obtain a printout of the logbook. The analyst listed on the logbook should sign and date the page near their printed initials. The logbook page is kept with the samples with which it is associated.

25.5 The entry of correct prep data is peer reviewed (correct dates, times, weights, volumes, SOP/revision, spikes, spike amounts, and reagent information, etc.) Once data are reviewed, the batch is statused to DONE in AlphaLIMS, the logbook is signed and dated by the reviewer, and the batch is ready for analysis. A copy of the prep logbook sheet is kept in the metals prep lab and is bound and given a control number when sufficient numbers of sheets are collected.

26.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 LABORATORY WASTE

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

28.0 REFERENCES

28.1 Test Method for Evaluating Solid Waste; Laboratory Manual Physical/ Chemical Methods, Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils," Revision 2, December 1996.

28.2 1992 Annual Book of ASTM Standards, Standard D1193-91, "Standard Specification for Reagent Water."

28.3 16 CFR Part 1303

29.0 HISTORY

Revision 21: Updated performance characteristics section; MDLs are performed annually and MDLVs are performed quarterly.

Revision 22: Removed 16 CFR Part 1303 reference.

Revision 22: Clarified DI water. Updated metals list of elements in method summary section.

APPENDIX 1: SAMPLE PREP LOGBOOK

(For illustrative purposes only)

Prep LogBook

Analyst: AJM
Batch: 10607
Prep Date: 07-FEB-2000 14:00
Lab SOP: GL-MA-E-013

Type	Sample Id	Lot Id	Spike Amount	Spike Units
LCS	1000023152	5385	.25	mL
LCS	1000023152	5386	.25	mL
MS	1000023155	5385	.25	mL
MS	1000023155	5386	.25	mL
MSD	1000023154	5385	.25	mL
MSD	1000023154	5386	.25	mL

Type	Sample id	Parent Sample	Method	Initial Wt.	Final Volume	Prep Factor	Comments	Matrix
MB	1000023151		200.2/200.7 Full List For QC	50mL	50mL	1		Water
SAMPLE	21426001		200.2/200.7 Selenium	50mL	50mL	1		Waste Water
LCS	1000023152		200.2/200.7 Full List For QC	50mL	50mL	1		Water
SAMPLE	21426002		200.2/200.7 Selenium	50mL	50mL	1		Waste Water
SAMPLE	21426003		200.2/200.7 Selenium	50mL	50mL	1		Waste Water
SAMPLE	21426004		200.2/200.7 Selenium	50mL	50mL	1		Waste Water
SDILT	1000023153	21426004	200.2/200.7 Full List For QC	50mL	50mL	1		Water
MSD	1000023154	21426004	200.2/200.7 Full List For QC	50mL	50mL	1		Water
MS	1000023155	21426004	200.2/200.7 Full List For QC	50mL	50mL	1		Water

General Engineering Laboratories Page#________

30-Sep-2013

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

GAMMA SPECTROSCOPY SYSTEM OPERATION

(GL-RAD-I-001 REVISION 19)

GEL

GEL's Document Control Officer certifies this document to be a true copy of the fully executed original.

SDR

TABLE OF CONTENTS

1.0 STANDARD OPERATING PROCEDURE FOR GAMMA SPECTROSCOPY SYSTEM OPERATION

2.0 METHOD OBJECTIVE, PURPOSE, CODE AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for gamma isotopes using the Gamma Spectroscopy System.

2.2 Gamma emitting isotopes within the sample matrix are identified and quantified using gamma spectrometry. A sample aliquot is placed in a calibrated geometry and placed in the detector chamber. The germanium crystal therein produces a corresponding electrical pulse for the gamma photons that interact with the detector. The cumulative pulses are analyzed using software capable of quantifying gamma-emitting isotopes from the spectral data.

3.0 APPLICABLE MATRIX OR MATRICES

This is a nondestructive test for the measurement of gamma emitting isotopes in all matrices for which there is an available calibration standard.

4.0 METHOD SCOPE, APPLICABILITY AND DETECTION LIMIT

4.1 The aliquoted sample activity or sample position should be adjusted so that the detector system dead time remains less than 15%.

4.2 Method Detectable Activity: The MDA is based upon sample volume, instrument background, detector efficiency, count time and other statistical factors, as well as specific isotopic values such as abundance and half-life.

5.0 METHOD VARIATIONS

Not applicable

6.0 DEFINITIONS

6.1 Abundance: The combination of the isotopic decay branching ratio and the expected gamma emissions per disintegration of an isotope at a particular energy.

6.2 Key Line: The line chosen by the builder of the library to be the prominent line of the isotope. This line is used for the purposes of calculating activity, error and MDA.

6.3 AlphaLIMS: The Laboratory Information Management System used to store and report data.

6.4 National Institute of Standards and Technology (NIST): For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

7.0 INTERFERENCES/LIMITATIONS

7.1 Some gamma isotopes emit gamma lines that may overlap with those from other isotopes. If the energies of the two isotopes are within the energy tolerance setting, the peaks may not be resolvable and may give a positive bias to the result. This problem is minimized by careful review of the peak search.

8.0 SAFETY PRECAUTIONS AND WARNINGS

Follow safety precautions as outlined in GL-LB-N-001 for the Safety, Health and Chemical Hygiene Plan.

9.0 APPARATUS, EQUIPMENT AND INSTRUMENTATION

9.1 Apparatus and Equipment

9.1.1 Compaq/DEC Alpha Station with OpenVMS

9.1.2 Canberra Genie-ESP Application Software

9.1.3 High purity germanium detector

9.1.4 Pulse processing electronics

10.0 REAGENTS AND STANDARDS

10.1 Standards

10.1.1 NIST traceable mixed gamma standards in geometries and densities, closely approximating analytical samples, used to calibrate the instrument.

11.0 SAMPLE HANDLING AND PRESERVATION

Refer to GL-RAD-A-013 The Determination of Gamma Isotopes.

12.0 SAMPLE PREPARATION

Refer to GL-RAD-A-013 The Determination of Gamma Isotopes.

13.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

Refer to GL-RAD-A-013 The Determination of Gamma Isotopes.

14.0 INSTRUMENT CALIBRATION, STANDARDIZATION AND PERFORMANCE

14.1 Calibration Standard

14.1.1 Mixed Gamma calibrations typically use a standard with 8-12 photons emitted over a range from approximately 45 keV to approximately 2000 keV.

14.1.2 Single nuclide calibrations typically use a standard comprised of the nuclide of interest.

14.2 Verification Standard

14.2.1 Mixed Gamma calibrations- A second source (from different manufacturer or if from the same manufacturer, a different lot number) is used for verification. The lines from Am-241, Cs-137 and Co-60 are used to verify the efficiency curve. These encompass the low, middle and high portions of the energy range.

14.2.2 Single nuclide calibrations – A second source (from a different manufacturer or if from the same manufacturer, a different lot number) is used for verification.

14.3 Standardization

14.3.1 High Voltage Adjust

14.3.1.1 See appropriate instrument manual for operation of electronics.

14.4 Calibration – Energy and efficiency calibrations are performed annually, upon initial instrument setup, after major repair or service, or when performance checks indicate a need.

NOTE: Expiration dates will match the last day of the month in which the calibration data was acquired.

14.4.1 Count Calibration Spectrum

14.4.1.1 Place the radioactive source on the detector.

14.4.1.2 Select **Calibration | Count a Calibration Standard** from the *Calibration* menu and click **OK**.

14.4.1.3 Enter the **Preset Live (secs):** in seconds and click **OK**. Count the standard until a minimum of 10,000 counts is acquired in each peak of interest.

14.4.2 Initial Energy & Shape Calibration

14.4.2.1 Select **Calibration|Initial Energy & Shape Calibration** from the *Calibration* menu and click **OK**.

14.4.2.2 Select the detector.

14.4.2.3 Select the **Certificate File** from the drop down list. Click **OK**.

14.4.2.4 From the *Energy Calibration* dialog box highlight one of the energy lines listed.

14.4.2.5 Move the cursor in the MCA window to the corresponding channel expected for that energy line.

14.4.2.5.1 The apex of the peak of interest should be at the expected channel.

14.4.2.5.2 From the *Energy Calibration* dialog box click the **Cursor** button.

14.4.2.6 Repeat the previous step until all energy lines listed have been referenced with a corresponding channel.

14.4.2.7 From the *Energy Calibration* dialog box select the **OK** button.

14.4.2.8 The system will ask "Do you want to do a full energy and shape calibration?" Select **YES**.

14.4.2.9 The energy and shape calibrations will now be performed with all of the lines from step 14.4.2.6. Verify the energy and shape curve generated. Select **OK** to continue or **Cancel** to abort the calibration.

14.4.2.10 A new page will appear with the Energy Calibration Report and the FWHM Calibration Report. Review the columns marked difference. For the energy calibration, the absolute value of the difference must be less than 1.0 and for the FWHM calibration, the absolute value of the difference must be less than 0.5. Regardless of the results, select **Dismiss.**

14.4.2.11 A new pop-up screen will appear. If the results from the previous step were less than a 0.2 keV difference, select **OK**. If the results were greater than a 0.2 keV difference select **Cancel** and begin the energy calibration process again at step 14.4.1.

14.4.3 Energy Re-Calibrate

14.4.3.1 Select **Calibrate** | **Re-Calibrate** | **Energy and Shape Calibration** from the main menu and click **OK**.

14.4.3.2 Select the detector.

14.4.3.3 Select the certificate file and select the **OK** button.

14.4.3.4 The energy and shape calibrations will now be performed with all of the lines from step 14.4.2.6. Verify the energy and shape curve generated. Select **OK** to continue or **Cancel** to abort the calibration.

14.4.3.5 A new page will appear with the Energy Calibration Report and the FWHM Calibration Report. Review the columns marked difference. For the energy calibration, the absolute value of the difference must be less than 1.0 and for the FWHM calibration, the absolute value of the difference must be less than 0.5. Regardless of the results, select **Dismiss.**

14.4.3.6 A new pop-up screen will appear. If the results from the previous step were less than a 0.2 keV difference, select OK. If the were greater than a 0.2 keV difference select Cancel and begin the energy calibration process again. If it fails after re-calibration contact Group or Team Leader for further instructions.

14.4.4 Efficiency Calibrate

14.4.4.1 Select **Calibrate** | **Efficiency Calibrate** from the main menu.

14.4.4.2 Select the geometry that represents the standardized radioactive source and click **OK**. If the geometry doesn't exist select **Create New Geometry**, enter the name of the new geometry and select **OK**.

14.4.4.3 Select the certificate for the calibration standard and select the **OK** button.

14.4.4.4 The efficiency calibration curve will be displayed for review. Select Empirical fit, and Log scale.

14.4.4.5 To accept the calibration select **OK**, or select **Cancel** to abort.

14.4.4.6 Dismiss the Calibration report displayed to complete the calibration procedure.

14.4.4.7 In the DECterm type **EFFPlot,** then press ENTER the type **EFFPRINT** then hit ENTER. This will print the efficiency curve.

14.4.5 Efficiency Verifications

14.4.5.1 Verification counts are performed as a normal sample count starting at step 15.2.3 of this SOP.

14.4.5.2 No batch ID is assigned to verification counts, typically "VER" is used.

14.4.5.3 Select the only sample identification available regardless of how it is named.

14.4.5.3.1 You may be asked if you would like to extend the count. Select **NO**.

14.4.5.3.2 When the screen to enter the sample information appears (step 15.2.8), use the date and time indicated on the manufacturer's certificate file for decay correction and change the sample identification using the following naming convention: VER_DETECTOR_GEOMETRY, for example VER_GAM01_CAN.

14.4.5.4 Once the count has completed, in the DECterm, type "@print_virtual sample, where sample equals the same identification used in step 14.4.5.3.2. This will print out the raw data of the verification count.

14.4.5.5 Several pages will print out. The only pages needed are the background-subtracted peak report, which should be the first page, and the nuclide line activity report.

14.4.5.6 Place the results from the "Decay Corr" column into the appropriate Master Verification Spreadsheet located at S:\RAD\FORMS\EFF_VER where S:= sdrive on 'radserver' under the column named **Measured Activity**.

14.4.5.7 If necessary, enter the emission rate for the standard used for verification on the Master Verification Spreadsheet. This can be found on the manufacturer's certificate file for the standard. The spreadsheet will then calculate the **Calibrated Activity**. If a column for the emission rate does not exist on the spreadsheet, the **Calibrated Activity** can be calculated by using the values from the Decay Correct Source page in Alpha LIMS

(http://prodsvr01.gel.com:7778/pls/lims/de_ref_material.decay_correction).

14.4.5.8 The percent difference between the **Calibrated Activity** and **Measured Activity** is calculated by the spreadsheet and is displayed under the column marked **Difference**. The verification is considered acceptable if all values in the **Difference** column are less than 10%. If the **Difference** is 10% or greater, the verification is considered invalid and must be performed again. If two verifications fail notify Group Leader or Team Leader for further action.

14.5 Performance Checks

14.5.1 Daily Quality Control Calibration Check (QCC)

14.5.1.1 The QCC should be counted daily or prior to sample counting. If no samples are being counted this check is not required.

14.5.1.2 Load the QCC check source on the detector(s). If multiple QCC checks are being started skip to step 14.5.1.5.

14.5.1.3 From the PROcount window, select **QC│Calibration Check.**

14.5.1.4 Select the detector and select **OK**.

14.5.1.5 To start multiple QCC checks at once, select **QC│Multi Calibration Checks** from the PROcount window.

14.5.1.6 Highlight each detector you wish to start by clicking once on the detector name. Once you have highlighted all of the detectors you wish to start, select **OK**.

14.5.2 Daily Quality Control Background Check (QCB)

14.5.2.1 The QCB should be counted daily or prior to sample counting. If no samples are being counted this check is not required.

14.5.2.2 Ensure the detector shield(s) are empty prior to running the QCB. If multiple QCB checks are being started, skip to step 14.5.2.5.

14.5.2.3 From the PROcount window, select **QC│Background Check.**

14.5.2.4 Select the detector and select OK.

14.5.2.5 To start multiple QCB checks at once, select **QC│Multi Background Checks** from the PROcount window.

14.5.2.6 Highlight each detector you wish to start by clicking once on the detector name. Once you have highlighted all of the detectors you wish to start, select OK.

14.5.3 Weekly Environmental Background

14.5.3.1 Ensure the detector shield(s) is (are) empty. The same process will be used to start single and multiple weekly environmental background counts.

14.5.3.2 Select **Count | Start MultipleBackgrounds** from the PROcount window.

14.5.3.3 highlight each detector you wish to start by clicking once on the detector name. Once you have highlighted all of the detectors you wish to start, select **OK.**

14.5.4 Generating the Daily and Weekly Check Reports

14.5.4.1 Daily check reports will generate every day following the completion of the QCC and QCB counts for each detector that will be in operation.

14.5.4.2 In the DECterm, type the command "**@QA_REPORT D**" then hit ENTER.

14.5.4.3 Weekly check reports will be completed once per week, typically Monday, following the completion of the weekly background subtraction counts.

14.5.4.4 In the DECterm, type the command "**@QA_REPORT B**" then hit ENTER.

15.0 PROCEDURE FOR ANALYSIS AND INSTRUMENT OPERATION

15.1 Prepare the sample as outlined in GL-RAD-A-013 for The Determination of Gamma Isotopes.

15.2 Sample Counting

15.2.1 Prior to starting a sample count the detector used must be scanned into AlphaLIMS. In a web browser, enter the following address:

http://prodsvr01.gel.com:7778/pls/lims/inst_instrument.start_count

15.2.2 Each sample and detector are labeled with a Universal Product Code (UPC). First scan the UPC code for the detector and then scan the UPC code for the sample. Continue doing so for any additional sample counts. Once this has been done, select Submit on the web page.

15.2.3 Load the sample on the detector.

15.2.4 Select **Count | Start a Count** from the *ProCount Main Menu.*

15.2.5 Select a detector and select **OK**.

15.2.6 Enter the batch to be started and select OK.

15.2.7 Select the sample to be counted.

15.2.8 Enter the sample specific information into the Sample Information screen and select OK.

15.2.9 Select the Analysis Sequence file used for analysis and select OK.

15.2.10 Select the counting geometry and select OK.

16.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to GL-RAD-I-010 for Counting Room Instrumentation Maintenance.

17.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

Data recording, calculation and reduction take place in accordance with GL-RAD-D-003 and GL-RAD-D-006.

18.0 POLLUTION/CONTAMINATION

Ensure all samples are bagged prior to counting to prevent instrument contamination.

19.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

Refer to GL-RAD-D-003 for Data Review, Validation, and Data Package Assembly.

20.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action for out-of-control data might require instrument maintenance, re-analysis, using a new spike mix, or a more complex set of actions. When trouble-shooting measures (refer to Section 21) fail to bring an analytical process or data into control, a data exception report and/or corrective action should be initiated in accordance with GL-QS-E-004.

21.0 CONTINGENCIES FOR HANDLING THESE SITUATIONS

Troubleshooting the instrument is a function of analyst experience. In-house service is obtained from GEL's Group Leader or other qualified personnel. If vendor assistance is needed, then the appropriate vendor is contacted. Maintenance logbooks are kept for each instrument and contain entries for both routine and non-routine maintenance procedures.

22.0 RECORDS MANAGEMENT

22.1 Each sample analysis that is performed is documented in the instrument run log in accordance with GL-LB-E-009 for Run Logs.

22.2 All raw data printouts, calculation spreadsheets, and batch checklists are filed with the sample data for archival in accordance with GL-RAD-D-003 for Data Review, Validation, and Data Package Assembly.

22.3 Instrument maintenance is recorded in accordance with GL-LB-E-008 for Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms and Other Recordkeeping Devices.

22.4 Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

23.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

24.0 REFERENCES

24.1 United States Department of Energy, Environmental Measurements Laboratory, HASL-300 The Procedures Manual of the Environmental Measurements Laboratory, 28th Edition, "Gamma Radioassay," Ga-01-R (Vol. 1), February 1997.

24.2 United States Environmental Protection Agency, Prescribed Procedures for Measurement of Radioactivity in Drinking Water, Method 901.1, August 1980.

24.3 American National Standards Institute, American National Standard for Calibration and Use of Germanium Spectrometers for the Measurement of Gamma-Ray Emission Rates of Radionuclides, ANSI N42.14-1999.

24.4 Canberra Model 480720 ProCount-ESP Users Manual, September 2000.

24.5 Canberra Model 480726 Genie-ESP System Users Manual, September 2000.

24.6 Canberra Model 480198 Genie VMS Users Manual, 2000.

24.7 ASTM, International, Standard Practice for Setup, Calibration, and Quality Control of Instruments Used for Radioactive Measurements, D7282-6, Nov. 2010.

25.0 HISTORY

Revision 15: Procedural updates made to SOP to reflect the process currently being used.

Revision 16: Added criteria for acceptance of FWHM calibration.

Revision 17: Updated sections 14.4.3.6 and 14.4.5.2 for clarification.

Revision 18: Added note to section 14.4 to clarify instrument calibration expiration dates.

Revision 19: Revised to include new GL-RAD-D-006 for calculations.

Attachment B

Gamma Spectroscopy Library

Nuclide Library Editor: ND_SC_LIB:AECOM1   16-JUN-2014 16:20:10.12

Title: AECOM1

Nuclide Name	Nuclide Type	Half Life	Key Line?	No Wtmean?	Energy (keV)	%Abn
K-40		1.25E+09Y	*		1460.82	10.66
CO-60		1925.28D			1173.23	99.85
			*		1332.49	99.98
BA-137M		2.55M	*		661.66	89.90
CS-137		30.08Y	*		661.66	85.10
TL-208		3.05M			277.37	6.60
			*		583.19	85.00
					860.56	12.50
PB-210		22.20Y	*		46.54	4.25
BI-211		2.13M	*		351.06	12.92
PB-211		36.10M	*		404.85	3.78
					427.09	1.76
					832.01	3.52
BI-212		60.55M	*		727.33	6.67
					785.37	1.10
					1620.50	1.47
PB-212		10.64H	*		238.63	43.60
					300.09	3.30
BI-214		19.90M	*		609.32	45.49
					768.36	4.89
					1120.29	14.92
					1238.12	5.83
					1764.49	15.30
PB-214		26.60M			242.00	7.25
					295.22	18.42
			*		351.93	35.60
RN-219		3.96S			271.23	10.80
			*		401.81	6.60
FR-223		21.80M			50.09	34.00
					79.65	8.70
			*		234.75	3.00
RA-223		11.43D			144.24	3.27
					154.21	5.70
			*		269.46	13.90
					338.28	2.84
TH-227		18.72D			50.13	11.40
					235.96	17.50
			*		256.23	9.50
					329.85	4.00
AC-228		6.25H			338.32	11.27
					463.00	4.40
					794.95	4.25
					835.71	1.61
			*		911.20	25.80
					968.97	15.80
PA-231		3.28E+04Y	*		283.69	1.70
					300.07	2.42
					302.65	2.20

			330.06	1.40
TH-231	25.52H		81.23	0.90
		*	84.21	6.60
			89.95	1.00
			163.10	0.15
PA-234M	1.16M		766.42	0.32
		*	1001.03	0.84
TH-234	24.10D	*	63.29	3.70
			92.59	4.23
U-235	7.04E+08Y	*	143.76	10.96
			163.33	5.08
			185.72	57.20
			205.31	5.01
AM-241	432.60Y	*	59.54	35.90

Attachment C

Radioisotope Calculation Spreadsheet

EXAMPLE TABLE
GAMMA SPECTROSCOPY RESULTS AFTER 28-DAY INGROWTH PERIOD

PINES AREA OF INVESTIGATION
SUPPLEMENTAL SOIL CHARACTERIZATION

	Measured				Calculated	Measured								Calculated	Calculated	Calculated	Measured		Calculated	Measured
Sample I.D.	**Be-7**	**Am-241**	**K-40**	**Ba-137m**	**Cs-137 (a)**	**Co-60**	**Tl-208**	**Pb-210**	**Bi-212**	**Pb-212**	**Bi-214**	**Pb-214**	**Ac-228**	**Ra-228 (b)**	**Ra-226 (c)**	**Total Ra (d)**	**Pa-234m**	**Th-234**	**U-238 (e)**	**U-235**
GS001	1.0	1.0	1.0	1.0	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	1.0	1.0	1.0	1.0
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				
					0.0									0.0	0.0	0.0				

Notes: Equations:

(a) Cs-137 = 0.946 x Ba-137m
(b) Ra-228 = Ac-228
(c) Ra-226 = (Pb-214 + Bi-214) / 2
(d) Total Ra = Ra-228 + Ra-226
(e) U-238 = (Pa-234m + Th-234) / 2

Appendix C

Field Standard Operating Procedures

AECOM **Radiological Service Technical Practice Group Standard Operating Procedure**	PROCEDURE NO. RS-TPG, SOP 001 DATE: March 20, 2014 APPROVED: Radiological Service TPG Leader
Portable Detection Equipment	

Standard Operating Procedure

PORTABLE DETECTION EQUIPMENT

AECOM's Radiological Service Technical Practice Group (RS-TPG) is responsible for the issuance, revision, and maintenance of this policy. This procedure has also been provided to the South Carolina Department of Health and Environmental Control (SC DHEC) as part of AECOM's "decommissioning license" application. Therefore, any deviations from the procedures set forth in this document require approval of the RS-TPG Leader and the SC DHEC license Radiation Safety Officer (RSO). This SOP supersedes all previous SOPs on this topic.

SC DHEC License RSO Approval: ____________________ March 20, 2014

1 PURPOSE

The purpose of this procedure is to provide instruction for operating portable radiation detection instrumentation. For aspects of instrumentation operation not covered in this procedure, refer to the instrument technical manual.

2 SCOPE

This procedure provides guidance for the response and source checks of portable instrumentation and area radiation monitors. Response and source checks are the periodic checks to verify that the instrument is properly functioning within the manufacturer's specifications. Guidance is also provided for removing from service, shipping and receipt of instruments returned from repair and calibration.

3 ALARA POLICY

It is AECOM's policy to plan and conduct its radiological activities safely and in such a fashion as to protect the health and safety of its employees, subcontractors, members of the public, and the environment. To achieve this, AECOM shall confirm that efforts are taken to reduce radiological exposures and releases to the environment as low as is reasonably achievable (ALARA), taking into account social, technical, economic, practical and public policy considerations. AECOM's RS-TPG is committed to implementing this procedure and maintain radiation detection equipment in a manner to reflect this policy.

4 PRECAUTIONS

4.1 When operating a battery powered instrument, the batteries shall be checked each time the instrument is used and batteries changed when required.

4.2 Handle instruments with care. Do not drop or allow them to bang against hard surfaces. Use only instruments possessing a current calibration.

4.3 Care should be taken when using thin window detectors (pancake and scintillation detectors) near sharp objects so that the window and detector shall not damaged.

4.4 Slowly enter areas of unknown radiation with instruments on the high scale to avoid off-scale readings and subsequent prolonged recovery time.

4.5 Minimize contact with the surface being surveyed. If lose/removable contamination is present, avoid contact with the surface and check instruments for contamination if contact occurs.

4.6 Occasionally verify instrument is responding properly if background appears outside the expected range.

4.7 When checking instruments, place the source in its holder or center it on the probe as required.

4.8 Carefully pack for shipment any instrument being sent to a facility to be calibrated or repaired to avoid damage in transit.

4.9 Radiation survey instruments and count rate instruments shall be calibrated at least every twelve months, after the instrument is repaired and at the start of each project.

5 PROCEDURE

5.1 Steps Prior to Using Instruments

5.1.1 Calibration Verification

5.1.1.1 All portable radiological instruments shall have a current calibration label.

5.1.1.2 The calibration date will be check daily prior to use of the instrument.

5.1.2 Physical Check

5.1.2.1 Inspect the general physical condition of the instrument and detector prior to each use.

5.1.2.2 Inspect for loose, damaged knobs, buttons, cables, connectors, broken/damaged meter movements/ displays, dented or corroded instrument cases, punctured/deformed probe/probe window(s), cables, etc., and any other physical impairments that may affect the proper operation of the instrument or detector.

5.1.2.3 Any instrument or detector having a questionable physical condition shall not be used until corrected.

5.1.3 Battery Check

5.1.3.1 Check that there is sufficient power being supplied to the detector and instrument circuitry for proper operation.

5.1.3.2 Document the battery check in the daily log or on the Radiological Instrument Daily Source Check Record, Attachment 1.

5.1.3.3 Perform this check in accordance with the instrument's technical manual; although, it is generally performed as follows:

5.1.3.3.1 Position the appropriate selector switch to the "Batt" position or depress the "Batt Check" button with the instrument on.

5.1.3.3.2 Observe the indication for the current battery condition. Typically, the current battery condition will be indicated by a meter deflection into the "Batt OK" region or "Batt OK" on the display, etc.

5.1.3.3.3 If unsatisfactory results are obtained, refer to the technical manual for replacement of the batteries and repeat the check. The instrument shall display a satisfactory battery check prior to use.

5.1.4 High Voltage (HV) Check

5.1.4.1 HV is adjusted appropriately during instrument calibration and does not require adjustment for normal operation.

5.1.4.2 A HV check is required for instruments with an “HV” check button prior to each use as applicable in accordance with the instrument technical manual.

5.1.4.3 Record the HV setting on the Radiological Instrument Daily Source Check Record, Attachment 1.

5.1.4.4 An instrument with suspected HV problems shall be reported to the Project Manager and RSO.

5.1.5 Instrument Source Check (Contamination Detectors)

This check is performed periodically to verify that the instrument will respond accurately to a known source of radiation. Locate the source for the instrument/detector being used and perform the response source check as described in the following.

5.1.5.1 Check the battery condition. If batteries are not in the allowed range, replace the batteries or clean contacts as necessary. If battery check is not satisfactory after corrective actions, then place instrument out of service and send to an authorized calibration facility for repair and calibration.

5.1.5.2 Determine the background radiation level. It must be low enough to allow a measurable response to the check source being used. Careful monitoring of changing background levels is necessary to obtain accurate instrument readings.

5.1.5.3 Perform source checks with appropriate sources. For on-contact readings, verify that the source to probe geometry is reproducible, in direct contact, and facing the probe.

5.1.5.4 Record the source check results on the Radiological Instrument Daily Source Check Record, Attachment 1.

5.1.5.5 Compare the source check counts against the response range calculated in accordance with Section 5.3.7. Instruments with source check responses that responded outside the acceptable range two out of three times will be removed from service and the Project Lead notified.

5.1.6 Daily Response Checks (Dose Rate/Exposure Rate Detectors)

This instrument check is performed to see if the instrument responds to a source of radiation. This is a qualitative check only.

5.1.6.1 Daily response checks of dose/exposure rate survey instruments shall be performed every day when in use. Documentation of these response checks is required.

5.1.6.2 Begin with the instrument on the highest range/scale and enable the audible device, if applicable.

5.1.6.3 Slowly move the detector towards the check source and observe for an increase in audible and/or visual response.

5.1.6.4 Change the range/scale of the instrument as appropriate to obtain a readable indication and to check each of the meter ranges/scales possible. If an appreciable response can not be obtained, even in the lowest range, evaluate instrument performance by comparison to previous source check data for the instrument.

5.1.7 Should the battery, source or response check be unsatisfactory, the instrument shall be removed from service. Record this on the instrument check form, Attachment 1. Send the instrument to an authorized calibration facility for repair and calibration.

5.1.8 When an instrument has reached its calibration due date, the instrument shall be sent to an authorized calibration facility.

5.2 Background Measurement for Scaler Instruments (Initial Setup)

5.2.1 Verify that the background area is free of radioactive sources. The detector geometry should be set up in the same configuration as that to be used when counting samples to produce the most accurate results.

5.2.2 Perform the background measurement for one minute and record the total counts measured (C_b) on the Scaler Instrumentation Background Setup Sheet, Attachment 2.

5.2.3 Repeat the background measurement 9 times, for a total of ten measurements. Record the total counts observed (C_b) for each measurement on the Scaler Instrumentation Background Setup Sheet, Attachment 2.

5.2.4 Calculate the average background counts ($\overline{C}_b$), the standard deviation (SD_b) and average background count rate ($\dot{C}$):

$$\overline{C}_b = \frac{\sum_i^n C_i}{N}$$

$$SD_b = \sqrt{\frac{\sum_i^n (C_i - \overline{C}_b)^2}{N - 1}}$$

$$\dot{C}_b = \frac{\overline{C}_b}{t_b}$$

where:

$\overline{C}_b$ = average background count

SD_b = standard deviation of the average background

N = number of measurements

Σ = summation

C_i = C_1 through C_n (C_{10} if 10 measurements are made)

$\dot{C}_b$ = average net background count rate

t_b = time in minutes of a background count

5.2.5 Record the average background counts ($\overline{C}_b$), the standard deviation (SD_b), and the average background count rate ($\dot{C}_b$) on the Scaler Instrumentation Background Setup Sheet, Attachment 2.

5.2.6 Calculate the limits for background and record on Attachment 3, Scaler Instrumentation Efficiency Sheet.

High limit $\dot{C}_b$ + 2SD$_b$

Low limit $\dot{C}_b$ - 2 SD$_b$ (if less than 0, record 0)

5.3 Instrument Efficiency for Scaler Instruments (E)

Efficiency is a quantitative measure of detector performance for a particular radioisotope. It provides the necessary relationship between counts per minute (cpm) as seen by the detector and disintegrations per minute (dpm) from source decay. Determine detector efficiency with a source of known activity of the nuclide (or of a nuclide with similar energy decay products) being monitored for as follows:

5.3.1 Correct source activity for decay as follows: (if necessary)

$$A = A_o e^{-\lambda T}$$

$$\textit{Where: } \lambda = \frac{0.693}{t_{1/2}}$$

where: A = present source activity.

A_o = source activity at initial assay.

λ = decay constant for the source isotope.

T = time elapsed since initial source assay*

$t_{1/2}$ = source isotope half-life

*Time units must be consistent (days, hrs., or min., etc.)

5.3.2 Correct source activity for backscatter: (if necessary)

$$A_c = A(1+B_s)$$

where: A_c = corrected activity (dpm)

A = present source activity.

B_s = percent backscatter (expressed as a decimal, i.e., 50% = 0.50 taken from source calibration sheet); $(1+B_s)$ can be found on page 127 of the Radiological Health Handbook.

5.3.3 Determine expiration date of source check limits by adding to the current date the value derived from dividing the $t_{1/2}$ of the source by 15. The limits will need to be recalculated in accordance with this section (5.4) after the expiration date.

Current date + $(t_{1/2})/15$ (of source) = Expiration date

If this date is later than the calibration due date record calibration due date as expiration date.

5.3.4 Count the source ten times (one minute each) and calculate the standard deviation (SD_n). Record the total counts measured (C_i) on the Instrument Efficiency Determination form, Attachment 3:

$$SD_g = \frac{\sqrt{\sum_i^{10} (C_i - \overline{C}_g)^2}}{N-1} = \sqrt{\frac{SS}{N-1}}$$

where: SS = sum of squares

$$SD_n = \sqrt{(SD_g)^2 + (SD_b)^2}$$

C_i = gross counts (source counts including background for a single count)
Σ = summation
N = number of measurements
SD_n = standard deviation of the average net counts.
SD_g = standard deviation of the average gross counts
SD_b = standard deviation of the average background counts (obtained from section 5.2)

Record the ten gross counts (C_g) and the standard deviations (SD_n and SD_g) on the Scaler Instrumentation Efficiency Sheet, Attachment 3.

5.3.5 Calculate the net count rate ($\dot{C}_n$):

$$\dot{C}_g = \frac{\overline{C}}{t_g}$$

$$\dot{C}_n = \dot{C}_g - \dot{C}_b$$

where: $\dot{C}_g$ = average gross count rate
$\overline{C}_g$ = average gross counts
t_g = time in minutes of a source count

C_b = average background count rate (obtain from Section 5.2)

Record on Attachment 3.

5.3.6 Calculate the detector efficiency (E) for the radioactive standard which equals of best approximates the potential contamination source as follows:

$$E = \frac{\dot{C}_n}{A_c} = \frac{cpm}{dpm}$$

where: $\dot{C}_n$ = average net cpm

A_c = corrected activity (dpm).

Record on Attachment 3.

5.3.7 Calculate the limits for source checks and record on Attachment 3.

High limit $\dot{C}_n$ + 2 SD_n

Low limit $\dot{C}_n$ - 2 SD_n

5.4 Estimated Minimum Detectable Concentration (MDC) for Scaler Instruments

5.4.1 The estimated minimum detectable activity is determined to verify that the detector being used will detect the presence of activity at or above the allowable limit under a given set of counting conditions. MDC is based on the estimated detection limit in counts (L_D) and detector efficiency. Determine the estimated L_D and MDC as follows:

$$L_D = k^2 + 2k\sqrt{B}$$

$$L_D = 3 + 4.65\sqrt{B}$$

Where:

k = Poisson probability sum for α and β (assuming a and b are equal)
= 1.645 for α and β both equal to 0.05 (95% confidence level)

B = number of background counts expect while performing the measurement (background rate x sample count time)

5.4.2 Record the calculated L_D on the Minimum Detectable Concentration Calculation form, Attachment 4.

5.4.3 Calculate the estimated MDC (in dpm/100 cm^2). For instances when the background and sample count time are the same:

$$MDC = \frac{L_D}{E \times A/100 \times t_b}$$

For instances when the background count time and the sample count time are different:

$$MDC = \frac{3 + 3.29\sqrt{C_b t_s \left(1 + \frac{t_s}{t_b}\right)}}{E \times t_s x \frac{A}{100}}$$

Where:

E = total detector 2-pi efficiency (in cpm/dpm) (from Section 5.3.6)

A = detector probe area (in cm^2)

t_s = sample count time

t_b = background count time

5.4.4 Record the calculated MDC in on Attachment 4.

5.5 Control Charts

5.5.1 Control charts should be used by the health physics technician to monitor for shifts, trends, or increases in variability. They are used as guides to indicate the need for investigative action, rather than for evaluating precise values.

5.5.1.1 The cpm for each background check should be plotted on a control chart with high and low limits.

5.5.1.2 The net cpm for each source check should be plotted on a control chart with high and low limits.

5.6 Calibration

Instruments used for monitoring and contamination control shall be:

- Periodically maintained and calibrated on an established frequency of at least once per year;
- Appropriate for the type(s), levels, and energies of the radiation(s) encountered;
- Appropriate for existing environmental conditions; and
- Routinely tested for operability.

5.6.1 Radiological instruments shall be used only to measure the radiation for which their calibrations are valid.

5.6.2 The ANSI N323 method for radiological instrumentation calibration will be adhered to.

5.6.3 Calibrations shall use National Institute of Standards and Technology (NIST) traceable sources.

5.6.4 Calibration records shall be maintained on-site and in an electronic project file.

5.6.5 Pocket and electronic dosimeters and area radiation monitors should be calibrated at least annually.

5.6.6 The effects of environmental conditions, including interfering radiation has on an instrument shall be known prior to use.

5.6.7 Functional tests should be used to assess instrumentation designs that include alarms or that involve a process control.

5.6.8 A functional test should be developed to test all components involved in an alarm or trip function and performed at least annually.

5.6.9 Special calibrations should be performed for use of instrumentation outside manufacturer's specifications.

5.6.10 The instrument should be adjusted, calibrated and labeled to identify the special conditions and used only under the special conditions for which it was calibrated.

5.6.11 Instruments should bear a label or tag with the date of calibration and date calibration expires.

5.6.12 For AECOM-owned instruments, the calibration will be performed by a vendor appropriately licensed by the NRC or an Agreement State. Calibrations will be performed at least once annually while the instrument is in service. Rented instruments will also have a valid calibration from a vendor appropriately licensed by the NRC or an Agreement State.

5.7 Receipt of Repaired/Calibrated Instrument

5.7.1 This section applies to instruments sent from a project site out for calibration and returned to the project site. It does not apply to rented equipment received on the project site for the first time.

5.7.2 Verify instrument has the correct calibration due date on the calibration sticker

5.7.3 Place the date the instrument was returned to service in the Out of Service Tracking Log, Attachment 5.

5.7.4 Perform a reference source check of the instrument using the appropriate source.

5.7.4.1 Repeat the procedure provided in Section 5.2 through 5.4 if the instrument's response is outside the original response range.

5.7.4.2 The new background, efficiency, and MDA obtained shall be used as the base line value for that instrument.

5.8 Instruments requiring calibration or repair at an off-site facility, as determined in Section 5.1, are treated as follows.

5.8.1 Remove the instrument from service and record information on instrument check form. In addition, fill out the appropriate information in the Out of Service Tracking Log, Attachment 5.

5.8.2 Instruments with delicate probe windows should have a probe cover secured to prevent damage. Any special instructions should be included with the instrument.

5.8.3 Carefully package the instrument and ship to the calibration facility.

The following procedures (5.8 – 5.11) are for general guidance only. Project-specific work plans will fully describe survey requirements.

5.9 Using Exposure and Dose Rate Instruments

5.9.1 General Area Surveys

Hold the detector at waist level with the most sensitive areas of the detector facing the item or areas being surveyed. Unless the radiation level on the item being surveyed is known, start on the high scale and work down scale until the instrument reading is between 1/4 and 3/4 (mid-scale) scale, if possible.

5.9.2 Direct Measurements

Hold the detector at about one inch from the surface of the item being surveyed.

5.9.3 Recording a Measurement

Allow the detector to stabilize 15-30 seconds before recording the measurement. If the analog or digital display is sporadic and it difficult to obtain an average response, record 10 instantaneous readings and calculate the average.

5.10 Using Gamma Scintillation Detectors

5.10.1 Direct Measurements

With the detector as close to the surface as possible or some other pre-determined position, collect a measurement for a length of time sufficient to provide an acceptable minimum detectable count rate. Record the measurement on the appropriate field survey form.

5.10.2 Walk-Over Surveys

With the detector as close to the ground as possible, move the detector in a serpentine pattern while advancing along a predetermined survey area transect at a rate of not more than 1 meter per second. For instruments mounted on carts, ensure that the detector height allows sufficient field of view considering the coverage requirements and the spacing of the survey area transect. Record the average and maximum count rates observed for a predetermined survey area or log the data using appropriate survey and position logging instruments.

5.11 Using Beta-Gamma Survey Meters

5.11.1 Counting Smears, Air Sample Filters, and Direct Measurements

Hold the detector no further than 1/2 inch from the smear, filter, or surface. Count smears/filters for a length of time such that the MDA is less than the removable contamination release criterion. Count surfaces for a length of time such that the MDA is less than the total contamination release criterion.

5.11.2 Frisking/scanning

Hold the detector within 1/2 inch of the surface being frisked/scanned. Move the detector no faster than two inches per second. Stop when positive indication is noted from audio response, allow meter indication to stabilize and record that value.

5.12 Using Alpha Survey Meters

5.12.1 Direct Measurements

Hold the detector no further than 1/4 inch from the surface. Count surfaces for a length of time such that the MDA is less than the total contamination release criterion.

5.12.2 Frisking/scanning

Hold the detector within 1/4 inch of the surface being surveyed. Move the detector no faster than two inches per second. Stop when positive indication is noted and allow meter indication to stabilize and record that value.

6 RECORDS

6.1 Radiological Instrument Daily Instrument Check Record, Attachment 1

6.2 Background Setup Record, Attachment 2

6.3 Instrument Efficiency Determination, Attachment 3

6.4 Minimum Detectable Concentration Calculation, Attachment 4

6.5 Out of Service Tracking Log, Attachment 5

ATTACHMENT 1

RADIOLOGICAL INSTRUMENT DAILY SOURCE CHECK RECORD

INSTRUMENT:____________________________ **SERIAL NO.:**______________________

CALIBRATION DUE DATE:__________________

DETECTOR:______________________________ **SERIAL NO.:**______________________

SOURCE CHECK MATERIAL:________________ **SERIAL NO.:**______________________

ACTIVITY:______________________________ **COUNT TIME:**_____________________

DATE	TIME	BATTERY CHECK	HV SETTING	SOURCE CPM	IN RANGE (Y/N)	TECHNICIAN INITIALS

Reviewed By:____

BACKGROUND SETUP RECORD

Technician:		**Date:**	
Location:		**Project:**	
Meter Model	**Meter S/N**	**Detector Model**	**Detector S/N**

Count Time (t_b):	minutes
Measurement #	**Counts (C_i)**
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
Average: $\overline{C}_b = \frac{\Sigma_1^{10} C_i}{N}$	
Standard Deviation: $SD_b = \sqrt{\frac{\Sigma_i^n (C_i - \overline{C}_b)^2}{N-1}}$	
$\dot{C}_b = \frac{\overline{C}_b}{t_b}$	cpm
High Limit : $\dot{C}_b + 2SD_b$	cpm
Low limit: $\dot{C}_b - 2\ SD_b$ (if less than 0, record 0)	cpm

Reviewed By:_______________________________________

$\overline{C}_b$ = average background count

SD_b = standard deviation of the average background

N = number of measurements (10)

Σ = summation

C_i = C_1 through C_n (C_{10} if 10 measurements are made)

$\dot{C}_b$ = average net background count rate

t_b = time in minutes of a background count

ATTACHMENT 3

INSTRUMENT EFFICIENCY DETERMINATION

Technician:		**Date:**	
Location:		**Project:**	
Source/Activity:		**Source S/N:**	
Meter Model	**Meter S/N**	**Detector Model**	**Detector S/N**

Count Time (t):	minutes	**Corrected Source 2-pi Activity (A_c):**	dpm
Measurement #	**Counts Gross**	**Counts Net**	**Equations**
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
Average			$\overline{C} = \frac{\Sigma_1^{10} C_i}{N}$
Average Count Rate ($\dot{C}_n$)			$\dot{C}_n = \frac{\overline{C}}{t}$
2-pi Efficiency (E)			$E = \frac{\dot{C}_n}{A_c} = \frac{cpm}{dpm}$
SD_g (gross)			See Attachment 2
SD_b (background)			See Attachment 2
SD_n (net)			$SD_n = \sqrt{(SD_g)^2 + (SD_b)^2}$
Upper Source Check Limit			$\dot{C}_n + 2SD_b$
Lower Source Check Limit			$\dot{C}_n - 2SD_b$

Reviewed By:_________________________________

MINIMUM DETECTABLE CONCENTRATION CALCULATION

Technician:		**Date:**	
Location:		**Project:**	
Meter Model	**Meter S/N**	**Detector Model**	**Detector S/N**

C_b = Background count rate (from Attachment 2)	cpm
t_b = background measurement count time	minutes
t_s = Sample/direct measurement count time	minutes
B = background counts expected during sample count (C_b x t_s)	counts
Minimum Detectable Count Rate (L_D)	cpm
E = 2-pi Efficiency (see Instrument Efficiency Determination, Attachment 3)	cpm/dpm
Detector Probe Area (A)	cm^2
Minimum Detectable Concentration (MDC)	dpm/100 cm^2

$$L_D = 3^* + 4.65^* \sqrt{B}$$

$$MDC = \frac{L_D}{E \times A/100 \times t_b}$$

* - derived constant based on the 95% confidence (α and β = 0.05)

$$MDC = \frac{3 + 3.29\sqrt{C_b t_s \left(1 + \frac{t_s}{t_b}\right)}}{E \times t_s x \frac{A}{100}}$$

Reviewed By:_______________________________________

ATTACHMENT 5

OUT OF SERVICE TRACKING LOG

Instrument [1]	Serial # [2]	Calibration Due Date [3]	Out of Service Date [4]	Remarks [5]	Returned to Service Date [6]

1. Instrument type
2. Instrument serial number
3. Calibration due date
4. Date removed from service
5. Reason instrument removed from service
6. Date instrument returned from service

Reviewed By:___________________________________

AECOM **Radiological Service Technical Practice Group Standard Operating Procedure**	PROCEDURE NO. RS-TPG, SOP 007 DATE: January 24, 2014 APPROVED:
Grid Systems and Surveys	Radiological Service TPG Leader

AECOM's Radiological Service Technical Practice Group (RS-TPG) is responsible for the issuance, revision, and maintenance of this policy. Any deviations from the procedures set forth in this policy require approval of the RS-TPG Leader. This SOP supersedes all previous SOPs on this topic.

1 PURPOSE

The purpose of this procedure provides instruction for establishing a reference grid system and performing radiological surveys for the established grids.

2 EQUIPMENT

Instrumentation shall be selected to accomplish the type of survey to be performed. All instrumentation shall be approved for use by a RS-TPG Certified Health Physicist (CHP) or Radiation Safety Officer (RSO). The following are examples of the instruments that can be used.

2.1 Gamma exposure rate and/or dose rate instruments such as the Ludlum Model 19 or Bicron MicroRem meters respectively.

2.2 Survey meters with gamma scintillation detectors for walk-over surveys, direct measurements, or down-hole gamma measurements.

2.3 Survey meters with Gieger-Mueller (GM), gas proportional, or scintillation detectors for alpha, beta, alpha/beta, or beta/gamma contamination.

2.4 Removable contamination sample counters such as a Ludlum Model 2929 with a thin window Zinc Sulfide Scintillator.

2.5 Crayons, permanent marker, or other markings devices depending on the type of surface to be marked.

2.6 The Ludlum Model 2224 Scaler with/239-1F detector or equivalent will be utilized to characterize flooring. The Model 2224 is battery capable and shall be mounted on a cart with a P-10 gas supply for easy handling and overall equipment protection.

3 PRECAUTIONS

Pre-operational checks shall be performed on all instruments prior to use to verify the following requirements per RS-TGP, SOP 001:

3.1 The instrument has been pre/post source checked for the day.

3.2 The instrument has been calibrated within the past 12 months.

3.3 The battery check is satisfactory (for portable instrumentation).

3.4 Overall physical condition of the instrument is satisfactory.

3.5 The instrument manufacturer’s specific operational checks have been accomplished.

4 PROCEDURE

4.1 Establishing Exterior Grids

4.1.1 Each exterior area shall be gridded prior to starting a walk-over or vehicle-assisted survey.

4.1.2 Each grid area with a size approved by the CHP/RSO shall be based on an alphanumeric numbering system.

4.1.3 Each gridded area shall begin in the northwest corner. The northwest grid corner shall be labeled as A1. Each subsequent grid to the east of that grid shall be labeled A2, A3, A4, etc. Each subsequent grid to the south of that grid shall be labeled B1, C1, D1, etc.

4.1.4 A variety of materials may be used to mark grids, including stakes, pin flags, marking paint, etc.

4.2 Surveying Exterior Grids

4.2.1 Grids will be surveyed based on their expected level of coverage. For 100% coverage, surveyors will walk grid transects spaced 1-meter apart at a pace typically not to exceed 1 meter per second. The detector will be swung side to side in a serpentine pattern across the straight-line transect. The transect spacing can be increased as the required coverage decreases.

4.2.2 When using carts (either manually operated or automated), the detector will be placed at a height that provides a sufficient field of view to provide the appropriate coverage of the survey area. Cart-mounted detectors will be pushed/pulled along straight lines if practical. The transect spacing is based on the required level of coverage and can be increased as the required coverage decreases.

4.2.3 When manually recording data, record the approximate average and maximum measurement for a pre-determined sub-section of the survey unit. This may be an individual grid square or a collection grid squares (depending on the size of the gird squares). Use Radiological Survey Report, Attachment 1 to RS-TPG SOP-011, to document the survey readings.

4.2.4 When recording survey data using a data logging instrument, download data at least daily.

4.3 Establishing Interior Grids

4.3.1 Each interior building, (rooms, walls and hallways) shall be gridded prior to starting the instrument survey.

4.3.2 Each interior 3m x 3m grid area or 1m x 1m grid area, dependent on the CHP/RSO, shall be based on an alphanumeric numbering system.

4.3.3 Each gridded area shall begin in the northwest corner. The northwest grid corner shall be labeled as A1. Each subsequent grid to the east of that grid shall be labeled A2, A3, A4, etc. Each subsequent grid to the south of that grid shall be labeled B1, C1, D1, etc.

4.3.4 A variety of materials may be used to mark grids, including chalk lines, paint, labels, tags, etc. Uniformity and reproducibility of results shall drive material selection.

4.4 Surveying Interior Floor Grids

4.4.1 All Interior grids classed as potentially contaminated shall be surveyed.

4.4.2 Interior grids classed as potentially uncontaminated shall have at least 10% of grids surveyed. Survey grids shall be selected based on areas of high probability for contamination.

4.4.3 When manually recording data, record the approximate average and maximum measurement for a pre-determined sub-section of the survey unit. This may be an individual grid square or a collection grid squares (depending on the size of the gird squares). Use Radiological Survey Report, Attachment 1 to RS-TPG SOP-011, to document the survey readings.

Note: There is an area for comments on the survey form. Surveying personnel are encouraged to check and comment on suspicious areas within the survey grid. Mark the areas on grid to correspond with comments.

4.5 Establishing Interior Wall Grids

4.5.1 Walls shall be identified as North, South, East, and West.

4.5.2 Walls shall be drawn on miscellaneous survey maps. Wall dimensions and descriptive material or equipment shall be indicated on map, to the extent it would aid in survey reproducibility

4.5.3 Potentially contaminated walls shall be marked with survey locations at one meter points, vertically corresponding to floor grids.

4.5.4 Survey locations shall be marked with paint, labels, tags or other methods to provide reproducibility.

4.5.5 Survey locations shall be marked numerically beginning from the northwest corner.

4.5.6 Potentially uncontaminated interior walls shall be marked in the same manner as above, but at a frequency of at least one survey location per 10 floor grids.

4.6 Establishing Survey Locations, Ceilings/Overhead

4.6.1 Ceilings shall not be gridded in the manner previously described for floors, walls, etc. Rather a prescribed number of survey locations shall be identified and marked on a per square meter basis determined by building classification.

4.6.2 Potentially contaminated rooms and/or buildings shall have at least one disk smear taken above each floor grid.

4.6.3 Potentially uncontaminated rooms and/or buildings shall have at least one disk smear taken above each 4 floor grids.

4.6.4 Survey locations shall be marked by paint, label, tag or other material.

4.6.5 Ceiling surveys shall be identified on miscellaneous survey maps

4.6.6 Survey locations shall be identified numerically, beginning in the northwest corner.

4.7 Surveying Ceilings/Overhead

4.7.1 Follow the gridding procedures listed in 4.4.1.

4.7.2 Obtain a miscellaneous survey form and draw the **ceiling as viewed from below.**

4.7.3 Add equipment, lights, vent ducts, etc., to the extent it would aid in survey reproducibility.

4.7.4 Establish survey locations pursuant to Section 4.4.6. Monitoring personnel shall select locations where contamination would be most probable.

4.7.5 Disk smears shall be taken at the frequency required by Sections 4.4.2 and 4.4.3.

4.7.6 Disk smears shall be counted for one minute on the Ludlum Model 2929 Alpha/Beta counting system or pancake probe if approved by the CHP or RSO.

4.7.7 Disk smears shall be taken when contamination is suspected, consideration will be given to the use of large area swipes. This shall be dependent on surface medium, access, and building use. This shall be determined on a building-by-building basis by the CHP or RSO.

4.7.8 When manually recording data, record the approximate average and maximum measurement for a pre-determined sub-section of the survey unit. This may be an individual grid square or a collection grid squares (depending on the size of the gird squares). All survey results shall be recorded on the Radiological Survey Report Form, Attachment 1 to RS-TPG SOP-011.

4.6 Final Status Survey

4.7.9 Survey grid for the final status survey will be established using the protocols in MARSSIM.

4.7.10 The number of direct measurements required for the final status survey will be established using the protocols in MARSSIM.

4.7.11 Distance between samples for final status survey will be established using the protocols in MARSSIM.

4.7.12 Other associated operations will be done in accordance with MARSSIM protocols.

5 REFERENCES

5.1 *Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM),* Revision 1, August 2000.

AECOM **Radiological Service Technical Practice Group Standard Operating Procedure**	PROCEDURE NO. RS-TPG, SOP 011 DATE: March 20, 2014 APPROVED:
Radiological Surveys	Radiological Service TPG Leader

Standard Operating Procedure

RADIOLOGICAL SURVEYS

AECOM's Radiological Service Technical Practice Group (RS-TPG) is responsible for the issuance, revision, and maintenance of this policy. This procedure has also been provided to the South Carolina Department of Health and Environmental Control (SC DHEC) as part of AECOM's "decommissioning license" application. Therefore, any deviations from the procedures set forth in this document require approval of the RS-TPG Leader and the SC DHEC license Radiation Safety Officer (RSO). This SOP supersedes all previous SOPs on this topic.

SC DHEC License RSO Approval: ______________________ March 20, 2014

1 PURPOSE

This document establishes the guidelines to be used for measuring radiation and contamination. It also provides guidelines for maintaining control of radioactive materials and areas that need to be surveyed.

2 SCOPE

This procedure provides guidance on properly performing radiological surveys conducted on temporary project sites where AECOM has either implemented its SC DHEC license or where RS-TPG leadership is involved with project implementation.

3 ALARA POLICY

It is AECOM's policy to plan and conduct its radiological activities safely and in such a fashion as to protect the health and safety of its employees, subcontractors, members of the public, and the environment. To achieve this, AECOM shall confirm that efforts are taken to reduce radiological exposures and releases to the environment as low as is reasonably achievable, taking into account social, technical, economic, practical and public policy considerations. AECOM's RS-TPG is committed to implementing this radiological survey procedure to reflect this policy.

4 EQUIPMENT

The following are examples of instrumentation that might be used to perform surveys.

- Beta-gamma contamination surveys are performed using a Ludlum model 2224 with a thin window Geiger-Mueller (GM) probe, a Ludlum Model 44-9, or equivalent.

- Alpha surveys are performed with a thin window gas flow proportional probe, a Ludlum model 2224 with 43-93 probe, or equivalent.

- Disk smears from equipment or buildings may be counted in the Ludlum Model 2929 attached to a zinc sulfide thin window scintillator, or equivalent

- The Ludlum Model 2224 Scaler with/239-1F detector or equivalent will be utilized to characterize flooring, during the characterization phase. The Model 2224 is battery-capable and will be mounted on a cart with a P-10 gas supply for easy handling and overall equipment protection.

- The Ludlum Model 19 or equivalent Micro-R meter will be used to document gamma exposure levels. The Model 19 is portable, battery powered and durable.

- The Bicron Micro-Rem Survey Meter or equivalent dose rate meter will be used to document tissue-equivalent gamma dose rates.

5 INSTRUMENT OPERATIONAL CHECKS

5.1 A pre-operational check will be performed on all instruments prior to use to verify the following requirements in accordance with RS-TPG SOP-001, *Portable Detection Equipment*, and RS-TPG SOP-002, *Swipe Counter*. In general:

5.1.1 The instrument must be source checked every day before use and at the end of each shift;

5.1.2 The instrument has been calibrated within the last year;

5.1.3 The battery check is satisfactory, and spare batteries are available (for portable instrumentation);

5.1.4 Overall physical condition of the instrument is satisfactory; and

5.1.5 A consistent low-background counting area must be selected for daily checks of the instruments.

6 PROCEDURES

The following procedures are for general guidance only. Project-specific work plans will fully describe survey requirements.

6.1 Exposure/Dose Rate Surveys

6.1.1 General Requirements

- Exposure/dose rate surveys are performed, using any of the exposure rate instruments approved for use, to provide an indication of the amount and type (e.g., beta or gamma) of external radiation exposure the workers will receive while performing routine work operations;
- A reasonable amount of care should be taken when performing exposure/dose rate surveys to identify items that are contributing to the general area exposure rates (i.e., barrels, equipment, etc.);
- Exposure/dose rates measurements should be observed continually while approaching a radiation source from a background area;
- All exposure/dose rates shall be recorded on a Radiological Survey Report Form, Attachment SOP011-1, or equivalent;
- Exposure/dose rates that are taken "on contact" shall be noted on the Radiological Survey Report Form, Attachment SOP011-1, or equivalent; and
- Items identified with exposure/dose rates greater than five times the general work area shall be recorded with an asterisk indicating "hot spot". As these items are identified, the surveyor should shield the item, or remove it from the area, if possible.

6.1.2 Gamma Surveys

- Gamma dose rates:
  - Allow instruments to stabilize for 15 to 30 seconds
  - Record measurements as mrem/hr or μrem/h
  - If the analog or digital display is sporadic and it difficult to obtain an average response, record 10 instantaneous readings and calculate the average.
- Gamma exposure rates:
  - Allow instruments to stabilize for 15 to 30 seconds
  - Use the detector slow response/integrating mode
  - Recorded measurements as mR/hr or μR/h

- If the analog or digital display is sporadic and it difficult to obtain an average response, record 10 instantaneous readings and calculate the average.

6.1.3 Beta Dose Rate Surveys

- Beta dose rates are recorded as mRad/hr (µGy/hr) or µRad/h;
- Beta dose rates are derived by the following formula:

mRad/hr = (OW - CW) x CF

OW = Open window exposure rate
CW = Closed window exposure rate
CF = Correction factor*

- The beta correction factor used for each instrument shall be determined by the calibration facility
- If the analog or digital display is sporadic and it difficult to obtain an average response, record 10 instantaneous readings and calculate the average.

6.2 Contamination Surveys

6.2.1 Contamination surveys are used as a tool to maintain control of work areas, verify clean areas, and establish protective clothing and requirements;

6.2.2 Removable contamination surveys are performed by using either disk smears or large area swipes (masslin cloth or similar). Disk smear surveys are performed by wiping a surface area approximately 100 cm^2.

6.2.3 Scan surveys may be performed with any approved count rate instrument. Consideration should be given to using the audible setting on the instrument, if so equipped, since audible response is quicker to respond to than the visual provided by the meter.

- When using the beta-gamma instrument, the detector should be held within 1/2 inch of the surface being frisked and moved no faster than 2 inches per second.

- When using the alpha instrument, the detector should be held within 1/4 inch of the surface being monitored and the probe moved no faster than 2 inches per second. Increased counts are an indication of alpha activity, when counts increase either by audible or visual, stop all detector motion until a stable count rate is determined.

6.2.4 Personnel contamination surveys ("frisking") shall be performed on individuals, materials, and equipment (M&E) exiting a radiologically controlled area by a qualified radiation professional or technician. Surveys are performed in accordance with Section 4.2.3. When surveying personnel, at a minimum, the bottoms of the shoes and hands should be scanned. During more detailed scans, detector movement should be paused at locations of potential contamination such as knees, elbows, and mouth.

6.2.5 General Requirements

- Count rate instruments approved for use shall be used for evaluating contamination levels of disk smears or wipes;
- Smears are counted in an area where the background is less than 100 cpm;
- Smears are placed 1/2" from the surface of the detector for 15 to 20 seconds to allow the count rate meter's indication to stabilize;
- Smear results are recorded on the Radiological Survey Report Form, Attachment 2-1, in disintegrations per minute.
- Disintegrations per minute per 100 square centimeters (dpm/100cm^2) shall be calculated from gross counts per minute (cpm) by the following formula. For smears, the area of the surface smeared (e.g., 100 cm^2) is substituted for the probe area.

$$dpm/100cm^2 = \frac{gross\ cpm - background\ cpm}{detector\ efficiency \times {}^{probe\ area}/_{100}}$$

Example:

$$dpm/100cm^2 = \frac{1200\ cpm - 100\ cpm}{20\% \times {}^{15cm^2}/_{100cm^2}}$$

6.3 Gamma Count Rate Surveys

6.3.1 With the detector as close to the surface as possible or some other pre-determined position, collect a measurement for a length of time sufficient to provide an acceptable minimum detectable count rate (MDCR). Record the measurement on the appropriate field survey form.

6.3.2 With the detector as close to the ground as possible, move the detector in a serpentine pattern while advancing along a predetermined survey area transect at a rate of not more than 1 meter per second. For instruments mounted on carts, ensure that the detector height allows sufficient field of view considering the coverage requirements and the spacing of the survey area transect. Record the average and maximum count rates observed for a predetermined survey area or log the data using appropriate survey and position logging instruments. When using data-logging instruments which also log position using GPS, follow additional instructions/procedure and download data at a frequency no less than once per day.

6.4 Survey Frequency

The frequency of routine surveys shall be determined at the start of the project by the Project Health Physicist based on the likelihood for contamination in the area. Survey coverage is generally described in a Survey Plan. Survey Plans will often be prepared according to the guidance in the Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM) but other guidance may be applicable under specific conditions. MARSSIM provides specific methods for determining the number of direct survey/sample locations.

6.5 Survey Documentation

Field surveys shall be documented on a Radiological Survey Report Form, Attachment 2-1, or equivalent. Final survey records documentation should include:

- Survey type
- The meter and probe model numbers and serial numbers
- Detector calibration dates
- Detector efficiencies
- Net measurement results (reported in dpm/100cm^2 or exposure/dose rate units)
- Minimum detectable concentrations (MDC)
- Date of the survey
- Name of individual performing the survey
- Maps, diagrams, or pictures.

6.6 Surveying Materials and Equipment (M&E).

- The surveying M&E (e.g., pipe, valves, tools, heavy equipment, vehicles, etc.) shall be performed and documented as in Sections 4.2 and 4.4.
- M&E surveys shall include a drawing, photograph, or description on the survey form and in the final survey record, to the extent it could be relocated and resurveyed. Measurement locations shall be identified.
- For projects involving a significant amount of surveys for the release of M&E, the Project Health Physicist should develop a separate Survey Plan in

accordance with the protocols described in the Multi-Agency Radiation Survey and Assessment of Materials and Equipment (MARSAME) Manual.

6.7 Posting Radiation and Contamination Areas.

- Posting of Radiation and Contamination Areas identified during radiological surveys will be done in accordance with RS-TPG, SOP 20, *License/Site Radiation Protection Program*.

7 RECORDS

7.1 Calibration Records and Daily Instrument Check Records (according to RS-TPG SOP-001, *Portable Detection Equipment.*

7.2 Radiological Survey Record, Attachment 1.

7.3 An electronic version of Attachment 1 can be obtained from the RS-TPG Leader.

ATTACHMENT 1
RADIOLOGICAL SURVEY RECORD

AECOM | **Project Name** | **Survey No.:** _____
Project No.

Surveyor: ______________________________ ____________

Reviewer: ______________________________ ____________

Date

Survey Meters

Total (Direct) β γ	Removable β γ	Removable α	Dose γ
Instrument #	Instrument #	Instrument #	Instrument #
Meter Model #	Meter Model #	Meter Model #	Meter Model #
Meter Serial #	Meter Serial #	Meter Serial #	Meter Serial #
Detector Model #	Detector Model #	Detector Model #	Detector Model #
Detector Serial #	Detector Serial #	Detector Serial #	Detector Serial #
Cal Due	Cal Due	Cal Due	Cal Due
Detector Efficiency (ε_i)	Detector Efficiency (ε_i)	Detector Efficiency (ε_i)	Detector Efficiency (ε_i)
Surface Efficiency (ε_s)	Surface Efficiency (ε_s)	Surface Efficiency (ε_s)	(Approximate)
Sample Time (T_s) (min)	Sample Time (T_s) (min)	Sample Time (T_s) (min)	Sample Time (T_s) (min)
Background Time (T_b) (min)	Background Time (T_b) (min)	Background Time (T_b) (min)	Background Time (T_b) (min)
BKG (R_b) (cpm)	BKG (R_b) (cpm)	BKG (R_b) (cpm)	BKG (R_b) (cpm)
Probe Area (A) (cm)	Swipe Area (A) (cm)	Swipe Area (A) (cm)	Probe Area (A) (cm)
MDC (dpm/100cm2)	MDC (dpm/100cm2)	MDC (dpm/100cm2)	MDC (dpm/100cm2)

		dpm/100cm^2	dpm/100cm^2	dpm/100cm^2	uR/hr
LOCATION:	Location	α/β/γ - Total	β/γ - Remov.	α - Remov.	γ - Dose
PURPOSE:	1				
	2				
	3				
	4				
	5				
	6				
	7				
	8				
	9				
	10				
	11				
	12				
	13				
	14				
	15				

Field Change Order Procedures

SOP Number 100Pines

Revision Number: 3.0

September 2013

AECOM Project Manager
September 24, 2013

AECOM Project QA Officer
September 24, 2013

AECOM
September 2013
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

FCO	Field Change Order
FSP	Field Sampling Plan
HASP	Health and Safety Plan
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
RI	Remedial Investigation
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes field change order (FCO) procedures applicable to AECOM sampling and analysis programs.

2.0 SUMMARY OF METHOD

Procedural changes in the field can be needed when the sample network is changed (i.e., fewer or more samples, adjustments to locations) or when field procedures require modification due to unexpected conditions. Changes made in the field will be documented on an FCO form (see Figure 1).

3.0 HEALTH AND SAFETY WARNINGS

Not applicable.

4.0 INTERFERENCES

Not applicable.

5.0 PERSONNEL QUALIFICATIONS

Individuals responsible for completing FCO documentation must be personnel working on the specific field program for which the change is necessary, have read this SOP, and have worked under the oversight of experienced personnel.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- FCO Form (Figure 1)
- Field project logbook/pen
- Approved plans (e.g., FSP, QAPP, HASP)

7.0 METHODS

7.1 Field Change Order

7.1.1 The field personnel and/or the Field Operations Leader will recommend a change in consultation with the AECOM Project Manager, the AECOM Remedial Investigation (RI) Task Manager, and/or the AECOM Project Quality Assurance (QA) Officer. The AECOM Project Manager, RI Task Manager, or QA Officer will approve the change, which will be implemented by the field personnel. Approval may initially be received verbally or electronically, but will be documented on the FCO, as detailed below.

7.1.2 The following information shall be completed on the FCO form (Figure 1):

- Date
- Project name
- Project number
- Description of change and reason and justification for change, including reference to section(s) of Work Plan(s) affected
- Field personnel or Field Operations Leader signature and date
- Project Manager, RI Task Manager, or QA Officer signature and date

7.1.3 Field changes will be implemented and documented in the field logbook. No field personnel will initiate field changes without prior communication of findings through the proper channels. Thus, communication will be documented in the field logbook and FCO form.

8.0 DATA AND RECORDS MANAGEMENT

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Quality control will consist of implementing the field change process as described above, including the appropriate approval process.

10.0 REFERENCES

Not applicable.

FIGURE 1 - Example Field Change Order Form

Field Change Order (FCO)
DATE: **PROJECT NAME:** **PROJECT NUMBER:**
DESCRIPTION OF CHANGE AND RATIONALE
SIGNATURE APPROVALS IN THE FIELD: ______________________________ DATE: ____________ MANAGEMENT: ______________________________ DATE: ____________

Management may include RI Task Manager, Project Manager and/or QA Officer.

Split Spoon Sampling for Geologic Logging

SOP Number 109Pines

Revision Number: 3.0

September 2013

AECOM Project Manager
September 24, 2013

AECOM Project QA Officer
September 24, 2013

AECOM
September 2013
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
FSP	Field Sampling Plan
HASP	Health and Safety Plan
IDEM	Indiana Department of Environmental Management
OSHA	Occupational Safety and Health Adminstration
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure
SPT	Standard Penetration Test
USCS	Unified Soil Classification System
USDA	United States Department of Agriculture

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the methods used to obtain subsurface soil samples for geologic logging and physical characterization. Subsurface soil samples are obtained in conjunction with soil boring programs, and provide information on the physical and/or chemical makeup of the subsurface environment.

The purpose of this SOP is to provide a description of a specific method or procedure to be used in the collection of subsurface soil samples. Subsurface soil is defined as unconsolidated material that may consist of one or a mixture of the following materials: sand, gravel, silt, clay, peat (or other organic soils), and/or fill material. Subsurface soil sampling conducted in accordance with this SOP will promote consistency in sampling and provide a basis for sample representativeness.

This SOP covers subsurface soil sampling by split-spoon only.

2.0 SUMMARY OF METHOD

Split-spoon subsurface soil sampling generally requires use of a drilling rig and, typically, the hollow-stem auger or other common drilling method to generate a borehole in which to use the split-spoon sampler. The split-spoon sampler is inserted through the augers (or other type of drill casing) and then driven into the subsurface soil with a weighted hammer. The sampler is then retrieved and opened to reveal the recovered soil sample. Soil samples may be collected at continuous intervals or at pre-selected vertically spaced intervals within the borehole.

3.0 HEALTH AND SAFETY WARNINGS

Subsurface soil sampling may involve chemical hazards associated with exposure to the constituents potentially present in the subsurface and physical hazards associated with use of drilling equipment. When subsurface soil sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result from cross-contamination between samples or sample locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per AECOM SOP No. 7600Pines – Decontamination of Field Equipment.

5.0 PERSONNEL QUALIFICATIONS

Soil sampling by split-spoon requires a moderate degree of training and experience as numerous drilling situations may occur that will require field decisions to be made. It is recommended that inexperienced personnel be supervised for several drilling locations before working on their own. Geologists or personnel with geologic experience should supervise drilling activities. The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana.

Field and subcontract personnel will be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It will be the responsibility of field personnel to ensure that subsurface soil sampling is conducted in a manner that is consistent with this SOP. Field personnel will observe all activities pertaining to subsurface soil sampling to ensure that the SOP is followed, and to record all pertinent data onto a boring log and/or field logbook. It is also the field personnel's responsibility to indicate the specific targeted sampling depth or sampling interval to the drilling subcontractor. Field personnel are also responsible for preparing a geologic description of the soils once the sampling device has been retrieved and opened. Field personnel are responsible for compiling a detailed log of the geologic materials encountered.

It will be the responsibility of the drilling subcontractor to provide a trained operator and the necessary materials for obtaining subsurface soil samples. This generally includes one or more split-spoon samplers in good, operating condition. It is the drilling subcontractor's responsibility to provide and maintain their own boring logs if desired.

6.0 EQUIPMENT AND SUPPLIES

In addition to those materials provided by the subcontractor, other field supplies include:

- Boring Log Forms (Figure 1)
- Plastic sheeting
- Trash bags
- Folding rule or tape measure
- Utility knife
- Equipment decontamination materials (as required by AECOM SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by HASP)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field project logbook/pen

7.0 METHODS

7.1 General Method Description

Split-spoon sampling devices are typically constructed of steel and are most commonly available in lengths of 18 and 24 inches and diameters of 1.5 to 3 inches. The split-spoon consists of a tubular body with two halves that split apart lengthwise, a drive head on the upper end with a ball-check valve for venting, and a hardened steel cutting shoe at the bottom. The soil sample enters the split-spoon through the cutting shoe as the device is driven into the ground. A replaceable plastic or metal basket is often inserted into the shoe to assist with retaining samples. Once the sampler is retrieved, the drive head and cutting shoes are removed and the split-spoon halves are then separated, revealing the sample.

Sample depth intervals are defined in the Field Sampling Plan (FSP). For this project, continuous split-spoon samples will be collected to enable development of detailed geologic boring logs.

7.2 General Procedures – Borehole Preparation

7.2.1 Advancing Casing/Augers

Soil borings that are completed for soil sampling purposes are typically advanced using hollow-stem augers and sometimes drive-and-wash or other casing methods, operated by a qualified subcontractor. The casing/augers must be of sufficient diameter to allow for soil sampling at a minimum. If hollow-stem augers are used, a temporary plug shall be used in the lead auger to prevent the auger from becoming filled with drill cuttings while drilling is in progress.

7.2.2 Obstructions

For those borings that encounter obstructions, the casing/augers will be advanced past or through the obstruction if possible. Caution should be exercised when obstructions are encountered and an effort made to identify the obstruction before drilling is continued. If the obstruction is not easily drilled through or removed, the boring should be relocated to an adjacent location, in consultation with the AECOM Remedial Investigation (RI) Task Manager. Such changes will be documented in accordance with AECOM SOP No. 100Pines – Field Change Order Procedures.

7.2.3 Use of Added Water

The use of added or recirculated water during drilling is permitted when necessary, for example, to control running sands. Based on previous experience at Yard 520, running sands, when encountered, are typically controlled by maintaining a head of water in the augers. Use of extraneous water should be minimized or avoided if possible because it may impact sample quality. Only potable water will be used, and water usage should be documented in the field logbook. Sampling and analysis of added or recirculated water may be required for quality assurance purposes. If a well is installed within the completed borehole, removal of the added water through well development is required (refer to AECOM SOP No. 7221Pines – Monitoring Well Development).

7.3 Split Spoon Sampling Procedure

7.3.1 Standard Penetration Test

The drilling subcontractor will lower the split-spoon into the borehole. Samples are generally obtained using the Standard Penetration Test (SPT) in accordance with American Society for Testing and Materials (ASTM) standards (ASTM D 1586-84). Following this method, the sampler will be driven using the 140-pound hammer with a vertical free drop of 30 inches using two turns of the rope on the cathead (or equivalent). The number of hammer blows required for every 6 inches of penetration will be recorded on the boring log by the field personnel. Blowcount information is used as an indicator of soil density for geotechnical as well as stratigraphic logging purposes. Once the split-spoon has been driven to its fullest extent, or to refusal, it will be removed from the borehole.

7.3.2 Sample Recovery

Sample recovery will be determined by field personnel who will examine the soil core once the sampler is opened. The length of sample shall then be measured with a folding rule or tape measure and recorded in the field logbook or boring log. Any portion of the split-spoon contents that are not considered part of the true sample (e.g., heaved soils) will be discarded.

7.4 Sample Logging

Geologic materials recovered from boreholes will be logged in accordance with the Unified Soil Classification System (USCS) protocols (see, for example, USEPA, 1991). Geologic descriptions will be entered on a boring log (see Figure 1). Specific information to be recorded on the log may include:

- Location identification and/or description
- Drilling subcontractor
- Geologist/field personnel name
- Drilling date
- Drilling equipment
- Split-spoon sample interval
- Blow counts
- Total depth of boring

Additional geologic description information to be recorded may include:

- Moisture content
- Color
- Grain-size
- Sorting
- Density
- Plasticity
- Other relevant observations

In accordance with Indiana Department of Environmental Management (IDEM) guidance (IDEM, 1988), additional information may also be recorded, such as U.S. Department of Agriculture (USDA) soil classification, rounding, effervescence, mineralogy, and bedding. Additional information concerning geologic logging protocols is attached to this SOP.

7.5 Equipment Decontamination

All equipment that comes into contact with soil and/or groundwater (e.g., drill rig, split-spoon) will be decontaminated in accordance with AECOM SOP No. 7600Pines – Decontamination of Field Equipment before moving to the next location.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding the split spoon sample collection should be documented in the boring log and field logbook. Additional information regarding each form of documentation is presented in the following paragraphs:

8.1 Boring Log

This form (Figure 1) will be used to record the geologic description of the split spoon samples collected. Logging protocols are attached to this SOP. Geologic logs will be reviewed by a geologist licensed to practice in Indiana.

8.2 Field Logbook

This logbook should be dedicated to the project and should be used by field personnel to maintain a general log of activities throughout the sampling program. This logbook should be used in support of, and in combination with, the sample collection record. Documentation within the logbook should be thorough and sufficiently detailed to present a concise, descriptive history of the sample collection process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana. Boring logs will be reviewed by the licensed Indiana geologist.

10.0 REFERENCES

ASTM D 1586-84. 1992. “Test Method for Penetration Test and Split-Barrel Sampling of Soils”.

AECOM SOP No. 100Pines – Field Change Order Procedures. Revision 3.0.

AECOM SOP No. 7221Pines – Monitoring Well Development.

AECOM SOP No. 7600Pines – Decontamination of Field Equipment. Revision 4.0.

IDEM. 1988. Technical Guidance Document, Volume 1 – Requirements for Describing Unconsolidated Deposits. Indiana Department of Environmental Management. Draft, Revised November 18, 1988.

USEPA. 1991. Description and Sampling of Contaminated Soils: A Field Pocket Guide. EPA/625/12-91/002. November 1991.

FIGURE 1 – EXAMPLE SUBSURFACE SOIL BORING LOG

AECOM	*Client:*	***BORING ID:***
	Project Number:	
	Boring Location:	
		Sheet: 1 of 1
	Drilling Method:	*Date/Time Started:*
	Weather:	
Logged By:		*Date/Time Finished:*
Drilled By:		

Depth (ft)	Sample Number	Sample Type	Recovery (ft)	Density (SPT)	U.S.C.S	**Lithologic Description**	Remarks	Well Construction Details
_1								
_2								
_3								
_4								
_5								
_6								
_7								
_8								
_9								
_0								
_1								
_2								
_3								
_4								
_5								
_6								
_7								
_8								
_9								
_0								

END OF BORING @ ' below ground surface (bgs)

NOTES:

Checked by:____________ Date:_______________

Chain-of-Custody Procedures

SOP Number 1007Pines

Revision Number: 5.0

September 2013

AECOM Project Manager
September 24, 2013

AECOM Project QA Officer
September 24, 2013

AECOM
September 2013
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

COC	Chain-of-Custody
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure
USEPA	United States Environmental Protection Agency

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes chain-of-custody (COC) procedures applicable to AECOM sampling and analysis programs.

2.0 SUMMARY OF METHOD

The National Enforcement Investigations Center of the U.S. Environmental Protection Agency (USEPA) defines custody of evidence in the following manner:

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

Samples are physical evidence and should be handled according to certain procedural safeguards described in of this SOP.

3.0 HEALTH AND SAFETY WARNINGS

Not applicable.

4.0 INTERFERENCES

Not applicable.

5.0 PERSONNEL QUALIFICATIONS

Individuals responsible for completing COC documentation must be personnel working on the specific field program, have read this SOP, and have worked under the oversight of experienced personnel.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Sample Labels

- COC Form (Figure 1)
- COC Tape (Figure 2)
- Field project logbook/pen

7.0 METHODS

7.1 Field Custody

7.1.1 The field personnel is required to complete the following information on the COC form (Figure 1):

- Project Number (not project name)
- Project Location
- Field Sample Identification Number
- Date and Time of Sample Collection
- Sample Matrix
- Preservative
- Analysis Requested
- Sampler's Signature
- Signature of Person Relinquishing Sample Custody
- Date and Time Relinquished
- Sampler Remarks
- COC Tape Number

7.1.2 The COC must be filled out completely and legibly in ink. Corrections will be made, if necessary, by drawing a single line through and initialing and dating the error. The correct information is then recorded with indelible ink. All transfers from field personnel to laboratory personnel are recorded on the COC form in the "Relinquished By" and "Received By" sections.

7.1.3 If samples are to be shipped by overnight commercial courier (e.g., Federal Express), the field personnel must complete a COC form for each package (e.g., cooler) of samples and place a copy of each completed form inside the associated package before the package is sealed. Each completed COC form must accurately list the sample identification numbers of the samples with which it is packaged, and must contain the identification number of the COC tape on the package. It is not necessary for the shipping company to sign the COC.

Sample packaging will be conducted in accordance with AECOM SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

7.1.4 If samples are hand carried to a laboratory, the person hand carrying the samples is the sample custodian. If the carrier is a different person than the one who filled out the COC form and packaged the samples, then that person must transfer custody to the carrier by signing and dating each form in the "Relinquished By" section. The carrier must then sign and date each form in the adjacent "Received By" section. When the carrier transfers the samples to the laboratory, he or she must sign and date each form in the next "Relinquished By" section, and the laboratory sample custodian must sign and date each form in the adjacent "Received By" section.

7.2 Laboratory Sample Receipt and Inspection

7.2.1 Upon sample receipt, the coolers or packages are inspected for general condition and the condition of the COC tape. The coolers or boxes are then opened and each sample is inspected for damage.

7.2.2 Sample containers are removed from packing material and sample label field identification numbers are verified against the COC form.

7.2.3 The following information is recorded in the laboratory's records:

- Airbill Number
- Presence/absence of COC forms and COC tape
- Condition of samples
- Discrepancies noted
- Holding time and preservatives
- Sample storage location

7.2.4 The COC form is completed by signing and recording the date and time of receipt.

7.2.5 The AECOM Project Manager or designate must be notified of any breakage, temperature exceedances, or discrepancies between the COC paperwork and the samples.

8.0 DATA AND RECORDS MANAGEMENT

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion, and in the files of the laboratories that have performed the sample analyses.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

The records generated in this procedure are subject to review during data validation, in accordance with the Quality Assurance Project Plan (QAPP).

10.0 REFERENCES

AECOM SOP No. 7510Pines - Packaging and Shipment of Environmental Samples.

FIGURE 1 EXAMPLE CHAIN OF CUSTODY FORM

AECOM

CHAIN OF CUSTODY RECORD

Page _1_ of _1_

Client/Project Name:	Project Location:	
Project Number:	Field Logbook No.:	
Sampler (Print Name)/(Affiliation):	Chain of Custody Tape Nos.:	
Signature:	Send Report to:	TAT: Standard

Analysis Requested

Container Type
P – Plastic
A – Amber Glass
G – Clear Glass
V – VOA Vial
O – Other
E – Encore

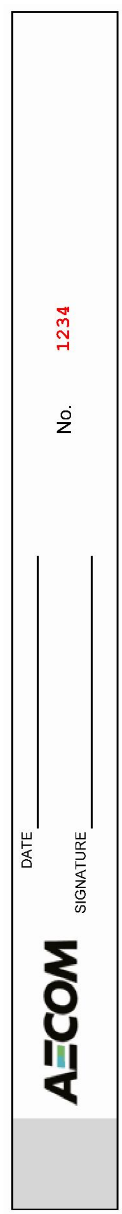
Preservation
1 – HCl, 4°
2 – H_2SO_4, 4°
3 – HNO_3, 4°
4 – NaOH, 4°
5 – NaOH/ZnAc, 4°
6 – $Na_2S_2O_3$, 4°
7 – 4°

Matrix Codes:
DW – Drinking Water
WW – Wastewater
GW – Groundwater
SW – Surface Water
ST – Storm Water
W – Water
S – Soil
SL – Sludge
SD – Sediment
SO – Solid
A – Air
L – Liquid
P – Product

Field Sample No./Identification	Date	Time	COMP	GRAB	Sample Container (Size/Mat'l)	Matrix	Preserv.	Field Filtered	Boron										Lab I.D.	Remarks

Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Analytical Laboratory (Destination):
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Sample Shipped Via: UPS FedEx Courier Other Temp blank: Yes No

FIGURE 2 EXAMPLE CHAIN OF CUSTODY TAPE



Packaging and Shipment of Environmental Samples

SOP Number 7510Pines

Revision Number: 5.0

September 2013

AECOM Project Manager
September 24, 2013

AECOM Project QA Officer
September 24, 2013

AECOM
September 2013
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

COC	Chain-of-Custody
DOT	Department of Transportation
HASP	Health and Safety Plan
OSHA	Occupational Safety and Health Adminstration
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
RCRA	Resource Conversation and Recovery Act
RI	Remedial Investigation
SOP	Standard Operating Procedure
USEPA	United States Environmental Protection Agency

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures associated with the packaging and shipment of environmental samples consisting of water, soil, and sediment submitted for routine environmental testing. Environmental samples are not considered a Resource Conservation and Recovery Act (RCRA) classified hazardous waste by definition; therefore, more stringent RCRA and Department of Transportation (DOT) regulations regarding sample transportation do not apply. Environmental samples do, however, require fairly stringent packaging and shipping measures to ensure sample integrity as well as safety for those individuals handling and transporting the samples.

This SOP is designed to provide a high degree of certainty that environmental samples will arrive at their destination intact. This SOP assumes that samples will often require shipping overnight by a commercial carrier service; therefore, the procedures are more stringent than may be necessary if a laboratory courier is used or if samples are transported directly to their destination by a field personnel. Should either of the latter occur, the procedures may be modified to reflect a lesser degree of packaging requirements.

2.0 SUMMARY OF METHOD

Sample packaging and shipment involves the placement of individual sample containers into a cooler or other similar shipping container and placement of packing materials and coolant in such a manner as to isolate the samples, maintain the required temperature, and to limit the potential for damage to sample containers when the cooler is transported.

3.0 HEALTH AND SAFETY WARNINGS

Sampling personnel should be aware that packaging and shipment of samples involves potential exposure and physical hazards primarily associated with handling of occasional broken sample containers and lifting of heavy objects. Adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Sample containers with presumed high constituent concentrations should be isolated within their own cooler with each sample container placed into a zipper-lock bag.

5.0 PERSONNEL QUALIFICATIONS

Sample packaging and shipment is a relatively simple procedure requiring minimal training and a minimal amount of equipment. It is recommended that initial attempts be supervised by more experienced personnel.

Field personnel should be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this SOP, quality assurance, and health and safety requirements outlined within the FSP, Quality Assurance Project Plan (QAPP), and HASP. Field personnel are also responsible for proper documentation in the field logbook.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Sample coolers
- Sample containers
- Shipping labels
- Chain-of-custody (COC) form (Figure 1)
- Custody tape (Figure 2)
- Bubble wrap
- Vermiculite (granular), or styrofoam pellets
- Ice
- Temperature blank
- Transparent tape, or rubber bands
- Fiber tape
- Duct tape

- Utility knife
- Zipper-lock plastic bags
- Trash bags
- Health and safety supplies (as required by the HASP)
- Field project logbook/pen

7.0 METHODS

7.1 Preparation

The extent and nature of sample containerization will be governed by the type of sample, and the most reasonable projection of the sample's hazardous nature and constituents. U.S. Environmental Protection Agency (USEPA) regulations (40 CFR Section 261.4(d)) specify that samples of solid waste, water, soil or air, collected for the sole purpose of testing, are exempt from regulation under RCRA when any of the following conditions are applicable:

- Samples are being transported to a laboratory for analysis;
- Samples are being transported to the collector from the laboratory after analysis;
- Samples are being stored (1) by the collector prior to shipment for analyses, (2) by the analytical laboratory prior to analyses, or (3) by the analytical laboratory after testing but prior to return of sample to the collector or pending the conclusion of a court case.

7.1.1 Laboratory Notifications

Prior to sample collection, the AECOM Remedial Investigation (RI)/Feasibility Study (FS) Task Manager or designee must notify the laboratory project manager of the number, type, and approximate collection and shipment dates for the samples. If the number, type, or date of sample shipment changes due to program changes that may occur in the field, the AECOM RI/FS Task Manager or alternate must notify the laboratory of the changes. Additional notification from the field is often necessary when shipments are scheduled for weekend delivery.

7.1.2 Cooler Inspection and Decontamination

Laboratories will often re-use coolers. Every cooler received at a project location should be inspected for condition and cleanliness. Any coolers that exhibit cracked interiors or exterior linings/panels or hinges should be discarded because the insulating properties of the coolers would be considered compromised. Any coolers missing one or both handles should also be discarded if replacement handles (i.e., knotted rope handles) can not be fashioned in the field.

The interior and exterior of each cooler should be inspected for cleanliness before using it. Excess strapping tape and old shipping labels should be removed. If the cooler interior exhibits visible contamination or odors it should not be used. Drain plugs should be sealed on the inside with duct tape.

7.2 Sample Packaging

7.2.1 Place plastic bubble wrap matting over the base of each cooler or shipping container as needed. A 2- to 3-inch thick layer of vermiculite may be used as a substitute base material.

7.2.2 Insert a clean trash bag into the cooler to serve as a liner.

7.2.3 Check that each sample container is sealed, labeled legibly, and is externally clean. Re-label and/or wipe bottles clean if necessary. Clear tape should be placed over the labels to protect them and keep them from falling off the container. Wrap each sample bottle individually with bubble wrap secured with tape or rubber bands. For aqueous samples in glass containers, each sample should be sealed in a zipper-lock bag to prevent leakage and cross-contamination in the case of breakage. Place bottles into the cooler in an upright single layer with approximately one inch of space between each bottle. Do not stack bottles or place them in the cooler lying on their side. If plastic and glass sample containers are used, alternate the placement of each type of container within the cooler so that glass bottles are not placed side by side.

7.2.4 Insert the cooler temperature blank supplied by the laboratory into each cooler (if any).

7.2.5 Place additional vermiculite, bubble wrap, and/or styrofoam pellet packing material throughout the voids between sample containers within each cooler to a level that meets the approximate top of the sample containers. Packing material may require tamping by hand to reduce the potential for settling.

7.2.6 Cubed ice in heavy duty zipper-lock plastic bags or loose ice may be used. Cold packs should be used only if the samples are chilled before being placed in the cooler.

7.2.7 Add additional bubble wrap/styrofoam pellets or other packing materials to fill the balance of the cooler or container.

7.2.8 Obtain two pieces of COC tape as shown in Figure 2 and enter the custody tape numbers in the appropriate place on the COC form (Figure 1). Sign and date the COC tape.

7.2.9 Complete the COC form per AECOM SOP No. 1007Pines – Chain-of-Custody Procedures. If shipping the samples involves use of a third party commercial carrier service, sign the COC record thereby relinquishing custody of the samples. Shippers should not be asked to sign COC records. If a laboratory courier is used, or if samples are transported to the laboratory by field personnel, the receiving party should accept custody and sign the COC records. Remove the last copy from the multi-form COC and retain it with other field notes. Place the original (with remaining copies) in a zipper-lock plastic bag and tape the bag to the inside lid of the cooler or shipping container.

7.2.10 Close the lid of the cooler or the top of the shipping container.

7.2.11 Place the COC tape at two different locations (i.e., one tape on each side) on the cooler or container lid and overlap with transparent packaging tape.

7.2.12 Packaging tape should be placed entirely around the sample shipment containers. A minimum of two full wraps of packaging tape will be placed at least two places on the cooler/container.

7.2.13 Repeat the above steps for each cooler or shipping container.

7.3 Sample Shipping

Transport the cooler/container to the package delivery service office or arrange for package pick-up at the site. Fill out the appropriate shipping form or airbill and affix it to the cooler/container. Some courier services may use multi-package shipping forms where only one form needs to be filled out for all packages going to the same destination. If not, a separate shipping form should be used for each cooler/container. The receipt for package tracking purposes should be kept in the project files, in the event a package becomes lost.

Each cooler/container also requires a shipping label that indicates point of origin and destination. This will aid in recovery of a lost cooler/container if a shipping form gets misplaced.

Never leave coolers/containers unattended while waiting for package pick-up.

Airbills or waybills will be maintained as part of the custody documentation in the project files.

7.4 Sample Receipt

Upon receipt of the samples, the analytical laboratory will open the cooler or shipping container and will sign "received by laboratory" on each COC form. The laboratory will verify that the COC tape has not been broken previously and that the tape number corresponds with the number on the COC record. The laboratory will note the condition of the samples upon receipt and will identify any discrepancies between the contents of the cooler/container and COC. The analytical laboratory will then forward the back copy of the COC record to the project Quality Assurance (QA) Officer to indicate that sample transmittal is complete.

8.0 DATA AND RECORDS MANAGEMENT

Documentation supporting sample packaging and shipment consists of COC records and shipping records. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

The potential for samples to break during transport increases greatly if individual containers are not snugly packed into the cooler. Packed coolers may be lightly shake-tested to check for any loose bottles. The cooler should be repacked if loose bottles are detected.

Environmental samples are generally shipped so that the samples are maintained at a temperature of approximately 4°C. Temperature blanks may be required for some projects as a quality assurance check on shipping temperature conditions. These blanks usually are supplied by the laboratory and consist of a 40-ml vial or plastic bottle filled with tap water. Temperature blanks should be placed near the center of the cooler.

10.0 REFERENCES

AECOM SOP No. 1007Pines – Chain-of-Custody Procedures. Revision 5.0.

FIGURE 1 - Example Chain of Custody Form

AECOM **CHAIN OF CUSTODY RECORD**

Page _1_ of _1_

Client/Project Name:	Project Location:		Analysis Requested
Project Number:	Field Logbook No.:		
Sampler (Print Name)/(Affiliation):	Chain of Custody Tape Nos.:		
Signature:	Send Report to:	TAT: Standard	

Container Type
P – Plastic
A – Amber Glass
G – Clear Glass
V – VOA Vial
O – Other
E – Encore

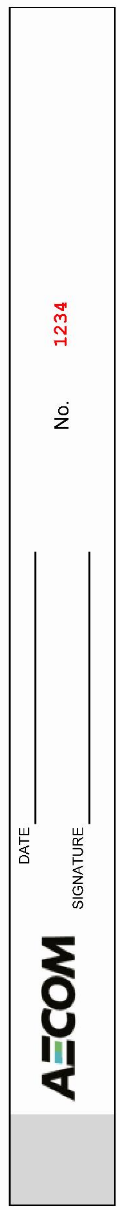
Preservation
1 – HCl, 4°
2 – H2SO4, 4°
3 – HNO3, 4°
4 – NaOH, 4°
5 – NaOH/ZnAc, 4°
6 – Na2S2O3, 4°
7 – 4°

Matrix Codes:
DW – Drinking Water
WW – Wastewater
GW – Groundwater
SW – Surface Water
ST – Storm Water
W – Water
S – Soil
SL – Sludge
SD – Sediment
SO – Solid
A – Air
L – Liquid
P – Product

Field Sample No./Identification	Date	Time	COMP	GRAB	Sample Container (Size/Mat'l)	Matrix	Preserv.	Field Filtered	Boron									Lab I.D.	Remarks

Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Analytical Laboratory (Destination):
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Sample Shipped Via: UPS FedEx Courier Other / Temp blank Yes No

FIGURE 2 - Example Chain of Custody Tape



Decontamination of Field Equipment

SOP Number 7600Pines

Revision Number: 4.0

September 2013

AECOM Project Manager
September 24, 2013

AECOM Project QA Officer
September 24, 2013

AECOM
September 2013
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
IDW	Investigation Derived Waste
OSHA	Occupational Safety and Health Administration
QC	Quality Control
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
QAPP	Quality Assurance Project Plan

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the methods to be used for the decontamination of field equipment used in the collection of environmental samples. Field equipment for decontamination may include a variety of items used in the field for monitoring or for collection of soil, sediment, and/or water samples, such as water level meters, water quality monitoring meters (turbidity meter, multi-parameter meter), split-spoon samplers, trowels, scoops, spoons, and pumps. Heavy equipment such as drill rigs also requires decontamination, usually in a specially constructed temporary decontamination area.

Decontamination is performed as a quality assurance measure and a safety precaution. Improperly decontaminated sampling equipment can lead to misinterpretation of environmental data due to interference caused by cross-contamination between samples or sample locations through use of contaminated equipment. Decontamination also protects field personnel from potential exposure to hazardous materials on equipment.

This SOP emphasizes decontamination procedures to be used for decontamination of reusable field equipment. Dedicated or disposable equipment will not need to be decontaminated.

2.0 SUMMARY OF METHOD

Decontamination is accomplished by manually scrubbing, washing, or spraying equipment with detergent solutions, tap water, distilled/deionized water, and/or solvents.

Generally, decontamination of equipment is accomplished at each sampling site between collection points. Waste decontamination materials such as spent liquids and solids will be collected and managed as investigation derived waste (IDW) for later management and/or disposal (refer to procedures outlined in the Field Sampling Plan (FSP) or Sampling and Analysis Plan (SAP)). All decontamination materials, including wastes, should be stored in a central location so as to maintain control over the materials used or produced throughout the investigation program.

3.0 HEALTH AND SAFETY WARNINGS

Decontamination procedures may involve chemical exposure hazards associated with exposure to soil, water, or sediment and may involve physical hazards associated with decontamination materials. When decontamination is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Equipment decontamination should be performed a safe distance away from the sampling area so as not to interfere with sampling activities, but close enough to the sampling area to maintain an efficient working environment.

5.0 PERSONNEL QUALIFICATIONS

Decontamination of field equipment is a relatively simple procedure requiring minimal training. It is recommended that the initial decontamination of field equipment be supervised by more experienced personnel. Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of field personnel to be familiar with the decontamination procedures outlined within this SOP, quality assurance, and health and safety requirements outlined within FSP, Quality Assurance Project Plan (QAPP), and HASP. Field personnel are responsible for decontamination of field equipment and for proper documentation in the field logbook.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Decontamination agents (which are specified in the FSP):
  - DETERGENT8®, or other non-phosphate and non-borate biodegradable detergent;
  - Tap water;
  - Distilled/deionized water; and/or
  - 10% nitric acid solution.
- Health and safety supplies (as required by the HASP)
- Chemical-free paper towels
- Waste storage containers: drums, 5-gallon buckets with covers, plastic bags
- Cleaning containers: plastic buckets or tubs
- Cleaning brushes

- Pressure sprayers
- Squeeze bottles
- Plastic sheeting
- Aluminum foil
- Zipper-lock bags
- Approved plans (e.g., HASP, QAPP, FSP)
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

7.1.1 New materials, such as well materials, are generally assumed to be clean and decontamination is not anticipated. However, they should be inspected and if they appear to be dirty, should be decontaminated.

Field equipment that is not frequently used should be wrapped in aluminum foil, shiny side out, and stored in a designated "clean" area. Small field equipment can also be stored in zipper-lock plastic bags to eliminate the potential for contamination. Field equipment should be inspected and decontaminated prior to use if the equipment appears dirty.

7.1.2 Heavy equipment (drill rigs, Geoprobes®, excavators) should be decontaminated upon arrival at the Area of Investigation, prior to beginning any work.

7.1.2 A decontamination station will be established within an area that is convenient to each sampling location. If single samples will be collected from multiple locations, then a centralized decontamination station or a portable decontamination station may be established.

7.1.3 One or more IDW containment stations should be established at this time also. In general, decontamination solutions are discarded as IDW between sampling locations.

7.2 Decontamination for Inorganic (Metals) Analyses

7.2.1 This procedure applies to equipment used in the collection of environmental samples submitted for inorganic constituent analysis. Examples of relevant items of equipment include split-spoons, trowels, scoops/spoons, and other small items. Submersible pump decontamination procedures are outlined in Section 7.4.

7.2.2 Decontamination is to be performed before sampling events and between sampling points, unless otherwise noted in the FSP or SAP.

7.2.3 After a sample has been collected, remove all gross contamination from the equipment or material by brushing and then rinsing with available tap water. This initial step may be completed using a 5-gallon bucket filled with tap water. A water pressure sprayer may also be used to remove solids and/or other contamination.

7.2.4 Wash the equipment with a non-phosphate and non-borate detergent and tap water solution. This solution should be kept in a 5-gallon bucket with its own brush.

7.2.5 Rinse with tap water or distilled/deionized water until all detergent and other residue is washed away. This step can be performed over an empty bucket using a squeeze bottle or pressure sprayer.

7.2.6 Rinse with 10% nitric acid.

7.2.7 Rinse with distilled/deionized water to remove any residual acid.

7.2.8 Allow the equipment to air-dry in a clean area or blot with chemical-free paper towels before reuse. Wrap the equipment in aluminum foil with the shiny side out and/or seal it in a zipper-lock plastic bag if it will not be reused immediately.

7.2.9 Dispose of soiled materials and spent solutions in the designated IDW disposal containers.

7.3 Decontamination of Submersible Pumps

7.3.1 This procedure will be used to decontaminate submersible pumps before and between groundwater sample collection points. This procedure applies to both electric submersible and bladder pumps. This procedure does not apply to discharge tubing if it will be reused between sampling points (see section 7.3.8 below).

7.3.2 Prepare the decontamination area if pump decontamination will be conducted next to the sampling point. If decontamination will occur at another location, the pump may be removed from the well and placed into a clean trash bag for transport to the decontamination area. Pump decontamination is easier with the use of 3-foot tall pump cleaning cylinders (i.e., Nalgene cylinder) for the various cleaning solutions, although the standard bucket rinse equipment may be used.

7.3.3 Once the decontamination station is established, the pump should be removed from the well and the discharge tubing and power cord coiled by hand as the equipment is removed. If any of the equipment needs to be put down temporarily, place it on a plastic sheet (around well) or in a clean trash bag. If a disposable discharge line is used it should be removed and discarded at this time.

7.3.4 As a first step in the decontamination procedure, use a pressure sprayer with tap water to rinse the exterior of the pump and power cord as necessary. Collect the rinsate and handle as IDW.

7.3.5 Place the pump into a pump cleaning cylinder or bucket containing a detergent solution (phosphate-free, borate-free detergent in tap water). Holding the power cord, pump solution through the pump system. A minimum of one gallon of detergent solution should be pumped through the system. Collect the rinsate and handle as IDW.

7.3.6 Remove the pump from the cylinder/bucket and if the pump is reversible, place the pump in the reverse mode to discharge all removable water from the system. If the pump is not reversible the pump and discharge line should be drained by hand as much as possible. Collect the rinsate and handle as IDW.

7.3.7 Using a pressure sprayer with distilled/deionized water, rinse the exterior of the pump and power cord thoroughly, shake all excess water, then place the pump system into a clean trash bag for storage. If the pump system will not be used immediately, the pump itself should be wrapped with aluminum foil before placing it into the bag.

7.3.8 If tubing will be reused between locations, the tubing will also need to be decontaminated. The tubing will remain attached to the pump and the decontamination steps (7.3.4 through 7.3.7) above will be followed. Additional volume of rinsate and distilled/deionized water will be used to compensate for the volume within the tubing. At a minimum, the volume of rinsate should be three times the capacity of the tubing.

7.4 Decontamination of Large Equipment

7.4.1 A temporary decontamination pad may be established for decontamination of heavy equipment. This pad may include a membrane-lined and bermed area large enough to drive heavy equipment (e.g., drill rig, backhoe) onto with enough space to spread other equipment and to contain overspray. Usually a small sump is necessary to collect and contain rinsate (a pump is used to remove these wastes from the sump). A water supply and power source is also necessary to run steam cleaning and/or pressure washing equipment.

7.4.2 Upon arrival at the Area of Investigation, all heavy equipment (such as drill rigs) should be thoroughly cleaned. This can be accomplished by steam cleaning or high pressure water wash and manual scrubbing.

Between each sample location (i.e., between boreholes), heavy equipment that has been in the ground must be cleaned by steam cleaning or high pressure water wash and manual scrubbing. This may be performed at the decontamination pad or in the vicinity of the drilling location.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding decontamination procedures should be documented in the project-specific field logbook. Documentation within the logbook should thoroughly describe the construction of any decontamination facility and the decontamination steps implemented in order to show compliance with the FSP or SAP. Decontamination events should be logged when they occur with the following information documented:

- Date, time, and location of each decontamination event
- Equipment decontaminated
- Method
- Solvents and/or acids used
- Notable circumstances
- Identification of equipment rinsate blanks
- Management of decontamination fluids
- Method, date, and time of equipment blank collection
- Disposition of IDW

Repetitive decontamination of small items of equipment does not need to be logged each time the item is cleaned.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

General guidelines for quality control check of field equipment decontamination usually require the collection of quality control (QC) samples such as equipment rinsate blanks. These requirements should be outlined in the QAPP and FSP or SAP.

Equipment rinsate blanks are generally made by pouring laboratory-supplied deionized water into, over, or through the freshly decontaminated sampling equipment and then transferring this water into a sample container. Equipment rinsate blanks should then be labeled as a sample (as per the QAPP and FSP) and submitted to the laboratory to be analyzed for the same parameters as the associated sample, or an appropriate subset thereof. Equipment rinsate blank sample numbers, as well as collection method, time and location should be recorded in the field logbook.

10.0 REFERENCES

Not applicable.

Surface Soil Sampling

SOP Number 7110Pines

Revision Number: 2.0

September 2013

AECOM Project Manager
September 24, 2013

AECOM Project QA Officer
September 24, 2013

AECOM
September 2013
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

HASP	Health and Safety Plan
IDW	Investigation-derived Waste
MS/MSDs	Matrix spike/matrix spike duplicates
OSHA	Occupational Safety and Health Adminstration
QAPP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This standard operating procedure (SOP) describes the method used for obtaining surface soil samples at the Pines Site for analysis of inorganic parameters. The purpose of this SOP is to provide a specific method and/or procedure to be used in the collection of surface soil samples which, if followed properly, will promote consistency in sampling and provide a basis for sample representativeness.

This SOP is generally applicable to surface and shallow depth soils which are unconsolidated and are of low to moderate density. Higher density or compacted soils may require use of drill rigs or other powered equipment to effectively obtain representative samples.

2.0 SUMMARY OF METHOD

Surface soil sampling generally involves use of hand-operated equipment to obtain representative soil samples from the ground surface and or from shallow depths below the ground surface exposed by excavating equipment. If soil conditions are appropriate, surface soil sampling, following the procedures described in this SOP, can provide representative soil samples in an efficient manner.

3.0 HEALTH AND SAFETY WARNINGS

Surface soil sampling may involve chemical exposure hazards associated with the type of contaminants present in surface soil. When surface soil sampling is performed, adequate Health and Safety measures must be taken to protect sampling personnel. These measures must be addressed in the project Health and Safety Plan (HASP). This plan must be approved by the project Health and Safety Officer before work commences, must be distributed to all personnel performing sampling, and must be adhered to as field activities are performed.

4.0 INTERFERENCES

Potential interferences could result from cross contamination. Minimization of the cross contamination will occur through the following:

- The use of clean, disposable plastic sampling tools at each location.

- Avoidance of material that is not representative of the media to be sampled. Material that has been in contact with the excavator bucket will not be sampled.

5.0 PERSONNEL QUALIFICATIONS

Surface soil sampling is a relatively simple procedure requiring minimal training and a relatively small amount of equipment. It is, however, recommended that initial attempts be supervised by more experienced personnel. Sampling personnel should be health and safety certified as specified by OSHA (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

6.0 EQUIPMENT AND SUPPLIES

6.1 Spoons, Scoops and/or Hand Auger

Commercially purchased plastic spoons or scoops may be utilized to collect the samples to be analyzed for inorganic parameters. These tools will be dedicated to each sampling location and will be discarded after use. A hand auger may be used to sample depths greater than one foot in depth and in areas requiring additional sampling volume. Non-disposable equipment shall be decontaminated after use in accordance with AECOM SOP 7600Pines – Decontamination of Field Equipment.

6.2 Collection Bowl

A plastic bowl will be used as the intermediate sample container between removal of the sample from the ground and containerization of the sample. Plastic bowls may be purchased new and dedicated to each sample location. Non-disposable equipment shall be decontaminated after use in accordance with AECOM SOP 7600Pines – Decontamination of Field Equipment.

6.3 Supporting Materials

- Sample kit (i.e., bottles, labels, custody records, cooler, etc.)
- Sample logs/boring logs
- Six-foot folding rule or tape measure for depth measurement
- Personal protective equipment (as required by the HASP)
- Field project notebook/pen

7.0 METHODS

7.1 Equipment Decontamination

Non-disposable sampling equipment (e.g., hand auger) will be decontaminated in accordance with AECOM SOP No. 7600Pines – Decontamination of Field Equipment prior to sampling and between sampling locations. When possible, clean, plastic equipment (trowels or spatulas and bowls) will be dedicated to each sample location and will be disposed of after each use.

7.2 Geologic Logging

Geologic materials recovered may be logged (if applicable) in accordance with the Unified Soil Classification System (USCS) protocols (see, for example, USEPA, 1991). Geologic descriptions will be entered on a surface soil sampling log (see Figure 1). Specific information to be recorded on the log may include:

- Location identification and/or description
- Geologist/field personnel name
- Date
- Equipment
- Total depth of sample

Additional geologic description information to be recorded may include:

- Moisture content
- Color
- Grain-size
- Sorting
- Density
- Plasticity
- Other relevant observations

In accordance with Indiana Department of Environmental Management (IDEM) guidance (IDEM, 1988), additional information may also be recorded, such as U.S. Department of Agriculture (USDA) soil classification, rounding, effervescence, mineralogy, and bedding. Additional information concerning geologic logging protocols is attached to this SOP.

7.3 Discrete Sampling Procedure

7.3.1 Insert the sampling tool into the soil and rotate the tool so that a representative "column" of soil is removed from the ground. One or more scoops of material may be needed until the desired sample volume is achieved.

7.3.2 Place each scoop into an intermediate sample container (plastic bowl) until sufficient sample volume is collected.

7.3.3 Once sufficient material has been collected, thoroughly homogenize the sample within the collection pan prior to bottling. Sample homogenizing is accomplished by manually mixing the entire sample in the collection pan with the sampling tool until a uniform mixture is achieved.

7.3.4 Fill the sample containers with material from the plastic bowl. The sampling tool may be used to fill the sample bottles. Use of fingers/hands to fill or pack sample containers is not allowed.

7.4 Composite Sampling Procedure

7.4.1 Insert the sampling tool into the soil and rotate the tool so that a representative "column" of soil is removed from the ground.

7.4.2 Place scoop into an intermediate sample container.

7.4.3 Move to additional composite sampling location(s) as needed and repeat the above two steps until the sufficient number of composite samples and volume have been reached.

7.4.4 Once sufficient material has been collected, thoroughly homogenize the sample within the collection pan prior to bottling. Sample homogenizing is accomplished by manually mixing the entire sample in the collection pan with the sampling tool until a uniform mixture is achieved.

7.4.5 Fill the sample containers with material from the plastic bowl. The sampling tool may be used to fill the sample bottles. Use of fingers/hands to fill or pack sample containers is not allowed.

7.5 Sample Handling and Preservation

7.5.1 Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.

7.5.2 Cap and label the container with the sample identifier, sampling date and time, preservation information, and analytical tests.
7.5.3 Place the sample containers into a cooler and maintain on ice.
7.5.4 Complete sample chain-of-custody and other documentation per SOP 1007Pines.
7.5.5 Package the samples for shipment to the laboratory per SOP 7510Pines.
7.5.6 Handle any investigation-derived waste (IDW) per the SAP.

8.0 DATA AND RECORDS MANAGEMENT

Various forms are required to ensure that adequate documentation is made of the sample collection activities. These forms include:

- Field log books
- Sample collection records
- Chain-of-custody forms
- Shipping labels

The field book will be maintained as an overall log of all samples collected throughout the study. Sample collection records are generated for each sample collected and include specific information about the sample (Figure 1). Chain-of-custody forms are transmitted with the samples to the laboratory for sample tracking purposes. Shipping labels are required if sample coolers are to be transported to the laboratory by a third party (courier service). Original and/or copies of these documents will be retained in the appropriate project files.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

- Collection of representative samples will be ensure through adherence to the procedures in this SOP and the sampling strategy outlined in the Sampling and Analysis Plan (SAP).
- The field quality control samples identified in the SAP must be collected. These samples include field duplicates and matrix spike/matrix spike duplicates (MS/MSDs)

10.0 REFERENCES

SOP 1007Pines. Chain-of-Custody Procedures.

SOP 7510Pines. Packaging and Shipment of Environmental Samples.

SOP No. 7600Pines. Decontamination of Field Equipment

AECOM Health and Safety Policy and Procedures Manual.

FIGURE 1 Surface Soil Sample Log

Surface Soil Sampling Log

AECOM

PROJECT:	SURFACE SOIL ID:
	LOCATION OF SAMPLE:
	DATE: / GPS:

ELEV.	Depth (feet)	U.S.C.S.	Description of Materials (color, grain size, sorting, etc.)	Remarks (sample time, sample depth, etc.)
0.0	0		Ground Surface	Time: Sample Depth:
	1			
	2			
	3			
	4			
	5			
	6			
	7			
	8			
	9			
	10			
	11			
	12			
	13			
	14			
	15			

Staff:

Underground Utilities and Subsurface Installation Clearance Process

SOP Number 417

Revision Number: 0.0

Novermber 2014

Americas

Underground Utilities and Subsurface Installation Clearance Process

S3NA-417-PR1

1.0 Purpose and Scope

1.1 Provides procedures designed to help prevent injuries to personnel working on the project and pedestrians, property damage, and adverse environmental impact as a result of potential hazards associated with encountering underground utilities, subsurface installations, and potential overhead hazards.

1.2 Provides the minimum requirements to be followed for underground work (e.g., excavations, drilling, boring, and probing work) to ensure that underground installations, and subsurface structures, are identified properly before work commences.

1.3 This procedure applies to all Americas-based employees and operations.

1.4 The Project Manager is responsible for meeting all the requirements in this procedure

1.5 A variance provision has been included for certain requirements of this procedure found in Sections 4.3.2, 4.7.1 and 4.9. Any variance from these procedures must be approved by the **District General Manager** or the **District SH&E Manager.**

1.6 AECOM's clients may have specific procedures which must be followed to identify and map utility and subsurface structures on their properties or facilities. Following the client's procedures over this procedure must be approved by the **District General Manager** or the **District SH&E Manager**.

2.0 Terms and Definitions

2.1 **Underground Utilities –** All utility systems located beneath grade level, including, but not limited to, gas, electrical, water, compressed air, sewage, signalling and communications, etc.

2.2 **Ground Disturbance (GD) –** Any indentation, interruption, intrusion, excavation, construction, or other activity in the earth's surface as a result of work that results in the penetration of the ground.

2.3 **Intrusive Activities –** Excavation of soil borings, installations of monitoring wells, installation of soil gas sampling probes, excavation of test pits/trenches or other man-made cuts, cavity, trench or depression in an earth surface formed by earth removal.

2.4 **Subsurface Installation –** Includes subterranean tunnels, underground parking garages and other structures beneath the surface.

3.0 References

3.1 S3NA-003-PR1 SH&E Training

3.2 S3NA-405-PR1 Drilling, Boring and Direct-Push Probing

3.3 American Public Works Association, Excavator's Damage Prevention Guide and One-Call System Directory International 1990-1991, Utility Location and Coordination Committee

3.4 Learning Management System (LMS)

4.0 Procedure

4.1 Roles and Responsibilities

4.1.1 **Project Manager –** Initial and authorize work to proceed using the *S3NA-417-FM2 Underground Utility and Subsurface Installation Clearance Checklist*. Authorizes (with Site Supervisor and District SH&E Manager's concurrence) if interrupted due to unexpected effect.

4.1.2 **District General Manager** and **District SH&E Manager –** Authorize any variances from this procedure. Authorization to proceed with drilling if interrupted due to unexpected effect occurs.

4.2 Flow Chart/Checklist

4.2.1 *S3NA-417-FM1 Underground Utilities and Subsurface Installation Clearance Requirements* is a flow chart of the key points to know in this procedure. Prior to any intrusive subsurface work, the *S3NA-417-FM2 Underground Utility and Subsurface Installation Clearance Checklist* must be filled out and signed by the AECOM Project Manager. If the answer to any question on the checklist is "No" or "N/A", no ground disturbance can take place without the approval of the **Project Manager**. The **Project Manager** must initial the form to authorize this approval.

4.3 Urban (or Non-Urban Areas without a one-call system)

4.3.1 Be aware that in urban areas there may be subsurface installations (e.g., underground garages) and utilities (e.g., public water, sewer, and gas pipelines) that are not covered by one-call systems. These subsurface installations and utilities require addition investigation and diligence beyond the one-call system. Additional investigation and diligence beyond the one-call system is also recommended for non-urban areas.

4.3.2 Private locates, as a minimum, and hand clearing, as appropriate, are also required in urban areas. Any variance from these requirements must be approved by the **District General Manager** or the **District SH&E Manager.** Private locates and hand clearing is also recommended for non-urban areas.

4.3.3 The presence of subsurface installations and utilities requires special care when obstructions/ refusal and voids are encountered and when unexpected absence of soil recovery occurs during drilling operations. Other indicators of subsurface installations and utilities are the presence of warning tape, pea gravel, sand, non-indigenous material, bentonite, red concrete (indicative of electrical duct banks) and any departure from native soil or backfill.

4.4 Permits and Access Agreements

4.4.1 All appropriate permits (e.g., government, working near rail road, etc.) will be identified, obtained, and adhered to.

4.4.2 All client on-site safety procedures shall be understood and adhered to, and all client permits will be obtained.

4.4.3 All access agreements will be obtained and adhered to.

4.4.4 Be aware of the Federal/State/Provincial/Territorial regulations that govern drill rig operations and exposed moving parts.

4.5 General Health and Safety

4.5.1 Health and Safety Plan – At a minimum, a health and safety plan (HASP) that includes task hazard analyses (THAs) shall be prepared prior to any drilling, boring, and direct-push probing activities. The HASP will address any required environmental monitoring including gas monitoring, dust, noise, metals, radiation or other monitoring as may be appropriate for site conditions. All HASP requirements will be followed by the AECOM project team.

4.5.2 Training

- All staff shall be trained in identifying underground utilities and subsurface installations and the requirements. Refer to the *S3NA-003-PR1 SH&E Training* and *Learning Management System (LMS).*
- All staff shall receive client-required training.

4.6 Identification and Mapping of Utility and Subsurface Structures

4.6.1 The locations of subsurface and overhead utilities and subsurface installations will be investigated, documented, and shown on a site plan (a scaled site plan shall be used when feasible). Refer to *S3NA-406-PR1 Electrical Lines Overhead* and *S3NA-417-FM2 Underground Utilities and Subsurface Installation Clearance Checklist.*

4.6.2 Documentation of utility and subsurface installation clearance along with the scaled site plan will be on site at all times of intrusive activities.

4.6.3 Identification and mapping of Utility and Subsurface Structures is iterative with the Site Walk and should be repeated as necessary following the Site Walk as appropriate.

4.7 Site Walk

4.7.1 A site walk shall be conducted by the AECOM project team/site manager with the objectives of reviewing all planned intrusive activity locations, the locations of subsurface and overhead utilities and the potential for subsurface installations, to determine the appropriate utility clearance activities, and to observe other physical hazards. If possible, particularly at urban and industrial sites, the client/property owner or someone knowledgeable about the site and site utilities will attend the site walk. Any variance from these requirements must be approved by the **District General Manager** or the **District SH&E Manager**.

4.7.2 The site walk is iterative with the Identification and mapping of Utility and Subsurface Structures and should be repeated as necessary following the Identification and Mapping of Utility and Subsurface Structures.

4.8 Proposed Subsurface Investigation Locations

4.8.1 All proposed subsurface locations will be reviewed in comparison to subsurface and overhead utilities and subsurface installations and adjustments made as necessary.

4.8.2 Minimum set back distances from subsurface and overhead utilities and subsurface installations will be established including 5 feet (1.5 meters) from any subsurface utility, 7 feet (2.1 meters) from the pad surrounding any underground storage tanks, and 10 feet (3 meters) from any overhead energized electrical line (or further depending on line voltage). These set back distances are a minimum; government regulations and utility requirements may dictate a greater set back distance.

4.9 Utility Clearance Investigation Location Confirmation

4.9.1 In urban areas, proposed subsurface locations will be hand cleared to 5 feet/1.5 meters (soil borings and wells) or 1 foot/0.3 meter (soil gas sampling probes) using non-mechanical methods. Hand clearance should be extended if locations of deep utilities and structures are not known. In non-urban areas, hand clearing should be conducted if possible. Any variance from these requirements must be approved by the **District General Manager** or the **District SH&E Manager.**

4.10 Surface Markings

4.10.1 Once the underground installation has been identified, proper surface markings shall be made in accordance with the guidelines from the One-Call System (811), guidance contained in this procedure or as contract-specified.

4.10.2 Color-coded surface marks (paints or similar coatings) shall be used to indicate the type, location, and route of buried installations. Additionally, to increase visibility, color-coded vertical markers (temporary stakes or flags) shall supplement surface marks.

4.10.3 All marks and markers shall indicate the name, initials, or logo of the company that owns or operates the installation and the width of the installation if it is greater than 2 inches.

4.10.4 If the surface over the buried installation is to be removed, supplemental offset marking shall be used. Offset markings shall be on a uniform alignment and shall clearly indicate that the actual installation is a specific distance away.

4.11 Uniform Color Coding

4.11.1 The colors and corresponding installation type are as follows unless otherwise contract-specified.:

Red: Electric Power Lines, Cables, Conduit, and Lighting Cables

Yellow: Gas, Oil, Stream, Petroleum, or Gaseous Materials

Orange: Communication, Alarm or Signal Lines, Cables, or Conduit

Green: Sewers and Drain Lines

White: Proposed Ground Disturbance area

Pink: Temporary Survey Markings

Blue: Potable Water

Purple: Nonpotable Water

5.0 Records

5.1 None

6.0 Attachments

6.1 S3NA-417-WI1 One-Call System Definition and Directory

6.2 S3NA-417-FM1 Flow Chart for Underground Utilities and Subsurface Installation Clearance

6.3 S3NA-417-FM2 Underground Utility and Subsurface Installation Clearance Checklist

6.4 S3NA-417-ST Underground Utilities-Jurisdictions/Regulations

Americas

One-Call System (811) Definition and Directory

S3NA-417-WI1

1.0 What Is It?

1.1 It is a Federally-mandated national “Call Before Your Dig” number, 811, to provide one telephone number for excavating contractors and the general public to call for notification of their intent to use equipment for excavating, tunneling, demolition, or any other similar work. This one-call system provides the participating members an opportunity to identify and locate their underground facilities.

As descrbied on their web site (http://www.call811.com), Common Ground Alliance (CGA) was “created specifically to work with all industry stakeholders in an effort to prevent damage to underground utility infrastructure and ensure public safety and environmental protection.” CGA also services as an organization to continuously update best practices amonth the growing underground industry. The CGA web site provides current one-call information for all states and proviences.

2.0 Why Is It Needed?

2.1 Damage to underground facilities increased considerably following the building boom of the 1950s, 1960s, and early 1970s when the trend was to go underground with utilities. Thousands of miles of underground facilities are vulnerable to excavating machines such as backhoes, and the resulting damage can interrupt utility service and threaten life, health, and property.

3.0 How to Get It

3.1 811 is the designated call before you dig phone number that directly connects you to your local one call center. Each state has different rules and regulations governing digging, some stricter than others. The CGA web site provides current contact inforatmation to find state-specific information as well as links to submit an online digging request where available

4.0 Disclaimer

4.1 The purpose of this directory is to illustrate the extent of one-call service available. Users must verify information is current including the extent and limit of service from local sources.

Province/State	One-Call Agency	Number
Canada	www.clickbeforeyoudig.com	
Alberta	Alberta One Call www.albertaonecall.com	1.800.242.3447
British Columbia	BC One Call www.bconecall.bc.ca	1.800.474.6886
Manitoba	Click Before You Dig www.clikckbeforeyoudigmb.com	Various – see website
Ontario	Ontario One Call www.on1call.com	1.800.400.2255
Québec	Onfo Excavation www.info-ex.com	1.800.663.9228
Saskatchewan	Sask 1st Call www.sask1stcall.com	1.866.828.4888
United States	www.call811.com	811
Alabama	Alabama 811	1.800.292.8525
Alaska	Alaska Digline, Inc.	1.800.478.3121
Arizona	Arizona 811	1.800.782.5348

Province/State	One-Call Agency	Number
Arkansas	Arkansas One Call	1.800.482.8998
California	(North & Central) USA North 811	1.800.227.2600
	(South) Dig Alert	1.800.227.2600
Colorado	Colorado 811	1.800.922.1987
Connecticut	Call Before You Dig	1.800.922.4455
Delaware	Miss Utility of Delmarva	1.800.282.8555
District of Columbia	District One Call	1.202.265.7177
Florida	Sunshine 811	1.800.432.4770
Georgia	Georgia 811	1.800.282.7411
Hawaii	Hawaii One Call	1.866.423.7287
Idaho	Dig Line, Inc.	1.800.342.1585
	(Bonner/Boundry) Pass Word	1.800.626.4950
	(Kootenai County) Pass Word	1.800.428.4950
	(Shoshone-Benewah) Pass Word	1.800.398.3285
Illinois	(Chicago) Digger -Chicago Utility Alert Network	312.744.7000
	(Outside of Chicago) JULIE	1.800.892.0123
Indiana	Indiana 811	1.800.382.5544
Iowa	Iowa One Call	1.800.292.8989
Kansas	Kansas 811	1.800.344.7233
Kentucky	Kentucky 811	1.800.752.6007
Louisiana	LA One Call	1.800.272.3020
Maine	Dig Safe	1.888.344.7233
Maryland	(West of Chesapeake Bay) Miss Utility of Maryland	1.800.257.7777
	(East of Chesapeake Bay) Miss Utility of Delmarva	1.800.282.8555
Massachusetts	Dig Safe System, Inc.	1.888.344.7233
Michigan	Miss Dig	1.800.482.7171
Minnesota	Gopher State One Call	1.800.252.1166
Mississippi	Mississippi 811	1.800.227.6477
Missouri	Missouri One Call System	1.800.344.7483

Province/State	One-Call Agency	Number
Montana	Montana 811	1.800.424.5555
	(Flathead and Lincoln Counties) Montana One Call Center	1.800.551.8344
Nebraska	Nebraska 811	1.800.331.5666
Nevada	USA North 811	1.800.227.2600
New Hampshire	Dig Safe System, Inc.	1.888.344.7233
New Jersey	New Jersey One Call	1.800.272.1000
New Mexico	New Mexico 811	1.800.321.2537
New York	(North of 5 Boroughs) Dig Safely New York	1.800.962.7962
	(5 Boroughs and Long Island) New York 811, Inc.	1.800.272.4480
North Carolina	North Carolina 811	1.800.632.4949
North Dakota	North Dakota One Call	1.800.795.0555
Ohio	Ohio Utilities Protection Service	1.800.362.2764
Oklahoma	Call Okie	1.800.522.6543
Oregon	Oregon Utilities Notification Center	1.800.332.2344
Pennsylvania	Pennsylvania One Call System, Inc.	1.800.242.1776
Puerto Rico	Puerto Rico Public Service Commission 811	
Rhode Island	Dig Safe System, Inc.	1.888.344.7233
South Carolina	South Carolina 811	1.888.721.7877
South Dakota	South Dakota One Call	1.800.781.7474
Tennessee	Tennessee 811	1.800.351.1111
Texas	Texas 811	1.800.545.6005
	Lone Star 811	1.800.669.8344
Utah	Blue Stakes of Utah	1.800.662.4111
Vermont	Dig Safe System, Inc.	1.888.344.7233
Virginia	Virginia 811	1.800.552.7001
Washington	Utility Notification Center	1.800.424.5555
West Virginia	WV 811	1.800.245.4848
Wisconsin	Diggers Hotline	1.800.242.8511
Wyoming	One-Call Of Wyoming	1.800.849.2476

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Key Points to Know Flow Chart for Underground Utilities and Subsurface Installation Clearance

S3NA-417-FM1

Before Any Underground Utilities and Subsurface Installation Clearance

PERMITS AND ACCESS AGREEMENTS

- Government and Utility/Infrastructure Permits
- Client permits and procedures
- Access Agreements

KEY POINT: Must obtain all permits and sign Access Agreement (if required)

GENERAL HEALTH and SAFETY

KEY POINT: Must prepare Health & Safety Plan, which includes a Task Hazard Analysis.

IDENTIFICATION & MAPPING OF UTILITY and SUBSURFACE STRUCTURES

KEY POINT: Must generate a comprehensive site map illustrating known locations of overhead/subsurface utilities, subsurface structures, and proposed boring locations.

SITE WALK

KEY POINT: Must perform a site walk utilizing site map and 360° view to verify known conditions and identify potential issues. Add discovered items/issues to map for use in location confirmation.

PROPOSED SUBSURFACE INVESTIGATION LOCATIONS

KEY POINT: Confirm that locations meet the minimum set-back distances described in Section 4.8

UTILITY CLEARANCE INVESTIGATION LOCATION CONFIRMATION

KEY POINT: Locations must be hand-cleared, as described in Section 4.9

Americas

Underground Utility and Subsurface Installation Clearance Checklist

S3NA-417-FM2

Location:		**Project #:**
Contractor:		**Client:**
Date:	**Time:**	**Weather:**
Inspector:		**Project Manager:**

Notes:

Questions must be answered prior to any intrusive subsurface work. DO NOT DISTURB GROUND if you have answered "No" or "N/A" to any of the questions without the approval of the AECOM Project Manager.

Any variance from this proceduremust be approved by the District General Manager.

		Yes	No	N/A
I.	**Permits and Access Agreements**			
1.	Have all appropriate permits been identified and obtained (e.g., drilling, encroachment, working near railroads, etc.)?	☐	☐	☐
2.	Have all client requirements, including client permits been identified and obtained?	☐	☐	☐
3.	If working off-site is(are) site access agreement(s) executed?	☐	☐	☐
II.	**General Health and Safety**			
1.	Has a Health and Safety Plan been prepared for AECOM employees?	☐	☐	☐
2.	Do on-site personnel have required-level PPE?	☐	☐	☐
3.	Do on-site personnel have required-level of training?	☐	☐	☐
III.	**Identification and Mapping of Utility and Subsurface Structures**			
1.	Is a Site Plan showing the proposed subsurface locations and utility locations attached to this check list?	☐	☐	☐
2.	Have utilities and subsurface installations been investigated as being present, including the following:	☐	☐	☐
	a. Steam, gas and electric?	☐	☐	☐
	b. Sewer and water?	☐	☐	☐
	c. Subterranean tunnels?	☐	☐	☐
	d. Fiber optics (Note routine utility geophysical survey will not identify fiber optic cables)?	☐	☐	☐
	e. Traffic control cables?	☐	☐	☐
	f. Others (identify)?	☐	☐	☐
3.	Have all Federal/State/Provincial/Territorial and other "One Call" providers marked their facilities or otherwise notified they do not have any facilities near the proposed subsurface/intrusive locations?	☐	☐	☐
4.	Has the Federal/State/Provincial/Territorial or other "One Call" provider identified what utilities and underground structures are ***not*** included in their provider system (e.g., non-utility underground structures)?	☐	☐	☐

Questions must be answered prior to any intrusive subsurface work. DO NOT DISTURB GROUND if you have answered “No” or “N/A” to any of the questions without the approval of the AECOM Project Manager. Any variance from this proceduremust be approved by the District General Manager.			
	Yes	**No**	**N/A**
5. Has a utility locating contractor performed geophysical and/or other surveys of the proposed subsurface/intrusive locations?	☐	☐	☐
6. Were all circuits on during subsurface checks if the checks were for identifying energized lines (e.g., circuits on timers or light sensing switches)?	☐	☐	☐
7. Are overhead utilities or obstructions present that may prevent the safe operation of drilling/excavation equipment and, if present, has the AECOM Overhead Electrical Line Acknowledgement Form been signed?	☐	☐	☐
8. Was there visual verification that each of the proposed locations does not lie on a line connecting two similar manhole covers (e.g., sanitary sewer or storm drain)?	☐	☐	☐
9. Was there visual verification that the ground in the vicinity of each of the proposed subsurface locations has not subsided, been excavated and patched, give the appearance it may be covering a former trench (e.g., linear cracks, sagging curbs, linear re-pavements) and do not lie on a line with any water, gas, electrical meters, utility cleanouts, or other utility boxes in the surrounding areas?	☐	☐	☐
IV. Site Walk			
1. Has a site walk been performed that includes the following:	☐	☐	☐
a. Reviewing all planned intrusive locations?	☐	☐	☐
b. Adjusting locations away from subsurface utilities and installations?	☐	☐	☐
c. Determining the appropriate utility clearance activities for each location?	☐	☐	☐
d. Determining the presence and location of overhead utilities and obstructions?	☐	☐	☐
e. Walk around perimeter of the site to observe physical hazards?	☐	☐	☐
f. Walk around 50 feet (15 meters) from perimeter of the site to observe physical hazards?	☐	☐	☐
g. Walk around 50 feet (15 meters) radius from each proposed subsurface intrusion location?	☐	☐	☐
V. Proposed Subsurface Investigation Locations*			
1. Are all of the proposed subsurface locations at least 5 feet (1.5 meters) from any subsurface utility?	☐	☐	☐
2. Are all of the proposed subsurface locations at least 7 feet (2.1 meters) from the pad surrounding any underground storage tanks (USTs) shown on the Site Plan?	☐	☐	☐
3. Are all of the proposed subsurface locations at least 5 feet (1.5 meters) from any subsurface utilities shown on the Public Right-of-Way street improvements?	☐	☐	☐
4. Are all proposed subsurface locations requiring a drill rig for installation at least 10 feet (3 meters) from any energized overhead power line (or further based on line voltage)?	☐	☐	☐
5. Are all of the proposed subsurface locations at least 5 feet (1.5 meters) from any subsurface utilities identified during any geophysical survey performed using ground-penetrating radar (GPR) in conjunction with other technology?	☐	☐	☐
** These set back distances are a minimum; government regulations and utility requirements may dictate a greater set back distance.*			

Questions must be answered prior to any intrusive subsurface work. DO NOT DISTURB GROUND if you have answered "No" or "N/A" to any of the questions without the approval of the AECOM Project Manager. *Any variance from this proceduremust be approved by the District General Manager.*			
	Yes	**No**	**N/A**
VI. Utility Clearance Investigation Location Confirmation*			
1. Have subsurface locations been hand cleared as follows? Hand clearance should be extended if locations of deep utilities and structures are not known. In non-urban areas hand clearing should be conducted if possible.	☐	☐	☐
a. For soil borings/monitoring wells excavate to a minimum of 5 feet (1.5 meters) below ground surface using non-mechanical methods.	☐	☐	☐
b. For soil gas sampling excavated to 1 foot (0.3 meter) below grade or below the bottom of a concrete floor prior to the installation of soil gas sample probe points?	☐	☐	☐
* *Exceptions to requirements of the utility clearance process include the following: sites where extensive utility mapping has been completed and/or where extensive activities have already been performed; locations where facility layout is well documented and understood; and sites or portions of large sites where utilities are known not to exist currently or to not have ever existed throughout the life of the facility, property or site.*			

Americas

Underground Utilities – Jurisdictions/Regulations

S3NA-417-ST

1.0 Regulations

1.1 Every province and territory has strict regulations governing the procedures and practices that MUST be followed. As these regulations vary slightly, before work can commence, the Project Manager MUST review these documents and identify how all of the hazards will be addressed and how the regulations will be adhered to:

1.1.1 Occupational Health and Safety Code

1.1.2 Regional or industry-specific regulations (e.g., Alberta EUB [Pipeline Act]).

2.0 Occupational Health and Safety Regulations

2.1 The following Occupational Health and Safety regulations apply directly to ground disturbance:

Jurisdiction	Regulation
United States	
OSHA	CFR 1926.651
Canada	
Alberta	OHS Code (2009) Sect 441 – 464, Schedule 9
British Columbia	OHS Regulation (1997) Sect 20.78 – 20.101
Manitoba	Workplace Health and Safety Regulation (217/2006) Sect 26.0 – 26.47
New Brunswick	OHS Regulation (91-191) Sect 93 – 94.1, 180 – 188
Newfoundland/Labrador	OHS Regulation (C.N.L.R. 1165/96) Sect 139 – 148
Nova Scotia	OHS Regulation (N.S. Reg. 44/99) Sect 153, 166 – 173
NWT/NU Territories	General Safety Regulations (R.R.N.W.T. 1990, c. S-1), Safety Act (SI-013-92) Sect 396 – 432
Ontario	O. Reg. 213/91 Sect 6, 7, 222 – 242
Prince Edward Island	OHS Regulations (EC180/87) Sect 12.1 – 12.15
Quebec	Safety Code for the Construction Industry (R.R.Q. 1981, c. S-2.1, r. 6) Sect 3.15.1 – 3.15.10
Saskatchewan	OHS Regulation (R.R.S., c. O-1, r. 1) Sect 257 – 265, Schedule Table 17
Yukon Territory	OHS Regulations (O.I.C. 2006/178) Sect 10.62 – 10.72

Appendix D

Response to Comments and USEPA Work Plan Approval

Appendix D-1

Responses to USEPA Comments Dated January 15, 2014

GENERAL COMMENTS

1. The Draft Supplemental Soil Characterization (SSC) Work Plan does not clearly indicate how many samples / surveys of what type will be collected. A table and text clearly providing this information would enhance the understanding of the intended sampling.

   Response: A table indicating the numbers and sampling/investigation types has been added to Section 3.1.

2. The Draft SSC Work Plan does not discuss circumstances under which the proposed activities (particularly the gamma survey) may need to be postponed.

   Response: AECOM has prepared a new subsection, 4.1.3, Work Restrictions, that addresses the field conditions under which gamma surveys would be postponed. These include weather events such as rain and snow.

   Section 1.3.1 also indicates that field work will not commence until all access agreements are in place.

3. Any changes/corrections made to address the specific comments (SCs) below should also be made to the appropriate sections of the Quality Assurance Project Plan (QAPP) in Appendix B of the Draft SSC Work Plan as well as any relevant Appendices.

   Response: Agreed, included with this response to comments is a Revision 1 version of the QAPP with the changes incorporated.

SPECIFIC COMMENTS

1. **<u>Page 1-3, Section 1.3, second paragraph:</u>** The intent of the phrase “specific sampling for radionuclides” should be explained.

   The Draft SSC Work Plan states: “Gamma surveys are typically used as screening tools to determine whether or not specific sampling for radionuclides is needed.” This should be revised to “Gamma surveys can be designed to collect gamma dose and gamma count rate information to support decisions regarding the collection of radionuclide samples.”

   The Draft SSC Work Plan states: “The purpose of including the gamma surveys here is to provide a comparison to gamma surveys conducted by the community; the results of the SSC surveys will be used to guide the selection of some of the soil sampling described in this work plan.” The gamma surveys, with sodium iodide (NaI) count rate and gamma dose rate measurements collected at background locations and investigation areas, should also help allay public concerns regarding risk due to naturally occurring radioactive materials (NORM) in coal combustion byproduct (CCB) materials.

   The Draft SSC Work Plan states: “The analytical results from these samples will be used to evaluate potential risks at these locations.” The receptors evaluated should be those considered in the HHRA, including a recreational user (such as a child at a park) and a construction worker performing excavation work in 100% CCB materials (both surface and subsurface activities).

Response: The requested changes have been made. Note that the second part of the comment provides the clarification requested in the first.

2. **<u>Page 1-4, Section 1.3.1, first paragraph:</u>** Section 1.3.1 discusses access agreements. The third full sentence states: "Where feasible, sample locations will be selected within public rights-of-way." As stated elsewhere in the Draft SSC Work Plan (for example, Sections 1.3.2 through 1.3.4), gamma surveys, coal combustion by-product (CCB) verification, and private property soil sampling will be conducted across all of each residential property. Sample locations cannot be restricted to the public rights-of-way for residential properties. Section 1.3.1 should be revised to clarify any discussion of substitution of other suitable properties (with EPA's approval) or the potential limiting of sample locations. Every effort should be made to gain access to the individual properties. The intent of the access agreement should explain that this supplemental soil characterization is a one-time event and if a property owner declines/refuses access for characterization, there will not be an opportunity to have the property characterized at a later time.

   Response: The preference for sample locations in rights-of-way applies to CCB visual inspection verification samples only. However, due to the confusion and the fact that the visual inspection verification sample locations have already been identified, this text has been removed from the document.

3. **<u>Page 1-4, Section 1.3.2:</u>** The stated objective of conducting gamma surveys is to establish a distribution of responses for the background areas and then to compare the background responses to the property specific distribution of responses to identify if there are any significant differences between the property specific and background surveys. Please explain how distributions of responses will be used if a background value and a numerical standard for total radium concentration above background are used.

   Response: As agreed with USEPA, data collected in the field will be recorded and documented, but to keep the data collection process objective, the data will not be reviewed in the field. Thus, no actions will be taken in the field based on subject property surveys (e.g., sampling, marking areas, communicating with the public, etc.). Therefore, there will be no numerical "decision levels" applied in the field based on measurements above background or total radium concentrations. At the completion of the gamma surveys, the data will be reviewed in conjunction with USEPA to determine whether additional actions, such as sampling, may be warranted.

   A paragraph was added to the end of Section 1.3.2 clarifying this.

4. **<u>Page 1-4, Section 1.3.2:</u>** This section does not indicate the number of gamma surveys planned. To be consistent with Sections 1.3.3 and 1.3.4.2, the number of gamma surveys planned should be clearly indicated.

   Response: Text was added to the first paragraph of Section 1.3.2 providing estimated numbers of surveys and noting that gamma surveys will be performed on each of the properties where access is provided.

5. **<u>Page 1-4, Section 1.3.4, fourth paragraph:</u>** The Draft SSC Work Plan discusses the collection of 5-point composite samples. The Incremental Sampling Methodology (ISM) should be considered. ISM is a structured composite sampling and processing protocol that reduces data variability and provides a reasonable estimate of a chemical's mean concentration for the volume of soil being sampled. More information can be found at the following Interstate Technology & Regulatory Council (ITRC) web links:

   - http://www.itrcweb.org/Team/Public?teamID=11

- http://www.itrcweb.org/Documents/ISM-InformationSheet_All_audiences.pdf

Response: In developing the original sampling plan, ISM was considered as one possible approach. However, the proposed quadrant approach was selected because it had been used by USEPA on a similar project in Region 5, and because ISM has the potential to be extremely intrusive on a residential property, depending on the numbers of depth of increments. Moreover, the ISM approach does not accommodate the judgmental sampling at play areas, gardens, and driveways where CCBs have been used. Text has been added to Section 3.4.2 to indicate this. These factors were discussed with USEPA during a meeting on January 31, 2014, and it was decided to retain the proposed sampling approach in the SSC Work Plan.

6. **Page 1-4, Section 1.3.4, fifth paragraph:** Section 1.3.4 discusses the proposed private property soil sampling. In the first sentence of Paragraph 5, the phrase "gamma radiological assessment results" is used. This phrase is not previously been defined. As discussed in Section 1.3.2, two types of gamma surveys will be conducted at each residence: a sodium iodide (NaI) gamma walk-over survey and a gamma dose rate survey. It is not clear if the phrase "gamma radiological assessment results" is meant to be the results from the two types of gamma surveys or something else. Section 1.3.4 should be revised to clearly define the phrase "gamma radiological assessment results."

   Response: The text has been deleted from this section.

7. **Page 1-5, Section 1.3.4.1, second paragraph:** Section 1.3.4.1 discusses the identification of analytical constituents. The second paragraph describes the step-wise process for identifying constituents of concern (COC) as "very conservative." The qualifier "very" is subjective; while some may consider the process "very conservative," others may consider the process conservative in a reasonably health-protective manner. Therefore, the qualifier "very" should be removed from the subject sentence.

   Response: "Very conservative" has been revised to "conservative."

8. **Page 1-6, Section 1.3.4.1, first full paragraph:** When samples are sent to a laboratory for analysis, specific reporting of the following radionuclides should be requested:

   - Gamma-emitting NORM radionuclides associated with CCBs: Uranium-238 series, Thorium-232 series, Uranium-235 series, and Potassium-40.
   - Man-made and longer lived radionuclides not associated with coal that, if present, could contribute to elevated gamma dose rate and count rate: Cs-137 and Cobalt-60.

   Count times should be sufficient to provide minimum detectable activities equal to 10% to 50% of normal background values for each of the individual radionuclides. Analysis and reporting by the lab for each sample should be sufficient to declare whether the above-mentioned radionuclides are present or absent at levels above typical background values, with sufficient measurement durations so that the reported measurement uncertainties for each radionuclide are reasonable and less than their respective reported activities.

   Also, this section requires editing to eliminate the use of terms for which acronyms have previously been supplied. Acronyms are also supplied again for the terms and then not subsequently used.

   Response: Select gamma emitting NORM radionuclides associated with the U-238 series, Th-232 series, and U-235 series, plus some additional non-NORM (e.g., Potassium-40 (K-40) will be reported by the laboratory. Details are provided in Appendix B, the QAPP. The EPA approved gamma spectroscopy library supplied by the laboratory (GEL) is provided in the QAPP (Attachment B of Appendix B).

The second part of the comment concerning count times and MDCs has been addressed in the updated QAPP (Appendix B).

9. **Page 1-6, Section 1.3.4.1:** In the first full paragraph, Table 1 is referenced as providing the preliminary remediation goals (PRGs) and background threshold values (BTVs) for the constituents of potential concern (COPCs). The BTV for the sum of Radium-226 and 228 is not presented in the table, but instead is provided in the footnote to the table. The BTV should be presented in the table. Additionally, footnote (e) referenced footnote (c); however, it should reference footnote (d).

   Response: Table 1 has been revised; note that the radionuclide PRGs were slightly updated in the FS, and those are presented here.

10. **Page 1-6, Section 1.3.4.2:** Section 1.3.4.2 discusses the identification of soil sampling locations. This section must be revised per the revisions identified for Appendix A of the Draft SSC Work Plan.

    This section is confusing as it lists the COPC then the number of residents to sample. This section implies that each property will be analyzed for different COPCs. For example, only nine properties will be analyzed for Arsenic, and only five properties will be analyzed for Radium 228. This is not the intent of the sampling program, and this section should be revised to more clearly explain and justify the number of properties to be sampled for chemical and radionuclide analyses.

    In addition to the identified locations, soil should be sampled wherever the gamma survey indicates radium concentrations are likely in excess of a value agreed upon with the EPA. In a previous section, the plan states that a complete library of gamma emitting naturally-occurring radioisotopes plus Cs-137 will be used. In this paragraph, it appears that the plan is saying that small and different numbers of samples will be analyzed for each radionuclide. Each sample should be analyzed for all the radionuclides in the complete library of gamma emitting naturally-occurring radioisotopes plus Cs-137.

    Response: See response to Comment 41. In addition, there was no intention to collect a different number of samples for different parameters. The language has been clarified in the revised plan.

    As previously discussed and agreed with USEPA, the criteria and need for additional discrete samples to be analyzed for radiological parameters will be determined in consultation with USEPA based on the results of the gamma surveys. This approach was discussed and confirmed with USEPA during a meeting on January 31, 2014.

11. **Page 3-1, Section 3.1:** This section describes the sampling / investigation locations. The associated Figure 1 does not clearly show all of the locations, primarily due to labels overlapping and scale issues. The use of call-out boxes for areas where points are overlapping should be considered. Figure 1 should be revised so that it clearly shows where the proposed sampling locations are. Additionally, it may be beneficial to provide a separate map of the proposed gamma survey locations, as was done for the proposed CCB sample locations, to provide a clear distinction between the two types of sampling.

    The plan should commit to collecting soil samples at the specified locations and at locations where the count rates indicate concentrations of radium in soil exceeding an agreed-upon value.

    Response: Figure 1 has been revised as recommended. Figure 1 shows all investigation locations. The existing Figure 4 shows the CCB visual inspection verification sample locations. A new Figure 7 shows the background gamma survey locations. A new Figure 8 shows the gamma survey locations based on the third-party gamma survey report. A new Figure 9 shows the properties were CCBs were identified in the RI CCB visual inspection program.

As previously discussed and agreed with USEPA, the criteria and need for specific samples to be analyzed for all COPCs will be determined in consultation with USEPA based on the results of the gamma surveys. This approach was discussed and confirmed with USEPA during a meeting on January 31, 2014.

12. **Page 3-1, Section 3.2.1:** As stated previously, if a specific standard is agreed upon, the objective of the gamma survey shall include identifying properties where gamma surveys indicate that the standard may potentially be exceeded.

    Response: As previously discussed and agreed with USEPA, the criteria and need for discrete samples to be analyzed for radiological parameters will be determined in consultation with USEPA based on the results of the gamma surveys. This approach was discussed and confirmed with USEPA during a meeting on January 31, 2014.

13. **Page 3-2, Section 3.2.2, second paragraph:** The Draft SSC Work Plan refers to "short-lived *decay daughters* of Ra-226 and Ra-228…" – please use the terminology "decay products" instead of "decay daughters.

    Response: "Decay products" has been used in place of "decay daughters."

14. **Page 3-2, Section 3.2.2, third paragraph:** The Draft SSC Work Plan discusses using a survey meter and detector "calibrated to optimize detector efficiency for the gamma energies associated with Ra-226 and its decay progeny." This phrase should be revised to read "calibrated to optimize detector efficiency for the gamma energies associated with the decay progeny of Ra-226, where Pb-214 and Bi-214 are generally regarded as the notable gamma emitters."

    Response: The last three paragraphs of Section 3.2.2 were significantly revised. The revised text incorporates the recommended edits.

15. **Page 3-2, Section 3.2.2:** The third paragraph indicates that each survey unit will receive 100% gamma walk-over coverage with a 2-inch by 2-inch NaI detector. This statement implies that every square inch of the survey unit will be covered during the gamma survey. This statement appears to be contradicted by the statement in the fifth paragraph, which indicates that the survey will be divided into 1-meter transects. This discrepancy should be resolved.

    Response: The last three paragraphs of Section 3.2.2 were significantly revised. The walk-over survey method described is consistent with the survey methods described in MARSSIM that provide 100% coverage of outside areas. However, to provide additional assurance of complete coverage, the transect width was reduced to 2 feet. Also, "100%" has been replaced with "complete."

16. **Page 3-2, Section 3.2.2:** The second sentence in the third paragraph states that the "minimum detectable activity goal is 2.5 pCi/g Ra-226 above background concentrations." Please define which background concentrations will be used (e.g., gamma-surveyed background concentrations or BTVs).

    Response: The revised Section 3.2.2 describes how the ambient background rate for each detector will be used to determine the minimum detectable count rate (MDCR) and the MDCR will be correlated to the approximate Ra-226 concentration in soil based on the measurements that will be made at the former Kerr McGee site in West Chicago.

17. **Page 3-2, Section 3.2.2, third paragraph:** This paragraph in this section references NuReg-1507. Draft NuReg-1507 describes minimum detectable concentrations that could be measured with typical survey instruments. The NuReg, never issued in a final form, describes using a different size detector, a Victoreen Model 489-55 3.2 cm x 3.8 cm detector and a survey meter that did not exist, a

Ludlum Model 12 ratemeter-scaler, for gamma surveys. The NuReg was based upon subjective interpretations of data by surveyors. It may be appropriate to establish a meter/detector-specific counts per minute (cpm) equivalent to an agreed upon number (e.g. 5 pCi/g) above background for total radium, and use that cpm equivalent as an indicator for the potential of exceedance of the total radium PRG.

Measurement depends upon many factors including the dimensions of the detector, whether or not it is shielded, the instrument background, the ambient background, and the detector and instrument resolving times. This requires interpretation of meter readings by a user to determine whether or not a value is exceeded. Using the audible output as the surveyor is frequently the most reliable survey technique particularly when investigating off-transect areas. Most human ears are far more sensitive to changes in count rate than the statistical methods suggest. Using audible output as an indicator of elevated concentrations can produce a lower MDC, less than 1 pCi per gram above background.

Response: According to the cover page of NUREG-1507 and the reference for NUREG-1507 in MARSSIM, the document was finalized by the NRC in 1997. However, the reference was changed to MARSSIM as the same methods are described in both guidance documents.

To maintain an unbiased collection of data and to reduce the impact of non-independent measurements, survey technicians will turn off the audible response of the detector during the surveys. Therefore, only processed data will be used to identify potentially elevated areas of radioactivity. Survey technicians will make detailed sketches of each subject property and identify the location of different types of groundcovers (e.g., grass, concrete, gravel, pavers, mulch, etc.). This is noted in the revised text of Section 3.2.2

18. **Page 3-2, Section 3.2.2, fourth paragraph:** The Draft SSC Work Plan states that, “NaI detectors will be calibrated by the manufacturer or a rental vendor who specializes in radiation survey equipment to optimize detector efficiency for the gamma energies associated with Ra-226 and its decay progeny.” This phrase should on one hand be revised for technical accuracy to “NaI detectors will be calibrated by the manufacturer or a rental vendor who specializes in radiation survey equipment to optimize detection efficiency for the gamma energies associated with the decay progeny of Ra-226, where Pb-214 and Bi-214 are generally regarded as the notable gamma emitters.” However, if such a calibration is expected to be performed, please specify the company that will be performing this calibration and provide the calibration procedure the company will follow.

    Response: The text has been revised as recommended in the first part of the comment. AECOM will rent survey equipment from ERG in Albuquerque, NM. ERG will send their instruments to Ludlum for calibration. The purchase order with ERG is in place, and the instruments have been sent to Ludlum for calibration. AECOM has requested Ludlum’s calibration procedures for USEPA to review.

19. **Page 3-2, Section 3.2.2:** The fifth paragraph indicates that, when the gamma survey is made while walking, the survey will be done in a serpentine pattern. Clarify whether or not a serpentine pattern will be used if survey buggies are used to conduct the survey and how 100% coverage of the property will be conducted with the use of a buggy.

    Response: The last three paragraphs of Section 3.2.2 were significantly revised. The revised text describes the differences in the survey types (buggy/cart or no buggy/cart).

20. **Page 3-2, Section 3.2.2, fifth paragraph:** The Draft SSC Work Plan states that a surveyor will be “walking at a pace of about 1 meter per second (m/s)” – the pace should be 0.5 to 1 m/s to accommodate the minimum detectable concentration (MDC) required.

The stated minimum detection goal should be expressed as a minimum detectable concentration (MDC) rather than as the minimum detectable activity in this section. The MDC goal should be for total radium rather than for Ra-226. Ra-226 appears throughout this section and should be corrected to read total radium.

The gamma survey walk-over surveys are unlikely to be capable of detecting radium-226 and radium-228 at concentrations expected to be relevant to these surveys. The surveys will quantify concentrations of those radionuclides through the use of surrogates (gamma emitting decay products of Ra-226 and Ra-228).

The described Ludlum Measurements, Inc. (Ludlum) Model 44-10 detector moved at 1 meter per second (m/s) may not be able to meet what should be the stated detection goal, 2.5 pCi/g total radium above the background concentration. The Ludlum web site has a link to a calculator, http://www.radprocalculator.com/ScanMDC.aspx, that provides the MDC for count rate survey meters. The MDC using the calculator could be in excess of 5 pCi/g total radium above background for the instrumentation described in the plan. A gamma survey may be more effective when it depends upon subjective evaluation of the instrument's audible output. Surveyors can be much more sensitive to changes in audible output than to analog or digital count rates.

Response: The last three paragraphs of Section 3.2.2 were significantly revised. The revised text directs technicians to use a slower pace during the walkover surveys if necessary to meet the MDC goal. Also, as previously stated, survey technicians will not listen to the audible detector response so that the surveys produce data points that are as independent as possible. All data will be analyzed both visually and statistically after the data are transmitted to the data analyst.

21. **Page 3-3, Section 3.2.3:** This section describes the Gamma Dose Rate Survey and defines a survey unit area as 2,000 square meters (m^2). However, there is no explanation of why the survey unit was chosen to be 2,000 m^2, even though the much-cited 40 *Code of Federal Regulations* (CFR) 192 standard uses 100 m^2. The use of 2,000 m^2 should be supported.

Response: AECOM used MARSSIM as a guide for determining the maximum size of the "survey unit." The text has been edited to clarify this. MARSSIM allows Class 1 land areas to be up to 2000 m^2. Considering the basis of the survey is to document site conditions and not demonstrate a successful cleanup, the MARSSIM guidance is considered sufficient. Also, see the response to SC #24 below. From MARSSIM (emphasis added):

"Survey units should be limited in size based on classification, exposure pathway modeling assumptions, and site-specific conditions. The suggested areas for survey units are as follows:

Classification	**Suggested Area**
Class 1 Structures	up to 100 m^2 floor area
Land areas	up to 2,000 m^2"

22. **Page 3-3, Section 3.2.3:** The use of a tissue equivalent gamma dose rate meter is appropriate. However, the attached SOP 007 describes measuring dose rate with an instrument, the Ludlum Model 19, which is not a dose rate instrument and is known to be highly energy dependent. Also, there is nothing in the SOP regarding the following:

- At a given survey location, allowing the meter to stabilize for approximately 15 to 30 seconds before collecting instrument readings.
- The Thermo Scientific™ Micro Rem meter has a mechanical dial (analog needle rather than a digital display), so the proper way to measure for data recording purposes is to determine the

average meter reading by collecting 10 instantaneous readings and calculating the average; then recording this average reading on the relevant data collection form. The 10 reading method will provide a more accurate meter reading that having the operator “eyeball” an average meter reading.

This section states that a daily dose response check, typically with the Cs-137 source, will be performed. The plan should describe how Department of Transportation regulations will be satisfied when the source is transported.

This section states: *“Given a probability factor assumed to be 0.92 (based on an assumed standard deviation of survey data), and acceptable Alpha/Beta decision factors chosen to be 1.645, the number of survey locations per survey unit is preliminarily estimated to be 10. The actual number of survey point locations (N) will be calculated during field activities based on the actual standard deviation of the data measured in the field.”*

So what this implies is that you’ll start with N=10, use that to determine "L” (the distance between survey locations on a triangular grid), collect a survey unit worth of data at 10 locations, then use the actual standard deviation of the data measured to calculate an “actual number of survey point locations.” Please elaborate.

Response: It should be noted that the reviewer was not provided the most current revisions of SOP 001 and SOP 011 and these SOPs are not intended to be project-specific. Not all discussions in the SOPs are applicable to the Pines project. However, SOP 007 has been revised to include a tissue equivalent gamma dose rate meter and SOP 011 was revised to include the reviewer’s comments in the bullets.

AECOM will only use exempt radioactive sources in the field. These will be transported in accordance with DOT regulations. The applicable shipping information will be provided.

AECOM will collect a set of at least 10 dose rate measurements on the first subject property and calculate a standard deviation (“actual standard deviation”). The number of measurements will be adjusted as necessary based on revised calculations. This information was added to the text for clarity.

23. **<u>Page 3-6, Section 3.4.2:</u>** This section discusses the identification of soil sampling locations. This section must be revised per the revisions identified for Appendix A of the Draft SSC Work Plan (see below).

    Response: See responses to Specific Comment 5 above, and to Specific Comment 41 below.

24. **<u>Page 3-7, Section 3.4.3:</u>** This section presents the depths of the quadrant composite samples. As presented in EPA comments on the revised FS Report, dated December 3, 2013, in the 40 CFR 192 standard, the concentration of radium in soil is to be averaged over 15-centimeter increments in depth. The use of different increments should be supported.

    Response: The objective of the proposed private property soil sampling is to provide data to evaluate the potential human health risk associated with CCB-derived constituents at properties within the Area of Investigation in the context of the methods used in the HHRA (AECOM, 2012c). The proposed soil depths are consistent with the HHRA evaluation.

    40 CFR 192 addresses remediation standards and states the following:

"**192.12 Standards.**

Remedial actions shall be conducted so as to provide reasonable assurance that, *as a result of residual radioactive materials from any designated processing site:*

(a) The concentration of radium-226 in land averaged over any area of 100 square meters shall not exceed the background level by more than—

(1) 5 pCi/g, averaged over the first 15 cm of soil below the surface, and

(2) 15 pCi/g, averaged over 15 cm thick layers of soil more than 15 cm below the surface."

The sampling described in the Work Plan is for site investigation purposes and is not designed to demonstrate compliance with a remediation standard.

Therefore, no changes to the text are recommended.

25. **Page 3-9, Section 3.4.4:** Consistent with a previous comment, the radionuclide analyte list should include the complete library of gamma-emitting naturally occurring radioisotopes (U-238 series, U-235 series, Th-232 series, K-40) plus Cs-137 and Co-60.

Response: The text has been modified.

26. **Page 4-1, Section 4.1.1:** See Specific Comment #2.

Response: See Response to Specific Comment 2.

27. **Page 4-2, Section 4.2.1:** The plan should specify that all major changes will require approval of the EPA.

Response: Text has been added to specify that all major changes will require approval from the USEPA.

28. **Page 4-2 and 4-3, Section 4.2.2.1:** It is not apparent that there is a data management plan or SOP that addresses the electronic data logging of the GPS and Ludlum 2221 ratemeter for the gamma walkover survey, nor is it apparent how gamma walkover survey related information will be accounted in the field log books. These issues should be addressed. Field log data of gamma dose rate measurements and the electronic data from the gamma walkover survey work (gamma count rate data and its associated geospatial coordinates) should also be compiled and ready to be provided to EPA upon its request. EPA may request this data as early as the end of daily gamma walkover survey activities.

Response: Additional information was added to address data management in Sections 3.2.4 and 4.2.2.1. However, with regard to the electronic data logged during the walkover surveys, only the raw data (count rate and position) will be available immediately at the end of the surveys (expected on a daily basis). Data will not be placed on survey maps or be subject to analysis until after the surveys are complete. This should be acceptable given the fact that the soil sampling activities will not be concurrent with the walkover surveys.

29. **<u>Page 4-3, Section 4.2.2.1:</u>** The 5th paragraph on this page discusses taking photographs. Photographs should be taken of all soil samples, both as retrieved from the ground and after mixing, so as to create a photographic record.

Response: Text has been added to specify photographs to be taken during implementation of the SSC Work Plan.

30. **<u>Page 4-4, Section 4.2.2.4:</u>** The plan should explain why soil samples to be analyzed for radiological components require chilling, and the consequences of exceeding the temperature range should be specified in the plan.

Response: It has been noted in the text that soil samples for gamma spectroscopy do not require chilling, however, samples for metals analysis require chilling to 4° ± 2°C. Data validation actions for samples exceeding the temperature range are described in the QAPP (AECOM, 2005).

31. **<u>Page 4-5, Section 4.2.3:</u>** The project files should also include electronic data such as those produced during gamma walkover survey activities, the associated GIS data, and mapping and data interpretation products.

Response: References to the electronic data acquired during the gamma surveys have been added to this section.

32. **<u>Page 4-5 and 4-6, Section 4.2.5:</u>** The plan should specify the equipment that must be surveyed using a suitable detector (such as a pancake probe), contamination limits, decontamination procedures (if necessary), and whether this equipment will be resurveyed before release.

Response: The radiological survey of <u>all</u> sampling equipment has been added to the decontamination procedure as both an initial and final step. The release limits requirements are "background" levels.

33. **<u>Page 4-8, Section 4.3.2.1:</u>** See Specific Comment #11, 13, 15, 18, 19, and 20.

Response: All previous comment Responses have also been incorporated into Section 4.3.2.1.

34. **<u>Page 4-8, Section 4.3.2.1:</u>** It is stated in this section that the Ludlum 2221 scaler/ratemeter and the Ludlum 44-10 2"x2" NaI detector will be "calibrated by the manufacturer or a rental vendor who specializes in radiation survey equipment to optimize detector efficiency for the gamma energies associated with Ra-226 and its decay progeny." How a calibrator will optimize detector efficiency for the gamma energies associated with the decay products of Ra-226 should be explained.

The Draft SCC Work Plan should also determine whether a Ludlum Model 2221 scaler/rate meter is the most effective instrument to use on this type of survey. The field investigation methodologies section lacks a commitment to perform a daily operational check for instrumentation used for the gamma walk-over survey. Operational checks should be performed daily (at a minimum), prior to performing measurement work, and at the completion of measurement work to ensure the validity of measurement work that was performed that day.

Response: Section 4.3.2.1 has been revised in the same manner as Section 3.2.2 to address Comment #18. A description of the vendor's calibration procedures is not necessary for this work plan but AECOM will request one for USEPA's review. The 2"x2" NaI detector is selected in part because it was the same detector used by third parties in past surveys. Daily operational instrumentation checks are described in the SOPs, specifically RS-TPG, SOP 001.

35. **Page 4-8, Section 4.3.2.2:** It is recommended that, at each sample location where a gamma dose rate measurement is collected, a gamma count rate measurement (using the equipment for the gamma walkover survey) is also collected at a fixed distance of 2 inches from the ground. This will provide a static measurement with a lower MDC than possible with the gamma walkover survey as well as measurements that are comparable to the static measurements collected by members of the Pines community.

    Response: AECOM will collect a direct gamma measurement using a 2" x 2" NaI detector at each of the locations of a gamma dose rate measurement. A two-minute count time will be used as this was the count time used by third parties.

36. **Page 4-8, Section 4.3.3:** The text states that, "[t]he sample will be visually inspected for the presence of CCBs in the same manner as the previous visual inspections and logged in accordance with the soil characterization portion of AECOM SOP 109Pines – Split Spoon Sampling for Geologic Logging." As stated in this SOP, the procedures cover subsurface soil sampling by split-spoon only. If only using the soil characterization portion of this SOP, the specific sections of the SOP that will be used should be identified and stated.

    Response: The specific section of AECOM SOP 109Pines – Split Spoon Sampling for Geologic Logging has been specified in the text.

37. **Page 4-9, Section 4.3.4:** See Specific Comment #24.

    Response: See Response to Specific Comment #24.

38. **Table 1.** As a note, these PRGs may be subject to revision based on comments made to the recently reviewed draft Feasibility Study.

    Response: The PRGs for radionuclides have been revised and are consistent with those presented in the FS submitted February 2014.

39. **Table 2.** It should be noted whether any of these proposed locations were also used as background locations for survey work conducted by the Pines community. If not, adding background survey locations used by the Pines community may be advisable, whether they are recognized as background locations or as additional gamma survey locations, in order to understand the distribution of gamma count rate measurements in areas regarded as background by the Pines community.

    Response: None of the locations on Table 2 were used as background locations during the 2009 Jensen survey. Two background survey locations from the Jensen 2009 survey are included in Table 4, see response to Specific Comment 40 below.

40. **Table 4.** It should be noted whether these locations would all be considered as survey units or if any are considered to be background reference areas.

    Response: The locations in Table 4 are all considered survey units. Although locations Q and R were identified as background survey areas during the 2009 Jensen survey, background locations for this program are those identified and agreed upon with USEPA in the FS submitted February 2014. Therefore, locations Q and R will be considered survey units. No changes are proposed to the table.

41. **Appendix A** presents the procedures used and results of the calculation of a representative number of properties to sample. The primary problem with the procedure used (including the particular equation used) is that the equation selected is based on the end goal of calculating a grand mean

across properties in two strata: those with CCBs and those without CCBs. However, there is no intention to actually calculate such a grand mean for the Pines site. The intention is to compare the concentration of each analyte at each of the selected properties to the analyte-specific BTV calculated based on the background data set. Appendix A must be revised to follow a streamlined data quality objective (DQO) process (EPA 2000) and also (1) clearly state the decision criteria that will be used as well as (2) select an appropriate sampling design with a related equation or process that is consistent with the identified decision criteria and which will estimate the necessary number of properties to be sampled.

Response: We acknowledge that the equation is intended to calculate a mean of each of the two strata. However, random sampling is needed to estimate a mean, and it has always been the intention to conduct biased sampling of the properties expected to have the highest percentage of CCBs. Thus, if sampling five properties containing CCBs is sufficient to calculate a mean, clearly it is sufficient and conservative to sample double that number (nine) to establish likely worst-case conditions. The text in Appendix A has been updated to include this rationale.

A streamlined 7-step DQO process has been added to Section 1.4 of the SSC Work Plan.

42. **Appendix B, Section A.6, page 1 of 2:** Item #1 "gamma surveys" should be replaced with "gamma count rate and gamma dose rate surveys."

    Response: The change was made as recommended.

43. **Appendix B, Section B.4.1, page 2 of 3:** In the third paragraph of Section B.4.1, it is indicated that the analysis performed by the R.J. Lee group will be by Photo Light Microscopy. This is different from what is described in Section 3.3.3 of the Draft SSC Work Plan, which describes the method as "Polarized Light Microscopy." This apparent discrepancy should be corrected.

    Response: The third paragraph of Section B.4.1 has been updated with "Polarized Light Microscopy."

44. **Appendix B, Section B.8, page 3 of 3:** This section lists analytical instrument calibration. Specifically, Table B-8 states that daily checks will be performed using a pulser. This depends upon a second instrument to validate the first instrument is operating correctly. Daily checks are better performed with a check source made up of several radionuclides. The acceptance limits for of all types of checks and calibrations are broad, within two or three standard deviations. A specific limit should be stated.

    Response: The QAPP was updated based on information provided directly from GEL with regard to their standard calibration protocols.

45. **Appendix B, Table A-4, page 4 of 18:** The data quality levels (DQLs)/Residential Soil PRGs are provided in the far right column, but the risk level used for their computation should be stated in the notes (probably 10^{-6}). It may be prudent to provide PRGs for risk levels of 10^{-4}, 10^{-5}, and 10^{-6} to cover the full EPA risk range. Also, considering that the DQL/PRGs were taken from the EPA Preliminary Remediation Goals for Radionuclides website tables, the isotopes listed in Table A-4 and their respective PRGs are incorrect. For example, Ra-226 should be listed as "Ra-226+D" (proper isotope selection). Then, the 1.21x10-2 pCi/g PRG is correct. In general for the listed isotopes, the "+D" version should be used to account for risk due to the primary isotope and its short lived decay products. Also, please refer to "daughters" as "decay products" or "short-lived decay products" as appropriate.

    Note that the minimum detectable activities (MDAs) for lead-210, radium-226, radium-228, and thorium-228 are greater than their respective DQLs/Residential Soil PRGs.

Response: "Decay products" has been used in the text. Table A-4 has been updated.

46. **Appendix B, Table A-5, page 5 of 18:** This table provides the quality control performance criteria for field and lab blanks as "<MDA" but the MDAs are not provided or otherwise specified. Please include all applicable MDAs. Also, an asterisk is present next to radium-226 but no note is provided; please provide the note.

    Response: Table A-5 was updated to include the revised gamma spec library based on conversations between GEL, AECOM, and EPA. The associated MDCs for the isotopes in the gamma spec library are indicated in Table A-4.

    The asterisk next to Ra-226 in Table A-5 was removed.

47. **Appendix B, Table B-1, page 8 of 18:** Please provide the basis for the preservation and holding time for radionuclides. A note is provided that the 45 days is a contractual rather than technical requirement, but a technical holding time or "not applicable" for technical requirements should be noted as appropriate.

    Response: The preservation for the radionuclides was changed to "None Required." The holding time for the radionuclides was changed to "Not Applicable."

48. **Appendix B, Table B-4, page 12 of 18:** It is recommended that the response check and instrument source check are performed daily at the start and again at the completion of a measurement work period to help ensure the validity of the measurements collected during that work period or, at least, at the beginning and end of the work day.

    Response: While it is not required in the procedure (RS-TPG SOP 001) to perform source checks at the beginning and end of each day, it is normally what is performed in the field. Section 4.3.2.2 has been modified to indicate that source checks will be done at the beginning and end of each work day.

49. **Appendix B, Table B-7, page 16 of 18:** What is labeled as a "Daily: Field calibration check" should be changed to "Daily: Field operational check" or "Daily: Field functional check." A field tech is not actually checking the calibration in the field but checking the instrument's response to a check source. The check source for the daily field operational/functional check does not need to be NIST-traceable. See ANSI N323B "American National Standard for Radiation Protection Instrumentation Test and Calibration, Portable Survey Instrumentation for Near Background Operation" for more information.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The current revision contains Attachment 1 for logging daily source checks. The form is titled "Radiological Instrument Daily Source Check Record." Table B-7 has been modified to indication that the field response checks will be with an exempt sealed gamma source, not a NIST traceable source.

50. **Appendix C, Procedure Number SARSG, SOP 001:** Specific procedures should be included in the manual for the instruments actually used on site.

    Response: The SOPs provided in Appendix C are general SOPs used by AECOM's radiolocation services technical practice group (RS-TPG) and they are not intended to be applicable to all site-specific needs. Site-specific survey details are provided in project work plans and survey plans. Unfortunately, the reviewers were not provided the most current revisions of SOPs 001, 007, and 011. These are now recognized by the procedure numbers RS-TPG SOP 001, RS-TPG SOP 007, and RS-TPG SOP 011.

51. **<u>Appendix C, Procedure Number SARSG, SOP 001, Section 4.4, page 2:</u>** The SOP states "[s]lowly enter areas of unknown radiation with instruments on the high scale to avoid off-scale readings and subsequent prolonged recovery time." This wouldn't be appropriate for assessments of environmental radioactivity. For example, when operating a Thermo/Bircon micro-rem tissue equivalent survey meter, one wouldn't want to have the instrument set on the highest x1000 scale (0 to 200,000 urem/hr) when operating in areas where near-background readings are expected (5 to 20 urem/hr where the x0.1 scale would be appropriate) or somewhat higher dose rates would be expected (20 to 200 urem/hr where the x1 scale would be appropriate).

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

52. **<u>Appendix C, Procedure Number SARSG, SOP 001, Section 4.5, page 2:</u>** The SOP states, "[a]lthough incidental contact with the surveyed surface will not generally contaminate the detector, minimize contact with the surface." Simply minimizing contact may be valid in cases of fixed contamination, but not where loose/removable contamination is present. When performing surface contamination surveys, contact with the surface should be avoided, but if contact does occur, the operator should check the response of the instrument and remove it from service if contamination is suspected.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). However, the comment was applicable to the current version and a change has been made as suggested.

53. **<u>Appendix C, Procedure Number SARSG, SOP 001, Section 4.6, page 2:</u>** The SOP states, "[o]ccasionally verify instrument is responding properly if background appears low." It's more appropriate to verify instrument operation if background is outside the expected range, where a higher background may indicate contamination of the instrument.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). However, the comment was applicable to the current version and a change has been made as suggested.

54. **<u>Appendix C, Procedure Number SARSG, SOP 001, Section 5.1.1.2, page 2:</u>** The SOP states, "[a] field calibration check will be performed daily prior to use of the instrument." Actually, what would be performed daily is a "source response check" or what is also commonly referred to as either a "functional check" or an "operational check." Section 5.1.5 refers to this as an "Instrument Source Check."

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

55. **<u>Appendix C, Procedure Number SARSG, SOP 001, Section 5.1.3.1, page 3</u>**: This section implies that a battery check checks the detector voltage. This only checks the condition of batteries and does not indicate whether or not the probe is being supplied with adequate voltage.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

56. **<u>Appendix C, Procedure Number SARSG, SOP 001, Section 5.1.5, page 3:</u>** These sections appear to be describing the same operation. It may be possible to combine them. Section 5.1.5.4 instructs the operator to "[r]ecord the source check results on the Radiological Instrument Daily Calibration Record, Attachment 1." Section 5.1.6.1 states, "[d]ocumentation of these response checks is not

required." Section 5.1.9 instructs "(o)n the first source check of the month, the source check label shall be replaced on the instrument." These three statements should be reconciled.

Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The current SOP requires that all response checks be documented.

57. **Appendix C, Procedure Number SARSG, SOP 001, Section 5.1.9, page 4:** The SOP states, "[o]n the first source check of the month, the source check label shall be replaced on the instrument." Is there an SOP that covers monthly source checks and the generation of "source check labels?" If the "source check label" is being replaced monthly, how is this being done? Usually, there is a calibration label applied to the instrument at the time of calibration, and this is replaced when the instrument is returned for calibration.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

58. **Appendix C, Procedure Number SARSG, SOP 001, Section 5.2.1, page 4:** This section describes the orientation of detectors. For instruments used to measure exposure rate, detectors with isotropic responses should be used because the source of radiation may be extended.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

59. **Appendix C, Procedure Number SARSG, SOP 001, Section 5.3, page 5:** This section should probably refer to the use of beta-gamma detectors (probes), such as the frequently used Geiger-Mueller (GM) "pancake" detector, for surface contamination count rate scanning.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

60. **Appendix C, Procedure Number SARSG, SOP 001, Section 5.3.1, page 5:** This section states, "[c]ount the smear for a minimum of five seconds, or if positive indication is noted, count for at least 15 seconds or until the meter indication stabilizes." If counting, the count time should be based on the desired minimum detectable activity. What this section suggests is the field screening of smears and air filters, where actual quantitative measurement of the smears and filters would be performed in a lab with more appropriate equipment.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

61. **Appendix C, Procedure Number SARSG, SOP 001, Section 5.4, page 5:** This section should probably refer to the use of alpha detectors (such as an alpha scintillation detector, a gas flow proportional detector, or a silicon PIPs detector) for surface contamination count rate scanning measurements. There should also probably be a subsection 5.4.1 called "Performing Surface Contamination Count Rate Scanning Measurements."

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure.

62. **Appendix C, Procedure Number SARSG, SOP 001, Section 5.6.1, page 5:** This section describes using a reference check source following receipt of the instrument. Instruments should be calibrated with reference check sources used at the point of calibration to verify that they have not changed in shipment. Section 5.5.3 or other sections do not specify or recognize applicable shipping

requirements for the check source that would be sent with the instrument when it's returned for calibration.

Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure. Since AECOM rents instruments on a project-by-project basis, instruments may not be received at the project site straight from calibration. The current procedure describes a source check following the receipt of an instrument that the project sends out for calibration.

63. **Appendix C, Procedure Number SARSG, SOP 001, Section 6.1, page 7:** This section states, "[r]eadings that deviate more than ± 20% from reference source check readings obtained at the time the instrument was first calibrated require instrument recalibration." The deviation intended is probably from the check source that's assigned to the instrument, and it's more likely from the "time the instrument was last calibrated" provided that the check source accompanied the instrument for its calibration and that a source response check was performed by the calibrator following calibration.

    Response: The reviewer was not provided the most current revision of SOP 001 (now RS-TPG SOP 001). The comment is not applicable to the current revision of the procedure. Since AECOM rents instruments on a project-by-project basis, instruments may not be received at the project site straight from calibration. The current procedure describes a source check following the receipt of an instrument that the project sends out for calibration.

64. **Appendix C, Procedure Number RS-PPG, SOP 007:** It is not clear how this SOP supports the performance of gamma walkover surveys (count rate) and gamma dose rate surveys. The gamma walkover survey is intended to be, in short, a gamma surface scan with NaI detector swinging while walking across a survey unit in a serpentine pattern on 1-meter transects; this is not covered by this SOP. The gamma dose rate survey is intended to consist of a collection of static measurements at points on a triangular grid; this is not covered by this SOP. Also, the SOP does not provide clear instructions on using the attached forms.

    Response: The reviewer was not provided the most current revision of RS-TPG SOP 007. The comment is not applicable to the current revision of the procedure.

65. **Appendix C, Procedure Number RS-PPG, SOP 007, Section 2.1, page 1:** gives an example of a Ludlum model 19 as a dose rate instrument. The Ludlum model 19 is energy dependent and it is not a suitable instrument for measurement of dose rate. A more suitable instrument is described in the text of the plan. This SOP should describe the same instrument as is in the plan.

    Response: The reviewer was not provided the most current revision of RS-TPG SOP 007. The comment is not applicable to the current revision of the procedure.

66. **Appendix C, Procedure Number RS-SARSG, SOP 011, Section 2.1:** This section states "[b]eta-gamma contamination surveys are performed using a thin window Geiger-Mueller (GM) probe, a Bicron or equivalent." "A Bicron" is the name of a manufacturer and not a specific probe model. Thin window GM probes can come in end-window or "pancake" versions, where the pancake GM is more commonly used for beta/gamma surface contamination measurements.

    Response: The reviewer was not provided the most current revision of SOP 011 (now RS-TPG SOP 011). The comment is not applicable to the current revision of the procedure.

67. **Appendix C, Procedure Number RS-SARSG, SOP 011, Section 2.5:** Note that the Ludlum Model 19 NaI scintillator is energy sensitive (energy dependent) and does not provide a linear response over the range of gamma energies that it detects. Therefore it shouldn't be suggested that a Bicron

Micro-Rem Tissue Equivalent Survey Meter (to be used for dose rate measurements) with its relatively linear energy response is equivalent to the Ludlum Model 19.

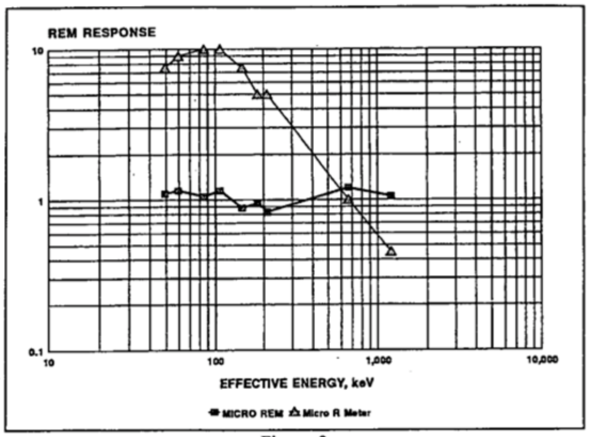


Figure 3
Rem Response value vs. Energy for
Bicron and conventional Micro R Meters.

Response: The reviewer was not provided the most current revision of SOP 011 (now RS-TPG SOP 011). The current revision of RS-TPG SOP 011 and RS-TPG SOP 001 distinguishes between microR and microRem meters.

68. **Appendix C, Procedure Number RS-SARSG, SOP 011, Section 3.1:** This section states, "[s]mears should be counted in an area where the background is less than 100 cpm for beta-gamma radiation." With which instrument (GM or Ludlum 2929) and under what conditions (field or lab) does this apply? This falls under Section 3.0 (Instrument Operational Checks). When is counting smears a part of instrument operation checks, unless the smear is considered to be a check source or calibration source? Eckert and Ziegler manufactures sources that mimic filters. Is that what is implied? An instrument operational checks section should really be instrument-specific.

Response: The reviewers did not have the most current revision of SOP 011 (now RS-TPG SOP 011). The current version of RS-TPG SOP 001 states that count times should be sufficient to have acceptable MDAs when compared to release criteria.

69. **Appendix C, Procedure Number RS-SARSG, SOP 011, Section 4.0:** This section should either specify the basis for posting radiological control areas (contaminated area, radiation area, airborne radioactive material, etc.) or refer to an SOP that does.

Response: The reviewer was not provided the most current revision of SOP 011 (now RS-TPG SOP 011). The current version of RS-TPG SOP 001 references RS-TPG SOP 020, *License/Site Radiation Protection Program*, for posting requirements. Such posting requirements will not be applicable to the Pines investigation survey/sampling efforts.

70. **Appendix C, Procedure Number RS-SARSG, SOP 011, Section 5.1:**

- Beta emitters do not directly produce exposure. The instruments described in other SOPs are not capable of measuring beta dose and the beta dose rate equation provided is correct only for a specific thickness beta shield and a limited range of energies.
- This work does not include exposure rate surveys. What are being proposed are gamma dose rate surveys and gamma count rate surveys.

- The text states that, "[g]amma exposure rates are recorded as mR/hr (uSv/hr), or (uR/hr)." For this work to be done for this site, gamma dose rates should be recorded as urem/hr or a similar metric unit (uSv/hr or nSv/hr).
- Beta dose rate recording and calculation are discussed using an instrument that has a sliding shield for beta measurements (found on survey meters such as the Thermo RO-20 ion chamber). It doesn't appear that this SOP is applicable to ion chamber according to Section 2.0 (Equipment) of this SOP.
- The text states, "[t]he beta correction factor used for each instrument shall be determined by the calibration facility". You probably won't get this for a Ludlum Model 19, a Bicron tissue equivalent survey meter, a Ludlum end-window, or a "pancake" GM.

Response: The reviewer was not provided the most current revision of SOP 011 (now RS-TPG SOP 011). However, the current revisions of both RS-TPG SOP 001 and RS-TPG SOP 011 address the types of surveys that will be conducted at the Pines sites in general terms. These SOPs are not designed for site-specific instructions. Site-specific instructions are provided in project work plans.

71. **Appendix C, Procedure Number RS-SARSG, SOP 011, Static MDCs:** Example static MDCs are provided for the Ludlum Model 43-89 alpha/beta scintillator and the Ludlum model 43-37 beta floor cart. It would probably be appropriate to include static MDCs for the instruments that will be used for this work.

    Response: The reviewer was not provided the most current revision of SOP 011 (now RS-TPG SOP 011). However, the current revisions of both RS-TPG SOP 001 and RS-TPG SOP 011 address the types of surveys that will be conducted at the Pines sites. The determination of the minimum detectable count rate is discussed in RS-TPG SOP 001.

    The details of converting gamma survey data (in cpm) to an estimated total radium activity (in pCi/g) will be addressed in final work plans after correlation measurements are made. This includes determination of the MDA.

72. **Appendix C, Procedure Number RS-SARSG, SOP 011, Scan MDCs:** Example scan MDCs are provided for the Ludlum model 44-9 "pancake" GM detector and the Ludlum model 43-37 beta floor cart. It would probably be appropriate to include scan MDCs for the instruments that will be used for this work. If necessary, a Ludlum model 44-9 "pancake" GM detector with an appropriate survey meter could be suitable for beta/gamma contamination monitoring, but this instrument was not previously mentioned in the SOP.

    Response: The reviewer was not provided the most current revision of SOP 011 (now RS-TPG SOP 011). However, the current revisions of both RS-TPG SOP 001 and RS-TPG SOP 011 address the types of surveys that will be conducted at the Pines sites.

73. **Appendix C, Procedure Number RS-SARSG, SOP 011, Section 5.3:** In short, this section should be revised to support the instruments that would be used for this work, if a radiological control program is necessary.

    Response: The reviewer was not provided the most current revision of SOP 011 (now RS-TPG SOP 011). However, the current revisions of both RS-TPG SOP 001 and RS-TPG SOP 011 address the types of surveys that will be conducted at the Pines Area of Investigation.

74. **Appendix C, Procedure Number RS-SARSG, SOP 011, Section 5.5:** References presumed SOPs (Re19, Re032v, Re033, etc.) that are not included in this document. "Grave Danger, Very High Radiation Area" is a posting required under 10 CFR 20 (NRC regs) if necessary but not specified by

OSHA. This is being mentioned because the Pines Area of Investigation isn't under a NRC license or subject to 10 CFR 20. The need for the postings described should probably be reviewed in the context of the work to be performed.

Response: The reviewer was not provided the most current revision of SOP 011 (RS-TPG SOP 011). This comment is not applicable to the revised procedure.

75. **Appendix C, SOP Number 7510Pines, Revision Number 5.0, Section 1.0:** The SOP states that "[e]nvironmental samples are not considered a Resource Conservation and Recovery Act (RCRA) classified hazardous waste by definition; therefore, more stringent RCRA and Department of Transportation (DOT) regulations regarding sample transportation do not apply."

It should be recognized that it is a shipper's responsibility to comply fully with the DOT and IATA regulations (and applicable courier requirements) when offering a dangerous good or hazardous material consignment for commerce.

It is recommended that you review 40 CFR Section 261.4(d), and especially 261.4(d)(2)(i) and 261.4(d)(2)(ii). The regulations at 261.4(d)(2)(ii) discuss requirements if the sample collector determines that DOT, USPS, or other shipping requirements do not apply to the shipment of the sample (IATA often looks at the consignment, which could be a collection of samples in one shipping container).

A summary on the shipment of samples is provided in the RCRA Waste Sampling Draft Technical Guidance (EPA530-D-02-002). Section 7.2.8.2 (Sample Shipping) of this guidance states the following:

In general, samples of drinking water, most ground waters and ambient surface waters, soil, sediment, treated waste waters, and other low concentration samples can be shipped as environmental samples; however, shipment of high concentration waste samples may require shipment as dangerous goods (not as "hazardous waste"). Note that RCRA regulations specifically exempt samples of hazardous waste from RCRA waste identification, manifest, permitting, and notification requirements (see 40 CFR §261.4(d)). The shipment of samples to and from a laboratory, however, must comply with U.S. DOT, U.S. Postal Service, or any other applicable shipping requirements. If a sample is a hazardous waste, once received at the laboratory, it must be managed as a hazardous waste.

In recent years, commercial overnight shipping services have adopted the regulations of the IATA for shipment of dangerous goods by air. The IATA Dangerous Goods Regulations contain all provisions mandated by the International Civil Aviation Organization and all rules universally agreed to by airlines to correctly package and safely transport dangerous goods by air. Contact IATA for a copy of the IATA Dangerous Goods Regulations and for assistance in locating suppliers of specialized packaging for dangerous goods.

Also, the following website provides information regarding the issue of DOT and sample preservation: http://www.epa.gov/osw/hazard/testmethods/resources.htm

Response: None of the samples collected and shipped during this investigation will meet the criteria of Hazardous Waste or Dangerous Goods.

Appendix D-2

Response to USEPA comments dated May 7, 2014 regarding Supplemental Soil Characterization Work Plan

TECHNICAL REVIEW COMMENTS ON "SUPPLEMENTAL SITE CHARACTERIZATION WORK PLAN, AOC II DOCKET NO. V-W-'04-C-784, APRIL 2014" PINES ARE OF INVESTIGATION, TOWN OF PINES, MAY 2014

GENERAL COMMENTS

1. The majority of EPA's comments dated January 15, 2014, have been adequately addressed, except as specified in the next section, below.

2. The revised SSC Work Plan still contains references to "radium-226" when it should be total radium (radium-226 and radium-228). Please update the language as appropriate throughout the document. A specific example is in Section 3.2.2, page 3-3, second paragraph "The concentration criterion in Subpart B of 40 CFR Part 192 for surface soil (5 picoCuries per gram (pCi/g) of Ra-226 over background)... "

   Response: The document has been reviewed and these changes have been made where appropriate.

3. Background sample locations SS016 and SS028 may be located in the wetlands area of the Site. If this is the case, alternate locations must be provided for EPA's review as gamma surveys cannot be conducted in saturated areas.

   Response: Note that there several of the final background locations, all of which have been determined by laboratory analysis to be free of CCBs are located in wetland areas, which can be inundated at certain times of the year. These two locations, SS016 and SS028, were inundated at the time the gamma surveys were conducted (May 14, 2014 through June 3, 2014). Alternate background sample locations from the CCB-free background locations were identified in a Field Change Order (FCO), titled *Supplementation of Background Locations for Gamma Surveys, Pines Area of Investigation – Supplemental Soil Characterization,* approved by USEPA May 21, 2014. A copy of the FCO will be provided as an appendix to the *Supplemental Soil Characterization Report*. Note that a gamma count rate meter from this field work effort has been retained for use on the original background properties once the high water subsides.

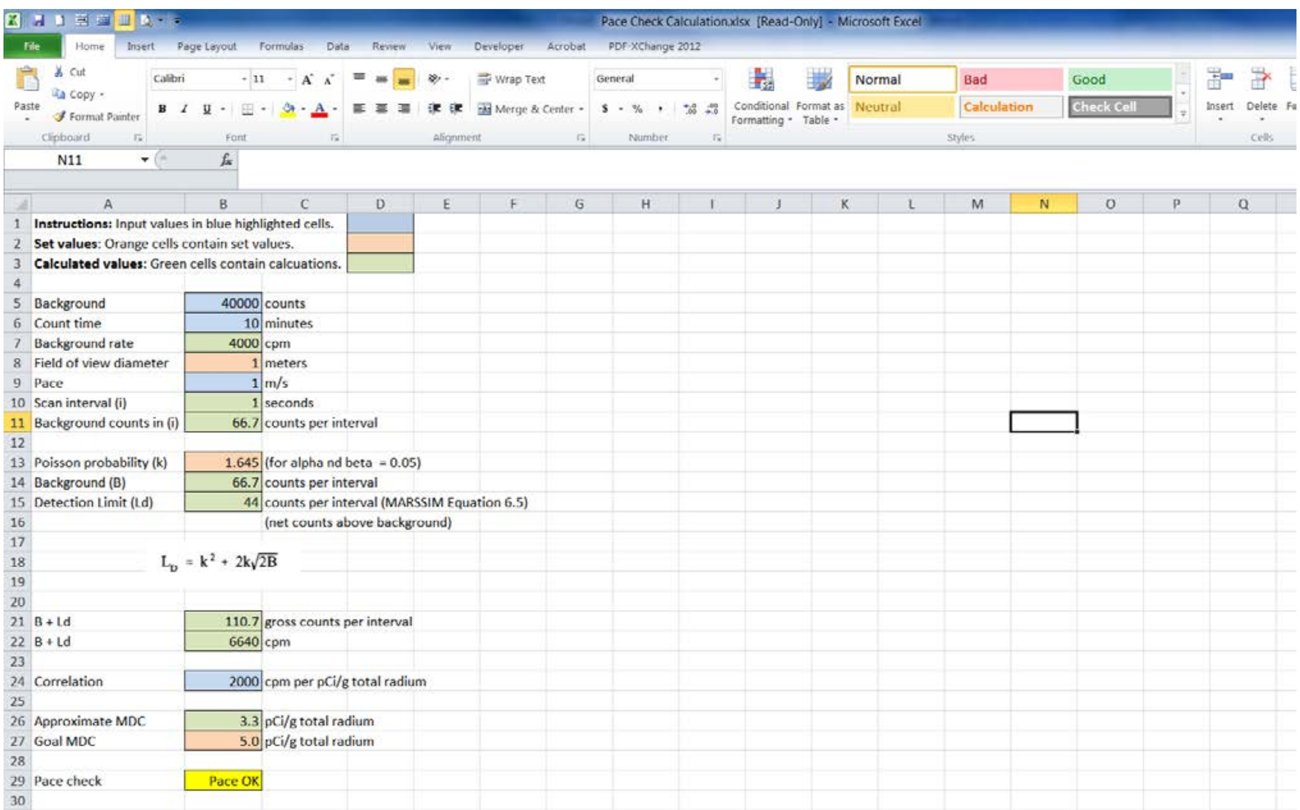
EPA COMMENTS NOT COMPLETELY ADDRESSED

Bullet 1 Specific Comment 8 (Page 1-6, Section 1.3.4.1, first full paragraph): Regarding the gamma spectroscopy library, the x-ray energies and excessive gamma energies should be eliminated from the list. The actinium series radionuclides from the library (provided in Attachment 1 in this comment letter) should be added based upon the type of detector. The N-type detectors have higher efficiency than the p-type detectors at low energies and may have poorer resolution and poorer efficiency at higher energies.

Response: The gamma spectroscopy library has been revised to address EPA's most-recent recommendations including the addition of actinium series isotopes. A revised gamma library was submitted to USEPA on July 16, 2014, and was approved by USEPA on August 26, 2014.

Bullet 2. Specific Comment 17 and 20 (Page 3-2, Section 3.2.2, third and fifth paragraphs): EPA's original comment suggests establishing a "meter/detector-specific counts per minute (cpm) equivalent as an indicator for the potential of exceedance of the total radium PRG." The SSC WP states that the surveyor will walk at a pace that will meet the MDC; however, the audible response of the detector will be turned off to maintain an unbiased collection of data. Please indicate how the surveyor will know what the correct pace will be to meet the MDC and whether or not the pace will be pre-determined after calibration against the radium blocks. The SSC WP suggests that the surveyor will be changing the pace to meet the MDC, but this will not be possible if the audio on the instrument is turned off.

Response: The pace will be set based on local background and the results of the correlations. This will be determined using "Pace Check Calculation" Excel spreadsheet and documented in field notes. The spreadsheet was submitted to USEPA May 12, 2014; an image of the calculation parameters is shown below. Muting the audible will not impact the surveyors' ability to keep a steady pace.



	A	B	C
1	**Instructions:** Input values in blue highlighted cells.		
2	**Set values:** Orange cells contain set values.		
3	**Calculated values:** Green cells contain calcuations.		
4			
5	Background	40000	counts
6	Count time	10	minutes
7	Background rate	4000	cpm
8	Field of view diameter	1	meters
9	Pace	1	m/s
10	Scan interval (i)	1	seconds
11	Background counts in (i)	66.7	counts per interval
12			
13	Poisson probability (k)	1.645	(for alpha nd beta = 0.05)
14	Background (B)	66.7	counts per interval
15	Detection Limit (Ld)	44	counts per interval (MARSSIM Equation 6.5)
16			(net counts above background)
17			
18	$L_D = k^2 + 2k\sqrt{2B}$		
19			
20			
21	B + Ld	110.7	gross counts per interval
22	B + Ld	6640	cpm
23			
24	Correlation	2000	cpm per pCi/g total radium
25			
26	Approximate MDC	3.3	pCi/g total radium
27	Goal MDC	5.0	pCi/g total radium
28			
29	Pace check	Pace OK	
30			

Bullet 3. Specific Comment 18 (Page 3-2, Section 3.2.2, fourth paragraph): Please provide EPA with the Ludlum calibration procedure as indicated in the Respondent's response to comments. Additionally, relating to the calibration procedure, the third paragraph of Section 3.2.2 states, "NaI detectors will be calibrated by the manufacturer (Ludlum) or a rental vendor who specializes in radiation survey equipment to optimize detection efficiency for the gamma energies associated with the decay products of Ra-226, where lead-214 (Pb-214) and bismuth-214 (Bi-214) are generally regarded as the notable gamma emitters." Please explain how the calibration procedure will optimize performance for total radium. The check source readings conducted during the survey efforts are to verify that the survey instrument is reading accurately; however, a check source reading should also be recorded both at the time and place of calibration of the instrument and after receipt of the instrument to verify that changes did not occur during shipment. Additionally, check sources whose activity will not change significantly over the duration of the project should be used.

Response: The calibration procedures and certificates for the Ludlum gamma dose rate meters (Thermo Microrem) to be used for the SSC work were sent to USEPA on May 5, 2014. Based on USEPA review of the certificates, certificates for two alternative meters were sent to USEPA on May 12, 2014. These alternative certificates, and the associated meters, were determined to be appropriate by USEPA for the SSC work. The original meters were returned, and the new meters were used for the SSC work. Note that the radiation survey equipment is rented, and as such, we cannot perform check source readings at the place of calibration.

Bullet 4. Specific Comment 22 (Page 3-3, Section 3.2.3): The daily dose response check is stated to be typically done with a Cs-137 button source; however, the revised SSC Work Plan still does not describe how Department of Transportation (DOT) regulations will be satisfied when the source is transported. Although the Cs-137 check source is exempt from licensing, it is not exempt for DOT regulations. Therefore, individuals involved in transporting the source will have to have training per Title 49 of the Code of Federal Regulations, Section 172, subpart H, or use a source check exempt from DOT regulations (such as Ba-133).

Response: The source will be shipped to AECOM by ERG. Chris Higgins, who has the proper DOT training, will control the source and ship the source back to ERG in accordance with applicable DOT requirements.

Bullet 5. Specific Comment 25 (Page 3-9, Section 3.4.4): The actinium series is not adequately represented. Please see Specific Comment 8, above.

Response: See the response to Bullet 1, above.

Bullet 6. Specific Comment 45 (Appendix B [Quality Assurance Project Plan], Table A-4, page 4 of 18): The term "Decay products" has been updated in the text; however, this language is not consistent throughout the document. Please update the SOPs, tables, and appendices, as appropriate.

Response: The document, including SOPs, tables, and appendices, has been reviewed and this change has been made.

NEW COMMENTS

1. **Figures 1 and 7:** Sample location SS038 is listed as a background location in Table 2 but the location is not depicted in Figures 1 or 7. Please add background sample location SS038 to these figures**.**

   Response: These sample locations have been added to Figures 1 and 7.

2. **Appendix C, SOP 001:** The SOP uses general terms such as "appropriate" and "periodically" which should be replaced with specific instructions. For example: "Section 5.1.5 – Instrument Source Check (contamination Detectors): This check is performed periodically to verify that the instrument will respond accurately to a known source of radiation."

   Response: We keep the language general in the SOP to leave room for client or regulator project-specific requirements. No change is required for the SOP. However, the Work Plan (Section 4.3.2.1) states that "Daily instrument operational checks on the 2-inch by 2-inch detector described in these procedures will be performed at the beginning and end of each day the instruments are in use."

3. **Appendix C, SOP 001, Section 4.6, page 2:** The SOP reads "Occasionally verify instrument is responding properly if background appears outside the expected range." The SOP lacks a step to determine background for rate reading survey instrument and guidance on "expected range" for background. The SOP goes into great detail about determining background for scaler instruments

   Response: The "expected range" is site specific and determined at the beginning of the field tasks (and updates as conditions may warrant). Trained staff will be able to establish background for these instruments without specific guidance in the SOP. Furthermore, net readings from rate reading instruments are not decision-making data and are not subject to the same level scrutiny. Direction on determining background for rate reading instruments will not be added to the SOP.

4. **Appendix C, SOP 001, Section 5.1.6.2, page 4:** Starting with the highest range is appropriate if entering an area with a possibly hazardous dose rate. However, in the case of the Pines Area of Investigation, the scale and expected reading for check sources must be known to enable comparison with an earlier reading.

   Response: AECOM's previous response indicated that this is not a Pines-specific SOP and that the comment refers to a cautionary statement in the SOP that applies to instances when dealing with unknown radiation sources. It is not intended to direct staff on the appropriate scale to set an instrument on for field measurements. Staff will choose the appropriate scale for measuring the check source and field data. The scale for the source will depend on its activity and the scale for the field measurements will be the lowest scale. Specific direction is not needed in the SOP.

5. **Appendix C, SOP 001, Section 5.6, pages 9-10:** Please see Specific Comment 18, above.

   Response: Please see the response to Bullet 3 Specific Comment 18, above.

Bradley, Lisa

From:	Hardin, Erik <hardin.erik@epa.gov>
Sent:	Friday, November 14, 2014 7:12 PM
To:	Bradley, Lisa
Cc:	Jablonowski, Eugene; Earle, William (wearle@onesullivan.com)
Subject:	Approval of Revison 2 of the SSC Workplan

Lisa:

By this email, EPA is approving Revision 2 of the SSC Workplan dated November 2014.

Thanks,
Erik

D. Erik Hardin
Remedial Project Manager
U.S. EPA, Region 5

Appendix E

Constituent Concentrations in Coal Combustion By-Products

Appendix E

Constituent List

This appendix provides the rationale for the list of constituents to be analyzed during the supplemental soil characterization (SSC) described in the main text of this Work Plan at the Pines Area of Investigation (AOC II – Docket No. V-W-'04-C-784)(2004). This list has been developed in discussions with the United States Environmental Protection Agency (USEPA).

The goal of the Superfund process and the human health risk assessment (HHRA) are to identify those constituents that pose potentially unacceptable risk to human health. Therefore, the first step of the HHRA was to select constituents of potential concern (COPC), as presented on Table E-1. As stated in USEPA guidance (USEPA, 1993):

> "Most risk assessments are dominated by a few compounds and a few routes of exposure. Inclusion of all detected compounds at a site in the risk assessment has minimal influence on the total risk. Moreover, quantitative risk calculations using data from environmental media that may contain compounds present at concentrations too low to adversely affect public health have no effect on the overall risk estimate for the site. The use of a toxicity screen allows the risk assessment to focus on the compounds and media that may make significant contributions to overall risk."

As shown on Table E-2, the COPC quantitative evaluation for metals and inorganics in the HHRA for the Pines Area of Investigation (AECOM, 2012) is consistent with similar evaluations of coal combustion by-products (CCB) data from a variety of sources, sources that were not available at the time the Municipal Water Service Extension (MWSE) sampling program was designed (USGS, 2011; ACAA, 2012; EPRI, 2009, 2010; USEPA Federal Register, Volume 75, No 118; USEPA, 2010). Of note is that 14 of the metals and inorganic constituents on the Extended List (i.e., the list of inorganic, metal, and radionuclide constituents analyzed during the Remedial Investigation) on Table E-1 do not have levels measured in any of the datasets (including the Pines MWSE dataset) exceeding the USEPA Regional Screening Level (RSL, USEPA, 2012) adjusted for a target hazard quotient of 0.1, as indicated by yellow highlighting in Tables E-1 and E-2. Also, six other metals and inorganic constituents on the Extended List (antimony, barium, beryllium, copper, molybdenum, and nickel) do not have levels in the Pines MWSE dataset that exceeded the adjusted RSLs. Table E-3 shows the same constituent information compared to the unadjusted RSLs for comparison.

Three of the radionuclide constituents were not detected in the MWSE dataset, indicated by green highlighting in Table E-1. Polonium-210, while technically a COPC, is included in the decay chain of lead-210 and is thus evaluated in the HHRA by the use of the lead-210 slope factor.

The constituents selected as COPCs were evaluated in a conservative and detailed HHRA (AECOM, 2012) approved by the USEPA. At the end of the HHRA, constituents of concern (COCs), as listed in Table E-1 were identified as those COPCs which potentially pose an excess lifetime cancer risk greater than $1x10^{-6}$ (the low end of USEPA's acceptable risk range) or a target endpoint specific hazard index of one. The COC selection was based on the assumption that residential properties contain 100% CCBs, which is conservative, as the maximum average percentage of CCBs identified on any property was 27%.

Based on the large body of information developed, collected and assessed with USEPA approval since the time of the MWSE sampling, the Respondents believe the COC list is appropriate for use with the private property sampling outlined in this SSC Work Plan. However, Respondents have agreed with USEPA not to limit the sampling to the COC list, but to expand the metals and inorganic list to test the samples from the private property sampling for the COPC list plus chromium and uranium, as listed below. a library of select gamma-emitting naturally occurring radioisotopes (Uranium-238 (U-238) series, Thorium-232 (Th-232) series, Uranium-235 (U-235) series, and Potassium-40 (K-40)) plus Beryllium-7 (Be-7), Americium-241 (Am-241), Barium-137 (Ba-137m), Cesium 137 (Cs-137) and Cobalt-60 (Co-60) (refer to Appendix B) will be used in the analytical program for the property-specific sampling under this SSC Work Plan.

Specifically, the metal and inorganic parameter list is, as follows:

- Aluminum
- Arsenic
- Chromium
- Chromium (hexavalent)
- Cobalt
- Iron
- Thallium
- Vanadium
- Uranium

References

ACAA. 2012. Coal Ash Material Safety. A Health Risk-Based Evaluation of USGS Coal Ash Data from Five US Power Plants. June 2012. available at: http://www.acaa-usa.org/displaycommon.cfm?an=1&subarticlenbr=109

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EPRI. 2009. Coal Ash: Characteristics, Management and Environmental Issues. Electric Power Research Institute, September 2009. Report No. 1019022. Available at www.epri.com.

EPRI. 2010. Comparison of Coal Combustion Products to Other Common Materials Chemical Characteristics. Final Report, September 2010. Report No. 1020556. Available at www.epri.com.

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USEPA. 1993. Selecting Exposure Routes and Contaminants of Concern by Risk-Based Screening. EPA/903/R-93-001. United States Environmental Protection Agency, Region III. Hazardous Waste Management Division. Office of Superfund Programs.

USEPA. 2010. Human and Ecological Risk Assessment of Coal Combustion Wastes. Regulation Identifier Number (RIN) 2050-AE81. USEPA. Draft. April 2010. Table A-3-1. 2002 data.

USEPA. 2012. Regional Screening Levels for Chemical Contaminants at Superfund Sites. November 2012. http://www.epa.gov/region9/superfund/prg/index.html.

USGS. 2011. Geochemical Database of Feed Coal and Coal Combustion Products (CCPs) from Five Power Plants in the United States. Data Series 635. Available at: http://pubs.usgs.gov/ds/635/; Data summarized in ACAA, 2012.

Tables

AECOM

TABLE E-1
COMPARISON OF CONSTITUENT LISTS
SUPPLEMENTAL SOIL CHARACTERIZATION WORK PLAN
PINES AREA OF INVESTIGATION

Constituent	COCs	COPCs	Extended List
Metals and Inorganic Constituents			
Aluminum		X	X
Antimony			X (d)
Arsenic	X	X	X
Barium			X (d)
Beryllium			X (d)
Boron			X (d)
Cadmium			X (d)
Calcium			X (e)
Chromium	X (a)	X (a)	X (d)
Chromium (hexavalent)	X	X	X
Cobalt		X	X
Copper			X (d)
Iron	X	X	X
Lead			X (d)
Magnesium			X (e)
Manganese			X (g)
Mercury			X (d)
Molybdenum			X (d)
Nickel			X (d)
Potassium			X (e)
Selenium			X (g)
Silicon			X (d)
Silver			X (c)
Sodium			X (e)
Sulfur			X (d)
Thallium	X	X	X
Uranium			X (f)
Vanadium		X	X
Zinc			X (d)
Radionuclide Constituents			
Lead-210	X	X	X
Polonium-210		(b)	X (b)
Radium-226	X	X	X
Radium-228	X	X	X
Thorium-228		X	X
Thorium-230		X	X
Thorium-232		X	X
Uranium-234		X	X
Uranium-235		X (c)	X
Actinium -227			X (c)
Protactinium-231			X (c)
Uranium-238	X	X	

Notes:
COC - Constituent of Concern (i.e, the constituents carried through the Feasibility Study).
COPC - Constituent of Potential Concern (i.e., the constituents evaluated in the human health risk assessment).
HHRA - Human Health Risk Assessment.
MWSE - Municipal Water Service Extension.
RSL - Regional Screening Level.
Yellow highlighting - Indicates metals and inorganic constituents not identified as COPCs in other national coal combustion by-product datasets using the residential soil RSLs adjusted for a target hazard quotient of 0.1 (see text, Table E-2, and the Final HHRA, AECOM, 2012).
Green highlighting - Indicates radionuclide constituents not detected in the MWSE dataset.
(a) - Chromium was not identified as a COPC or a COC; it is included for comparison to hexavalent chromium data.
(b) - Included in the HHRA as a decay product of Lead-210, therefore, while considered a COPC, the analytical data were not used as the evaluation of Lead-210 includes Polonium-210.
(c) - Not detected in MWSE samples.
(d) - Detected below USEPA RSLs adjusted to a hazard quotient of 0.1 in MWSE samples (AECOM, 2012).
(e) - Essential nutrient, not included as a COPC (AECOM, 2012 provides additional detail).
(f) - Uranium was not included in the MWSE sampling program, but was included in the Remedial Investigation background sampling program.
(g) - Shown to be consistent with background (AECOM, 2012).

AECOM

TABLE E-2

CONSTITUENT CONCENTRATIONS IN CCRs AND NATIVE MATERIALS (ADJUSTED RSLs)
SUPPLEMENTAL SOIL CHARACTERIZATION WORK PLAN
PINES AREA OF INVESTIGATION

Constituent	Pines MWSE Data - Suspected CCBs: Analyzed in MWSE Data	Pines MWSE Data - Suspected CCBs: COPC	Pines MWSE Data - Suspected CCBs: COC	USEPA RSLs (g) Adjusted (h) Residential Soil (mg/kg)	Pines MWSE Data (h) Suspected CCBs (mg/kg) Min	Pines MWSE Data (h) Suspected CCBs (mg/kg) Max	USGS Data (f) Fly Ash (mg/kg) Min	USGS Data (f) Fly Ash (mg/kg) Max	USGS Data (f) Bottom Ash (mg/kg) Min	USGS Data (f) Bottom Ash (mg/kg) Max	EPRI Ash Data Fly Ash (mg/kg) 10th %ile	EPRI Ash Data Fly Ash (mg/kg) 50th %ile	EPRI Ash Data Fly Ash (mg/kg) 90th %ile	EPRI Ash Data Bottom Ash (mg/kg) 10th %ile	EPRI Ash Data Bottom Ash (mg/kg) 50th %ile	EPRI Ash Data Bottom Ash (mg/kg) 90th %ile	EPRI Ash Data Source	USEPA Data CCR (d) (mg/kg) mean	USEPA Data Landfill Waste (e) (mg/kg) 50th %ile	USEPA Data Landfill Waste (e) (mg/kg) 90th %ile
Aluminum	X	X		7,700	5,220	44,600	NA	NA	NA	NA	70,000	NA	140,000	59,000	NA	130,000	(a)	NA	25,300	85,700
Antimony	X			3.1	1.4	1.4	0.982	22.4	0.401	3.2	BDL	BDL	16	BDL	BDL	BDL	(b)	6.32	15.6	46.2
Arsenic	X	X	X	0.39	3.6	97.2	7.3	93.8	1.24	18.1	22	71	261	2.6	7.2	21	(b)	24.7	27.9	105
Barium	X			1,500	47.4	346	336	5,730	474	2,990	381	932	5,064	378	768	3,604	(b)	246.75	222	1,050
Beryllium	X			16	0.63	5.5	1.69	32.7	2.99	10.3	2.2	10.6	26	0.21	5.8	14	(b)	2.8	4.1	17.6
Boron	X			1,600	45.9	151	NA	NA	NA	NA	118	322	1,018	2.7	82	335	(b)	NA	53.5	346
Cadmium	X			7	0.18	4.3	0.312	3.29	0.104	0.425	0.36	1.07	6.2	BDL	BDL	BDL	(b)	1.05	1.08	5.43
Calcium	X			EN	2,810	44,400	NA	NA	NA	NA	7,400	NA	150,000	5,700	NA	150,000	(a)	NA	NA	NA
Chromium	X			12,000	9.8	166	33.7	984	17.5	461	27	133	298	51	191	1,132	(b)	27.8	44.5	166
Chromium (hexavalent)	X	X	X	0.29	0.465	1.95	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--	NA	NA	NA
Cobalt	X	X		2.3	1.8	19.5	14.5	264	7.29	55	7.4	7.9	101	NA	NA	NA	(b)	NA	10.2	62.2
Copper	X			310	3.1	42.1	55.1	692	40.4	148	62	140	216	39	73	118	(b)	NA	36.1	228
Iron	X	X	X	5,500	6,270	142,000	NA	NA	NA	NA	33,575	69,100	128,838	40,339	101,200	158,850	(b)	NA	NA	NA
Lead	X			400	2.9	117	14.4	293	7.59	40	21	49	143	8.1	20	53	(b)	25	28.7	80.6
Magnesium	X			EN	825	9,500	NA	NA	NA	NA	3,900	NA	23,000	3,400	NA	17,000	(a)	NA	NA	NA
Manganese	X	(c)		180	41.8	737	105	966	145	347	91	189	700	85	262	892	(b)	NA	111	510
Mercury	X			2.3	0.01	0.06	0.0127	1.15	0.0123	0.155	0.01	0.11	0.51	0.004	0.018	0.08	(b)	0.18	0.328	1.63
Molybdenum	X			39	0.93	13.2	4.95	90.5	2.15	10.2	9	19	60	4	11	27	(b)	NA	12	34.7
Nickel	X			150	3.6	50.7	17.3	572	28.8	255	47	102	231	39	123	445	(b)	32	42.3	329
Potassium	X			EN	291	8,760	NA	NA	NA	NA	6,200	NA	21,000	4,600	NA	18,000	(a)	NA	NA	NA
Selenium	X			39	0.45	3.5	1.03	22.5	0.121	1.28	1.8	11	18	BDL	BDL	4.2	(b)	2.4	5.12	21.4
Silicon	X	(c)		NA	558	3,500	NA	NA	NA	NA	160,000	NA	270,000	160,000	NA	280,000	(a)	NA	NA	NA
Silver	X			39	BDL	BDL	NA	NA	NA	NA	BDL	BDL	7.6	BDL	BDL	BDL	(b)	0.70	1.72	13.7
Sodium	X			EN	116	1,310	NA	NA	NA	NA	1,700	NA	17,000	1,600	NA	11,000	(a)	NA	NA	NA
Sulfur	X			NA	31.7	514	NA	NA	NA	NA	1,900	NA	34,000	BDL	NA	15,000	(a)	NA	NA	NA
Thallium	X	X	X	0.078	0.47	5	0.312	21	0.102	1.96	BDL	2.4	45	BDL	BDL	0.88	(b)	1.75	3.23	20.8
Uranium				23	NA	NA	0.682	34.1	5.27	11	BDL	NA	19	BDL	NA	16	(a)	NA	NA	NA
Vanadium	X	X		39	23.8	89.9	106	1,660	69.4	591	59	254	364	BDL	161	250	(b)	NA	224	907
Zinc	X			2,300	22.4	255	33.1	848	26.5	152	63	152	683	16	59	367	(b)	NA	45.8	293

See notes on page 3 of this table.

TABLE E-2

CONSTITUENT CONCENTRATIONS IN CCRs AND NATIVE MATERIALS (ADJUSTED RSLs)
SUPPLEMENTAL SOIL CHARACTERIZATION WORK PLAN
PINES AREA OF INVESTIGATION

Constituent	Pines MWSE Data - Suspected CCBs			USEPA RSLs (g) Adjusted (h) Residential Soil (mg/kg)	EPRI Rock and Soil Data						
	Analyzed in MWSE Data	COPC	COC		Rock (mg/kg)			Soil (mg/kg)			Source
					10th %ile	50th %ile	90th %ile	10th %ile	50th %ile	90th %ile	
Aluminum	X	X		7,700	9,800	NA	96,000	15,000	NA	100,000	(a)
Antimony	X			3.1	0.08	0.3	1.8	BDL	BDL	1.3	(b)
Arsenic	X	X	X	0.39	0.50	1.60	14	2	5.8	12	(b)
Barium	X			1,500	67	420	1,390	200	500	1,000	(b)
Beryllium	X			16	0.10	1.30	4.4	BDL	BDL	2.0	(b)
Boron	X			1,600	BDL	0.33	220	BDL	30	70	(b)
Cadmium	X			7	BDL	BDL	3.6	BDL	0.2	0.5	(b)
Calcium	X			EN	6,000	NA	83,000	1,500	NA	62,000	(a)
Chromium	X			12,000	1.9	28	309	15	50	100	(b)
Chromium (hexavalent)	X	X	X	0.29	NA	NA	NA	NA	NA	NA	--
Cobalt	X	X		2.3	0.86	16	53	BDL	7	15	(b)
Copper	X			310	10	30	122	5	20	50	(b)
Iron	X	X	X	5,500	8,800	NA	95,000	7,000	NA	50,000	(a)
Lead	X			400	3.8	15	44	BDL	15	30	(b)
Magnesium	X			EN	700	NA	56,000	1,000	NA	15,000	(a)
Manganese	X	(c)		180	49	430	1,740	100	300	1,000	(b)
Mercury	X			2.3	0.1	0.7	2.0	0.02	0.05	0.19	(b)
Molybdenum	X			39	0.24	1.6	18	BDL	BDL	BDL	(b)
Nickel	X			150	2	18	220	5	15	30	(b)
Potassium	X			EN	4,000	NA	45,000	4,500	NA	25,000	(a)
Selenium	X			39	0.60	1.90	4.9	BDL	0.3	0.8	(b)
Silicon	X	(c)		NA	57,000	NA	380,000	230,000	NA	390,000	(a)
Silver	X			39	0.03	0.9	3	BDL	BDL	BDL	(b)
Sodium	X			EN	900	NA	34,000	1,000	NA	20,000	(a)
Sulfur	X			NA	200	NA	42,000	840	NA	1,500	(a)
Thallium	X	X	X	0.078	0.1	0.5	1.8	0.2	0.50	0.7	(b)
Uranium				23	0.84	NA	43	1.2	NA	3.9	(a)
Vanadium	X	X		39	2.6	52	232	20	70	150	(b)
Zinc	X			2,300	25	72	138	22	50	99	(b)

See notes on page 3 of this table.

TABLE E-2

CONSTITUENT CONCENTRATIONS IN CCRs AND NATIVE MATERIALS
(ADJUSTED RSLs)
SUPPLEMENTAL SOIL CHARACTERIZATION WORK PLAN
PINES AREA OF INVESTIGATION

Notes:
[green shading] > USEPA Residential Soil RSL, adjusted to a hazard quotient of 0.1 for noncarcingens.
[yellow shading] Not identified as a COPC in any coal ash data set.
EPRI - Electric Power Research Institute.
USEPA - United States Environmental Protection Agency.
BDL - Below Detection Limit.
CAS - Chemical Abstract Service
CCB - Coal Combustion By product.
CCR - Coal Combustion Residual.
COPC - Constituent of Potential Concern.
COC - Constituent of Concern.
EN - Essential Nutrient.
NA - Not Available/Not Analyzed.
RSL - Regional Screening Level.
(a) - EPRI. 2009. Coal Ash: Characterisitics, Management and Environmental Issues. Electric Power Research Institute, September 2009. Ranges (10th percentile - 90th percentile) in bulk composition of fly ash, bottom ash, rock, and soil, are presented in the table. Report No. 1019022. Available at www.epri.com.
(b) - EPRI. 2010. Comparison of Coal Combustion Products to Other Common Materials Chemical Characteristics. Final Report, September 2010. Report No. 1020556. Available at www.epri.com.
(c) - Data demonstrated statistically to be consistent with background.
(d) - Federal Register / Vol. 75, No. 118 / Monday, June 21, 2010 / Proposed Rules. Hazardous and Solid Waste Management System; Identification and Listing of Special Wastes; Disposal of Coal Combustion Residuals From Electric Utilities.
(e) - USEPA. 2010. Human and Ecological Risk Assessment of Coal Combustion Wastes. Regulation Identifier Number (RIN) 2050-AE81. USEPA. Draft. April 2010. Table A-3-1. 2002 data.
(f) - Data from USGS. 2011. Geochemical Database of Feed Coal and Coal Combustion Products (CCPs) from Five Power Plants in the United States. Data Series 635. Available at: http://pubs.usgs.gov/ds/635/ ; Data summarized in ACAA, 2012 available at: http://www.acaa-usa.org/displaycommon.cfm?an=1&subarticlenbr=109
(g) - USEPA. 2012. Regional Screening Levels for Chemical Contaminants at Superfund Sites. November 2012. http://www.epa.gov/region9/superfund/prg/index.html. Values for residential soil. Where RSL is based on a noncancer endpoint, the RSL is adjusted to a hazard quotient of 0.1 by multiplying the RSL by 0.1. The risk level is 1E-6 where the RSL is based on a cancer endpoint (arsenic and hexavalent chromium).
(h) - AECOM. 2012. Human Health Risk Assessment (HHRA). Pines Area of Investigation. Final. July 2012. Table 3-10.

TABLE E-3
CONSTITUENT CONCENTRATIONS IN CCRs AND NATIVE MATERIALS
(UNADJUSTED RSLs)
SUPPLEMENTAL SOIL CHARACTERIZATION WORK PLAN
PINES AREA OF INVESTIGATION

	Pines MWSE Data - Suspected CCBs			USEPA RSLs (g)	Pines MWSE Data (h)		USGS Data (f)				EPRI Ash Data							USEPA Data		
	Analyzed in MWSE Data	COPC	COC	Residential Soil (mg/kg)	Suspected CCBs (mg/kg)		Fly Ash (mg/kg)		Bottom Ash (mg/kg)		Fly Ash (mg/kg)			Bottom Ash (mg/kg)				CCR (d) (mg/kg)	Landfill Waste (e) (mg/kg)	
Constituent					Min	Max	Min	Max	Min	Max	10th %ile	50th %ile	90th %ile	10th %ile	50th %ile	90th %ile	Source	mean	50th %ile	90th %ile
Aluminum	X	X		77,000	5,220	44,600	NA	NA	NA	NA	70,000	NA	140,000	59,000	NA	130,000	(a)	NA	25,300	85,700
Antimony	X			31	1.4	1.4	0.982	22.4	0.401	3.2	BDL	BDL	16	BDL	BDL	BDL	(b)	6.32	15.6	46.2
Arsenic	X	X	X	0.39	3.6	97.2	7.3	93.8	1.24	18.1	22	71	261	2.6	7.2	21	(b)	24.7	27.9	105
Barium	X			15,000	47.4	346	336	5,730	474	2,990	381	932	5,064	378	768	3,604	(b)	246.75	222	1,050
Beryllium	X			160	0.63	5.5	1.69	32.7	2.99	10.3	2.2	10.6	26	0.21	5.8	14	(b)	2.8	4.1	17.6
Boron	X			16,000	45.9	151	NA	NA	NA	NA	118	322	1,018	2.7	82	335	(b)	NA	53.5	346
Cadmium	X			70	0.18	4.3	0.312	3.29	0.104	0.425	0.36	1.07	6.2	BDL	BDL	BDL	(b)	1.05	1.08	5.43
Calcium	X			EN	2,810	44,400	NA	NA	NA	NA	7,400	NA	150,000	5,700	NA	150,000	(a)	NA	NA	NA
Chromium	X			120,000	9.8	166	33.7	984	17.5	461	27	133	298	51	191	1,132	(b)	27.8	44.5	166
Chromium (hexavalent)	X	X	X	0.29	0.465	1.95	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	--	NA	NA	NA
Cobalt	X	X		23	1.8	19.5	14.5	264	7.29	55	7.4	7.9	101	NA	NA	NA	(b)	NA	10.2	62.2
Copper	X			3,100	3.1	42.1	55.1	692	40.4	148	62	140	216	39	73	118	(b)	NA	36.1	228
Iron	X	X	X	55,000	6,270	142,000	NA	NA	NA	NA	33,575	69,100	128,838	40,339	101,200	158,850	(b)	NA	NA	NA
Lead	X			400	2.9	117	14.4	293	7.59	40	21	49	143	8.1	20	53	(b)	25	28.7	80.6
Magnesium	X			EN	825	9,500	NA	NA	NA	NA	3,900	NA	23,000	3,400	NA	17,000	(a)	NA	NA	NA
Manganese	X	(c)		1,800	41.8	737	105	966	145	347	91	189	700	85	262	892	(b)	NA	111	510
Mercury	X			23.0	0.01	0.06	0.0127	1.15	0.0123	0.155	0.01	0.11	0.51	0.004	0.018	0.08	(b)	0.18	0.328	1.63
Molybdenum	X			390	0.93	13.2	4.95	90.5	2.15	10.2	9	19	60	4	11	27	(b)	NA	12	34.7
Nickel	X			1,500	3.6	50.7	17.3	572	28.8	255	47	102	231	39	123	445	(b)	32	42.3	329
Potassium	X			EN	291	8,760	NA	NA	NA	NA	6,200	NA	21,000	4,600	NA	18,000	(a)	NA	NA	NA
Selenium	X			390	0.45	3.5	1.03	22.5	0.121	1.28	1.8	11	18	BDL	BDL	4.2	(b)	2.4	5.12	21.4
Silicon	X	(c)		NA	558	3,500	NA	NA	NA	NA	160,000	NA	270,000	160,000	NA	280,000	(a)	NA	NA	NA
Silver	X			390	BDL	BDL	NA	NA	NA	NA	BDL	BDL	7.6	BDL	BDL	BDL	(b)	0.70	1.72	13.7
Sodium	X			EN	116	1,310	NA	NA	NA	NA	1,700	NA	17,000	1,600	NA	11,000	(a)	NA	NA	NA
Sulfur	X			NA	31.7	514	NA	NA	NA	NA	1,900	NA	34,000	BDL	NA	15,000	(a)	NA	NA	NA
Thallium	X	X	X	0.78	0.47	5	0.312	21	0.102	1.96	BDL	2.4	45	BDL	BDL	0.88	(b)	1.75	3.23	20.8
Uranium				230	NA	NA	0.682	34.1	5.27	11	BDL	NA	19	BDL	NA	16	(a)	NA	NA	NA
Vanadium	X	X		390	23.8	89.9	106	1,660	69.4	591	59	254	364	BDL	161	250	(b)	NA	224	907
Zinc	X			23,000	22.4	255	33.1	848	26.5	152	63	152	683	16	59	367	(b)	NA	45.8	293

See notes on page 3 of this table.

TABLE E-3
CONSTITUENT CONCENTRATIONS IN CCRs AND NATIVE MATERIALS
(UNADJUSTED RSLs)
SUPPLEMENTAL SOIL CHARACTERIZATION WORK PLAN
PINES AREA OF INVESTIGATION

Constituent	Pines MWSE Data - Suspected CCBs			USEPA RSLs (g)	EPRI Rock and Soil Data						
	Analyzed in MWSE Data	COPC	COC	Residential Soil (mg/kg)	Rock (mg/kg)			Soil (mg/kg)			Source
					10th %ile	50th %ile	90th %ile	10th %ile	50th %ile	90th %ile	
Aluminum	X	X		77,000	9,800	NA	96,000	15,000	NA	100,000	(a)
Antimony	X			31	0.08	0.3	1.8	BDL	BDL	1.3	(b)
Arsenic	X	X	X	0.39	0.50	1.60	14	2	5.8	12	(b)
Barium	X			15,000	67	420	1,390	200	500	1,000	(b)
Beryllium	X			160	0.10	1.30	4.4	BDL	BDL	2.0	(b)
Boron	X			16,000	BDL	0.33	220	BDL	30	70	(b)
Cadmium	X			70	BDL	BDL	3.6	BDL	0.2	0.5	(b)
Calcium	X			EN	6,000	NA	83,000	1,500	NA	62,000	(a)
Chromium	X			120,000	1.9	28	309	15	50	100	(b)
Chromium (hexavalent)	X	X	X	0.29	NA	NA	NA	NA	NA	NA	--
Cobalt	X	X		23	0.86	16	53	BDL	7	15	(b)
Copper	X			3,100	10	30	122	5	20	50	(b)
Iron	X	X	X	55,000	8,800	NA	95,000	7,000	NA	50,000	(a)
Lead	X			400	3.8	15	44	BDL	15	30	(b)
Magnesium	X			EN	700	NA	56,000	1,000	NA	15,000	(a)
Manganese	X	(c)		1,800	49	430	1,740	100	300	1,000	(b)
Mercury	X			23.0	0.1	0.7	2.0	0.02	0.05	0.19	(b)
Molybdenum	X			390	0.24	1.6	18	BDL	BDL	BDL	(b)
Nickel	X			1,500	2	18	220	5	15	30	(b)
Potassium	X			EN	4,000	NA	45,000	4,500	NA	25,000	(a)
Selenium	X			390	0.60	1.90	4.9	BDL	0.3	0.8	(b)
Silicon	X	(c)		NA	57,000	NA	380,000	230,000	NA	390,000	(a)
Silver	X			390	0.03	0.9	3	BDL	BDL	BDL	(b)
Sodium	X			EN	900	NA	34,000	1,000	NA	20,000	(a)
Sulfur	X			NA	200	NA	42,000	840	NA	1,500	(a)
Thallium	X	X	X	0.78	0.1	0.5	1.8	0.2	0.50	0.7	(b)
Uranium				230	0.84	NA	43	1.2	NA	3.9	(a)
Vanadium	X	X		390	2.6	52	232	20	70	150	(b)
Zinc	X			23,000	25	72	138	22	50	99	(b)

See notes on page 3 of this table.

TABLE E-3
CONSTITUENT CONCENTRATIONS IN CCRs AND NATIVE MATERIALS
(UNADJUSTED RSLs)
SUPPLEMENTAL SOIL CHARACTERIZATION WORK PLAN
PINES AREA OF INVESTIGATION

Notes:
[green] > USEPA Residential Soil RSL.
[yellow] Not identified as a COPC in any coal ash data set.
EPRI - Electric Power Research Institute.
USEPA - United States Environmental Protection Agency.
BDL - Below Detection Limit.
CAS - Chemical Abstract Service
CCB - Coal Combustion By product.
CCR - Coal Combustion Residual.
COPC - Constituent of Potential Concern.
COC - Constituent of Concern.
EN - Essential Nutrient.
NA - Not Available/Not Analyzed.
RSL - Regional Screening Level.
(a) - EPRI. 2009. Coal Ash: Characterisitics, Management and Environmental Issues. Electric Power Research Institute, September 2009.
Ranges (10th percentile - 90th percentile) in bulk composition of fly ash, bottom ash, rock, and soil, are presented in the table.
Report No. 1019022. Available at www.epri.com.
(b) - EPRI. 2010. Comparison of Coal Combustion Products to Other Common Materials Chemical Characteristics. Final Report, September 2010.
Report No. 1020556. Available at www.epri.com.
(c) - Data demonstrated statistically to be consistent with background.
(d) - Federal Register / Vol. 75, No. 118 / Monday, June 21, 2010 / Proposed Rules. Hazardous and Solid Waste Management System; Identification and Listing of Special Wastes;
Disposal of Coal Combustion Residuals From Electric Utilities.
(e) - USEPA. 2010. Human and Ecological Risk Assessment of Coal Combustion Wastes. Regulation Identifier Number (RIN) 2050-AE81. USEPA. Draft. April 2010. Table A-3-1. 2002 data.
(f) - Data from USGS. 2011. Geochemical Database of Feed Coal and Coal Combustion Products (CCPs) from Five Power Plants in the
United States. Data Series 635. Available at: http://pubs.usgs.gov/ds/635/ ; Data summarized in ACAA, 2012 available at: http://www.acaa-usa.org/displaycommon.cfm?an=1&subarticlenbr=109
(g) - USEPA. 2012. Regional Screening Levels for Chemical Contaminants at Superfund Sites. November 2012. http://www.epa.gov/region9/superfund/prg/index.html. Values for residential soil.
(h) - AECOM. 2012. Human Health Risk Assessment (HHRA). Pines Area of Investigation. Final. July 2012. Table 3-10.

Appendix F

Deleted

[As noted in Section 3.2.2, the Chicago blocks were available for calibration, thus, an alternative calibration method was not needed.]

Appendix G

Sampling and Analysis Plan Addendum

AECOM

Supplemental Soil Characterization Work Plan

Appendix G

Sampling and Analysis Plan Addendum

Pines Area of Investigation

AOC II

Docket No. V-W-'04-C-784

November 2014

Disclaimer

This document is a draft document prepared under a federal administrative order on consent. This document has not undergone formal review by U.S. Environmental Protection Agency (USEPA). The opinions, findings, and conclusions expressed are those of the author and not necessarily those of USEPA.

Table of Contents

List of Figures

List of Acronyms

bgs	Below Ground Surface
CCB	Coal Combustion By-product
CoC	Chain-of-Custody
EC	Emergency Coordinator
GPS	Global Positioning Satellite
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
ID	Identification
IDW	Investigation Derived Waste
K-40	Potassium-40
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NORM	Naturally Occurring Radioactive Material
PPE	Personal Protective Equipment
QAPP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
SSC	Supplemental Soil Characterization
SSO	Site Safety and Health Officer
Th-232	Thorium-232
U-235	Uranium-235
U-238	Uranium-238
USEPA	U. S. Environmental Protection Agency

1 Introduction

This Sampling and Analysis Plan Addendum (SAP) is prepared as a supplement to the Supplemental Soil Characterization (SSC) Work Plan, April 2014 (draft) and provides additional details regarding the properties selected for sampling and sampling procedures. This SAP also includes procedural modifications to the existing SSC Work Plan and Quality Assurance Project Plan (QAPP) Addendum (e.g., utility clearance procedures, sample collection methods, sample nomenclature), and incorporates comments provided by the U.S. Environmental Protection Agency (USEPA) dated May 7, 2014. (The QAPP Addendum is provided as Appendix B of the SSC Work Plan.)

2 Property Selection

To meet the objectives stated in the SSC Work Plan, data collection tasks include gamma surveys, CCB visual inspections, and soil sampling at a statistically-defined subset of properties. The CCB visual inspections and gamma surveys were completed in June 2014 and data summaries were provided to USEPA. Based on the data summaries, and with input from the community, USEPA selected nine properties for soil sampling: Properties 6, 14, 15, 24, 29, 34, 35, 37, and 38 (Figures G-1 through G-9).

In addition to the selected properties, and at the request of USEPA, a sample will be collected from the mulch pile located at the south end of Illinois Avenue (near US Highway 20 and Railroad Avenue). As the property owners in the general area of the mulch pile did not grant access to the property, the sample will be collected from mulch material, if any is present within the public right-of-way.

3 Health and Safety

The project Health and Safety Plan (HASP) has been updated to include the tasks outlined in the SSC Work Plan. The procedures outlined in the HASP will be followed by AECOM personnel and AECOM's subcontractors during all site work. Matt Laub is AECOM's designated Site Supervisor and Site Safety & Health Officer (SSO). Mr. Laub is also AECOM's designated Emergency Coordinator (EC), in the event of a site emergency. Mr. Laub, or his designee, will be present during all field work to fulfill his health and safety duties.

4 Pre-Field Activities

4.1 Access Agreements and Property Owner Notices

Access agreements for the properties to be sampled were acquired prior to the gamma surveys. Residents will be notified via mail that their property has been selected by USEPA for soil sampling activities at least one week prior to the start of field activities.

4.2 Utility Clearance

Utility clearance activities will be conducted in accordance with AECOM Standard Operating Procedure (SOP) S3NA-417-PR Underground Utilities and Subsurface Installation Clearance Process (see Appendix C of the SSC Work Plan). Clearance of utilities located in the work area is necessary prior to performing subsurface field activities. Public utilities may include municipal water, electricity, cable television, telephone, gas, and storm sewer. Private utilities may include electricity, propane, and septic. At least two full working days, but no more than 20 calendar days prior to the start of intrusive field work, the field staff will contact Indiana811:

Indiana811

1-800-382-5544
www.indiana811.org

The field staff will provide Indiana811 with the county and the township as well as a street address and cross street of the locations necessary for utility clearance. Where possible, the field staff will mark areas where field work may affect any subsurface utilities with white marking paint or white flags (where paint is not applicable) prior to calling Indiana811. Marking areas with white paint/flags will guide Indiana811 on where to concentrate their locating efforts.

Where subsurface work takes place on private property, a private utility locator will be retained, in addition to the Indiana811 service, to screen the proposed sampling locations for underground utilities. Field staff will work with the property owners to supplement the Indiana811 and private utility locate information, where possible.

Indiana811 underground facility members and the private utility locator will mark or otherwise identify facilities according to the following color codes in accordance with Damage to Underground Facilities, Indiana Code 8-1-26-18:

Utility	Marking Color
Electric power distribution and transmission	Safety Red
Municipal electric systems	Safety Red
Gas distribution and transmission	High Visibility Safety Yellow
Oil distribution and transmission	High Visibility Safety Yellow
Dangerous materials, product lines & steam lines	High Visibility Safety Yellow
Telephone and telegraph systems	Safety Alert Orange
Cable television	Safety Alert Orange
Police and fire communications	Safety Alert Orange
Water systems	Safety Precaution Blue
Sewer systems	Safety Green
Proposed construction	White

Additional information on contacting and providing the necessary information can be found on the Indiana811 website at www.indiana811.org.

5 Sampling Locations

As outlined in the SSC Work Plan, preliminary quadrant and sample collection locations have been identified. Each property selected for sampling has been divided into four approximately equally-spaced quadrants (designated A through D). Additional "quadrants" were added to the initial four to address three specific property conditions:

- A vegetable or flower garden
- An unpaved driveway where coal combustion by-products (CCBs) are present

- A child's play area, based on the presence of swing sets and/or other outdoor play equipment

Within each quadrant defined as described above, five approximately equally-spaced sample locations have been identified. Preliminary quadrant layouts and sampling locations are shown in Figures G-1 through G-9.

Additionally, a sample will be collected from the mulch pile located on the south end of Illinois Avenue. As the property owners in the general area of the mulch pile did not grant access to the property, the sample will be collected from mulch material, if any, that is present within the public right-of-way.

The quadrant layouts and sampling locations for each property will be verified with USEPA in the field. If any of the specific property conditions identified above are noted at the selected properties, particularly at those properties that were not inspected due to delays in receiving access agreements, additional quadrants will be added, as appropriate. Quadrant boundaries and discreet sampling locations will be logged with a global positioning satellite (GPS) unit.

6 Sampling Methods

Samples will be collected using hand-cart mounted direct-push sampling equipment and/or by using hand tools such as a hand auger. Direct-push drilling will be the primary sampling method. Hand augering will be used where access to sampling locations is restricted for the drilling machine or in areas where sampling in close proximity to utilities will be necessary. The sampling and logging procedures will be completed in accordance with SOP 7110Pines Surface Soil and/or SOP 7116Pines Subsurface Soil Sampling by Geoprobe Methods (Appendix C and Section 4.2.2.1 of the SSC Work Plan).

Samples collected at each of the five locations will be composited over specific depth intervals, such that one sample from each sampling depth from each quadrant will be obtained. The sample depths will be:

- 0 to 6 inches below ground surface (bgs) – to be referred to as "surface soil."
- 6 to 18 inches bgs – to be referred to as "near-surface soil."
- 1.5 feet (or 18 inches) to maximum depths of 5 feet bgs, or to the maximum depth possible if less than 5 feet bgs (e.g., based on borehole collapse or refusal) – to be referred to as "subsurface soil."

Thus, in each quadrant, a total of up to three samples will be obtained, each representing a composite over one of the three designated depth intervals. One composite surface soil sample (0 to 6 inch bgs) and one composite near-surface soil sample (6 to 18 inch bgs) will be submitted for analysis from each of the quadrants sampled. If CCBs are not visually observed within the deeper, subsurface soil horizon (1.5 to 5 feet bgs) at any of the five sample locations within a quadrant, then no sample from this horizon will be submitted for analysis. If CCBs are observed at one or more sample locations within the subsurface soil horizon in a quadrant, then a 5-point composite sample from the subsurface horizon will be submitted for analysis. The field logs will note the depth at which CCBs are no longer observed, or whether they appear to extend beyond the maximum depth of a sample location.

For each depth interval, the full sample volume from each of the five equal-volume discrete samples will be placed into a plastic bowl or similar non-metal container and thoroughly homogenized. A single composite sample will then be withdrawn from the homogenized material and placed into appropriate laboratory-supplied containers.

Photographs will be taken of each quadrant to document conditions before and after the sampling/property restoration. Photographs will be taken of all soil samples as retrieved and also after homogenization in order to create a photographic record of the soil sampling. Additional photographs will be taken throughout the field program as appropriate. Whenever photographs are taken, a digital camera will be used, and the camera picture frame number, date, direction facing, and subject will be recorded in the logbook and/or on the appropriate field form. Where sufficient accuracy may be achieved by field personnel, a GPS unit will be used to determine the locations of samples collected and quadrant boundaries. Photographs will be collected as described in Section 4.2.2 of the SSC Work Plan.

The sample from the mulch pile at the south end of Illinois Avenue will be collected using a hand trowel, following the appropriate soil SOP. A GPS unit will be used to identify the location of the sample, and a photograph of the location will be taken.

7 Quality Control Samples

Quality control samples will be collected and analyzed as specified in the QAPP Addendum, which is provided as Appendix B of the SSC Work Plan. Field duplicate and Matrix spike/matrix spike duplicates (MS/MSDs) samples will be analyzed to assess the quality of data resulting from these sampling activities. For completeness and ease of implementation, quality control samples will be collected on a per-property basis, rather than on a total-sample-number basis. It is estimated that a minimum of 8 soil samples (two per four quadrants) and a maximum of 15 soil samples (three per five quadrants) will be collected at each property.

Field duplicates will be collected by alternately dividing portions of the sample material between two identical sets of containers for laboratory analysis. The samples will be labeled as two separate samples and carried through analysis and reporting. The field duplicate will be analyzed for the same parameters as its associated field sample. Field duplicate samples will be collected at a frequency of one per property. As described above, this equates to a duplicate sampling frequency of one duplicate per 8 to 15 field samples.

MS/MSD samples will be collected in the same manner as the original samples, with double sample volume (or the amount requested by the laboratory) collected to provide sufficient material for the analysis. Field duplicate samples will be collected at a frequency of one per property. As described above, this equates to a duplicate sampling frequency of one duplicate per 8 to 15 field samples.

Equipment rinsate blanks will be collected by pouring laboratory-grade, organic free water (provided by the laboratory) through non-dedicated sampling equipment (soil probe rod and/or hand-auger) and collecting the rinsate in the appropriate sample containers. Equipment rinsate blanks will be collected at a frequency of one per property per equipment used to sample the property. Equipment rinsate blanks will be collected after equipment decontamination and upon completion of sampling at each property, ensuring that equipment rinsate blanks are collected to represent each collection method (soil probe and/or hand auger) used at each property.

8 Sample Identification

Immediately upon collection, an adhesive sample label will be affixed to each container, including the unique sample identification (ID), as described below, the time and date of sample collection, the sampler's initials, parameters to be analyzed, and preservation, if applicable. The project name will not be shown on the label. The unique sample identification will be an alphanumeric code consisting of the following elements:

- Name of property in three characters (e.g., Property 6 = P06). These location names will correspond to field logs, as well as sample locations posted on maps.
- Two letters signifying the quadrant identification. QA, QB, QC, QD for the minimum four quadrants. QG will signify garden quadrants, QP for play area quadrants, QZ for driveways, and QX for all other locations, should additional locations be identified in conjunction with USEPA based on in-field observations. Location designations will be recorded in the field notes.
- Two letters signifying the sample matrix (SS for surface soil (0 to 6-inch depth), NS for near surface soil (6 to 18-inch depth) and SB for subsurface soil (>18-inch depth).
- Sampling date consisting of the number corresponding to the month (2 digits), day (2 digits) and year (2 digits), for example, 111214 for samples collected on November 12, 2014.
- One letter denoting the type of sample. Codes for this field include: S – sample; D – field duplicate; B – rinsate blank.

No dashes will be used to separate fields. An example sample ID would be: P14QCNS111214D, indicating a soil sample collected at Property 14, quadrant C, at the near-surface depth interval, on November 12, 2014. The actual depth intervals will be recorded on field boring log forms. This example indicates the sample is a field duplicate as indicated by the "D" at the end of the sample ID.

The mulch pile sample ID will include the location ("PM"), the sampling date, as described above, and the designation "S" for field sample. For example: PM111214S, indicating the much pile sample collected on November 12, 2014.

Rinsate blank sample names will include the property ID, sampling date, B to indicate a blank sample, and number to indicate which equipment was rinsed to generate the blank sample, where 1 indicates the soil probe rod and 2 indicates the hand auger. For example: P06111214B1 would indicate a rinsate blank sample collected following sampling at Property 6 on November 12, 2014, where the sample was collected by rinsing the soil probe rod.

MS/MSDs will have the same name as the original field sample and "MS/MSD" will be noted in the comments field of the chain-of-custody (CoC) form.

The sample ID code will be recorded on the label, in the field logbook/field forms, and on the CoC form. The sample ID will be carried through the analytical process to reporting. Sample chain-of-custody procedures and packaging and shipment of samples will be completed in accordance with SOP 1007Pines Chain-of-Custody Procedures and SOP 7510Pines Packaging and Shipment of Environmental Samples (Appendix C of the SSC Work Plan).

9 Sample Custody

The field sampler(s) are responsible for the care and custody of the samples, including shipping to the laboratory. Field samplers will complete the CoC in accordance with AECOM SOP No. 1007Pines – Chain-of-Custody Procedures (**Appendix C of the SSC Work Plan**).

10 Sample Packaging and Shipping

Samples will be packaged for shipment to the laboratory under the CoC procedures described in AECOM SOP No. 1007Pines – Chain-of-Custody Procedures and AECOM SOP No. 7510Pines – Packaging and Shipment of Environmental Samples (Appendix C of the SSC Work Plan).

After sample containers are labeled and filled, samples may be placed in plastic zipper-lock bags to contain material in the event of container spillage during shipment. Containers will then be packaged in a cooler for shipment, using inert packing material (e.g., bubble wrap, rubber foam, or equivalent) to prevent breakage during shipment. For samples submitted for metals analysis, the cooler will be packed with sufficient ice to maintain a temperature of 4° ±2° Celsius (C) for overnight delivery. Samples submitted for radiological analysis and for PLM analysis will not be required to be shipped on ice. A multi-form CoC form will be completed. An example CoC form is presented in AECOM SOP No. 1007Pines – Chain-of-Custody Procedures (see Appendix C of the SSC Work Plan). The original CoC will be placed in a zipper-lock bag that is taped to the lid inside each cooler of samples being submitted to the laboratory for analyses. The back copy of the CoC will be maintained with the field records. The cooler will be locked or sealed, and custody seals placed on the outside of the cooler in such a way that the cooler cannot be opened without breaking the seals.

Sampling, analytical holding times, and shipping and receiving of samples will require close attention and coordination between field staff and laboratory staff. During the time period between collection and shipment, samples will be stored in ice-filled coolers or refrigerated, if applicable, and maintained under sample custody. Samples will be shipped to the laboratory via commercial overnight courier (e.g., Federal Express).

11 Decontamination of Non-Dedicated Sampling Equipment

Decontamination of non-dedicated sampling equipment will be completed in accordance with SOP 7600Pines Decontamination of Field Equipment (Appendix C of the SSC Work Plan). All non-dedicated sampling equipment will be decontaminated prior to sampling. Decontamination of drilling/sampling equipment will take place between each quadrant. Dedicated (i.e., disposable) sampling equipment will not be decontaminated.

In general, equipment used will be decontaminated using the following procedure:

- Tap water rinse to remove gross contamination;
- Non-phosphate, non-borate detergent (e.g., DETERGENT8®) and water rinse;
- Tap water rinse;
- Distilled/deionized water rinse;
- 10% nitric acid rinse;
- Distilled/deionized water rinse; and

- Air dry.

As a final step, all decontaminated equipment will be screened with a pancake probe or other suitable detector to confirm that residual radioactivity is within background levels. If the decontaminated equipment will be stored until later use, it will be wrapped in aluminum foil to prevent recontamination. Water generated during decontamination of sampling equipment will be handled as described in Section 12, below.

12 Investigation Derived Waste (IDW) Management

Investigation-derived waste (IDW) for the field investigation program will be managed in accordance with applicable USEPA and IDEM regulations. It is anticipated that IDW materials will be generated during the field investigation. These materials may include:

- Decontamination fluids,
- Used PPE,
- Used sampling equipment, and
- Excess soil from soil borings.

These wastes will be handled in the following manner:

- Water used for decontamination will be disposed of at Yard 520.
- Excess soil from soil borings will be returned to respective boreholes within each quadrant as backfill.
- Used PPE, such as sampling gloves, paper towels, or other materials will be bagged and sealed prior to disposal as general refuse.
- Used disposable sampling equipment, such as trowels and empty bottles, will be disposed of with the PPE as general refuse.

13 Property Restoration

Property restoration will be performed upon completion of sampling activities. Boreholes will be backfilled with excess soil collected from respective quadrants. If additional soil is required to fill the boreholes, sand will be added to the borehole and the borehole will be topped with site soil or other material consistent with the surrounding ground surface. The ground surface will be smoothed of ruts and/or divots and returned to pre-sampling condition to the extent practical. If necessary, a seed mix will be applied to areas where grass has been removed. Photographs will be taken of each quadrant to document conditions before and after the sampling/property restoration.

14 Laboratory Analysis

Soil samples will be analyzed for designated inorganics, and radionuclides, as specified in the SSC Work Plan and listed below. The samples will be submitted to the ALS Group (formerly Columbia Analytical Services, Inc.) for designated inorganics analyses, and GEL Laboratories, LLC for the radionuclide gamma spectroscopy analysis and total uranium by inductively coupled plasma–mass spectroscopy (ICP-MS) analysis. Additional details on the analytical methods are provided in the project QAPP Addendum, which is provided as Appendix B of the SSC Work Plan.

15 Data Evaluation

Laboratory analytical data will be reviewed and validated in accordance with the project QAPP Addendum (Appendix B of the SSC Work Plan). The results of the analyses will be provided to USEPA in the SSC Report, as outlined in the SSC Work Plan.

Figures

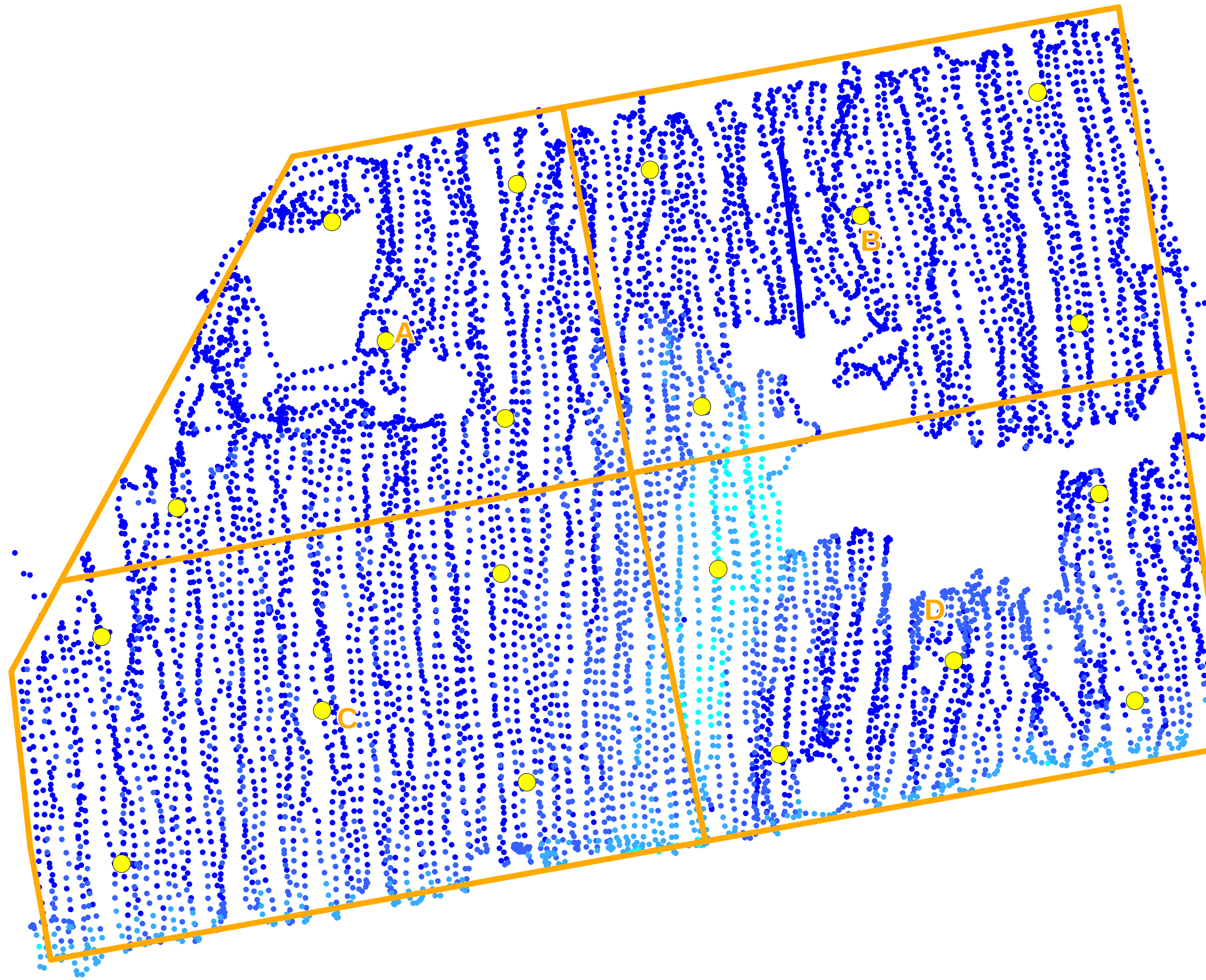
Sampling Quadrant

Sample Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000

19,453 cpm Approximating background + 5 pCi/g



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-1
Property 6
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

N

40 20 0 40 Feet

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

AECOM

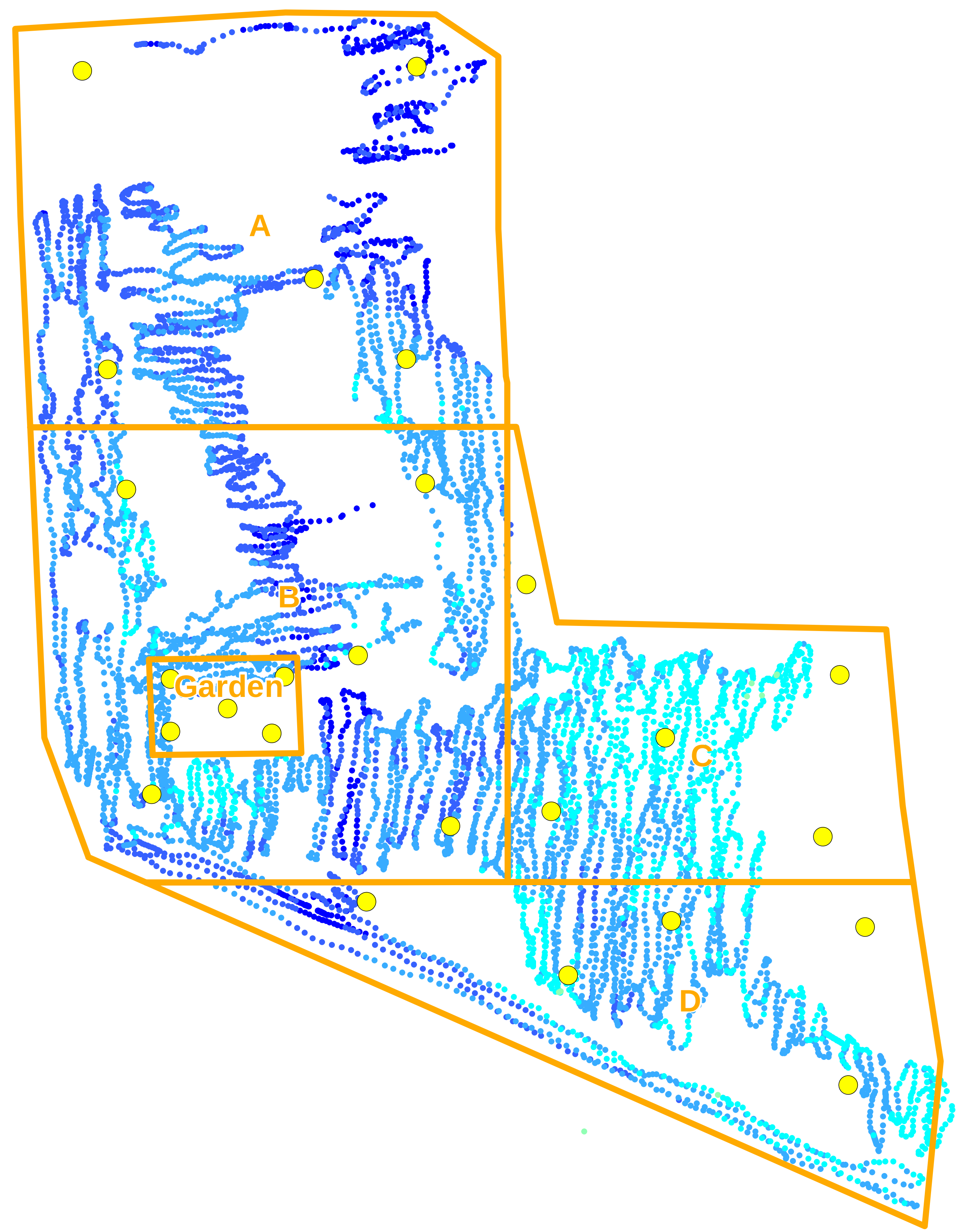
Sampling Quadrant

Sampling Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000

19,453 cpm Approximating background + 5 pCi/g



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-2
Property 14
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

50 25 0 50 Feet

N

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

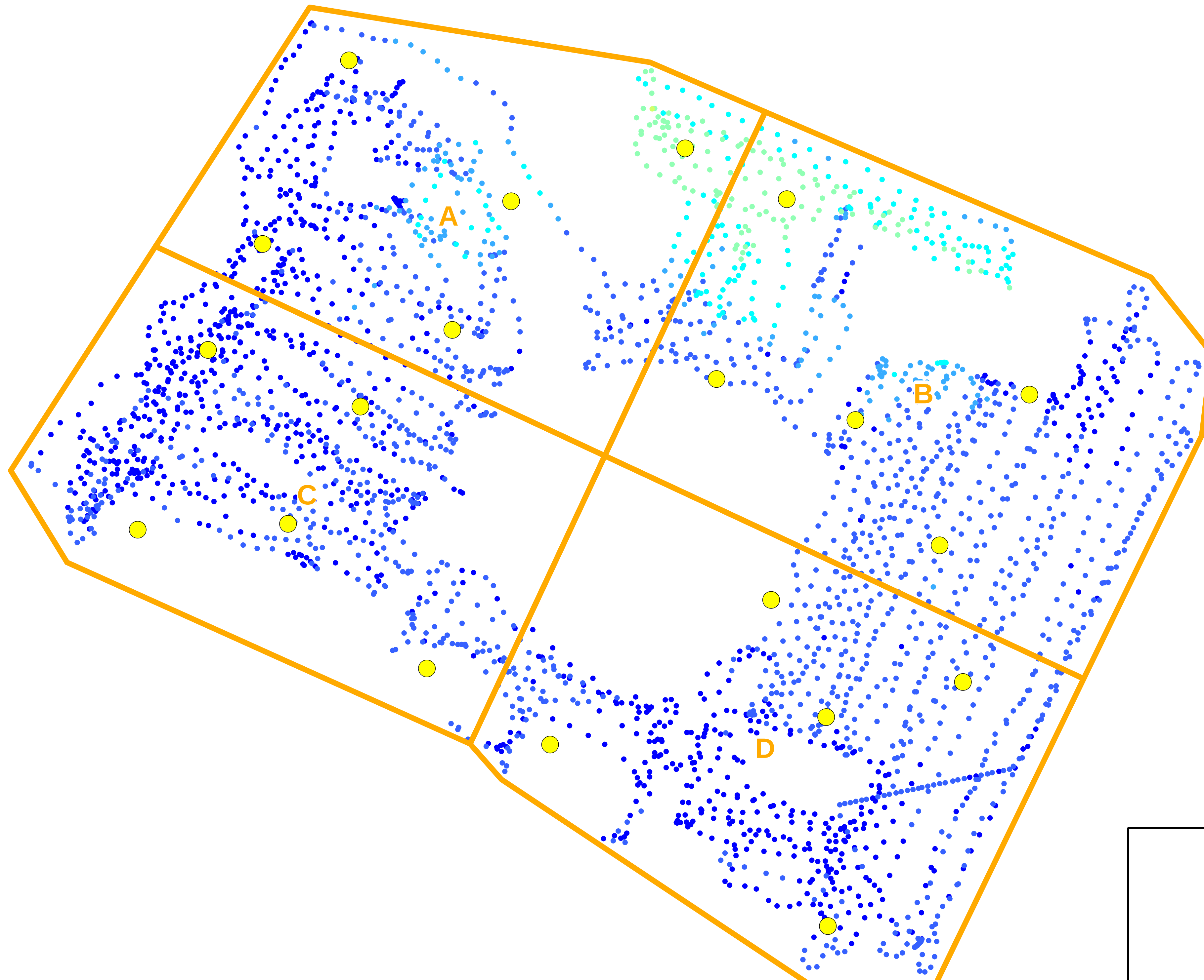
AECOM

Sampling Quadrant
Sampling Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000

19,453 cpm Approximating background + 5 pCi/g



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-3
Property 15
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

25 12.5 0 25 Feet

N

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

AECOM

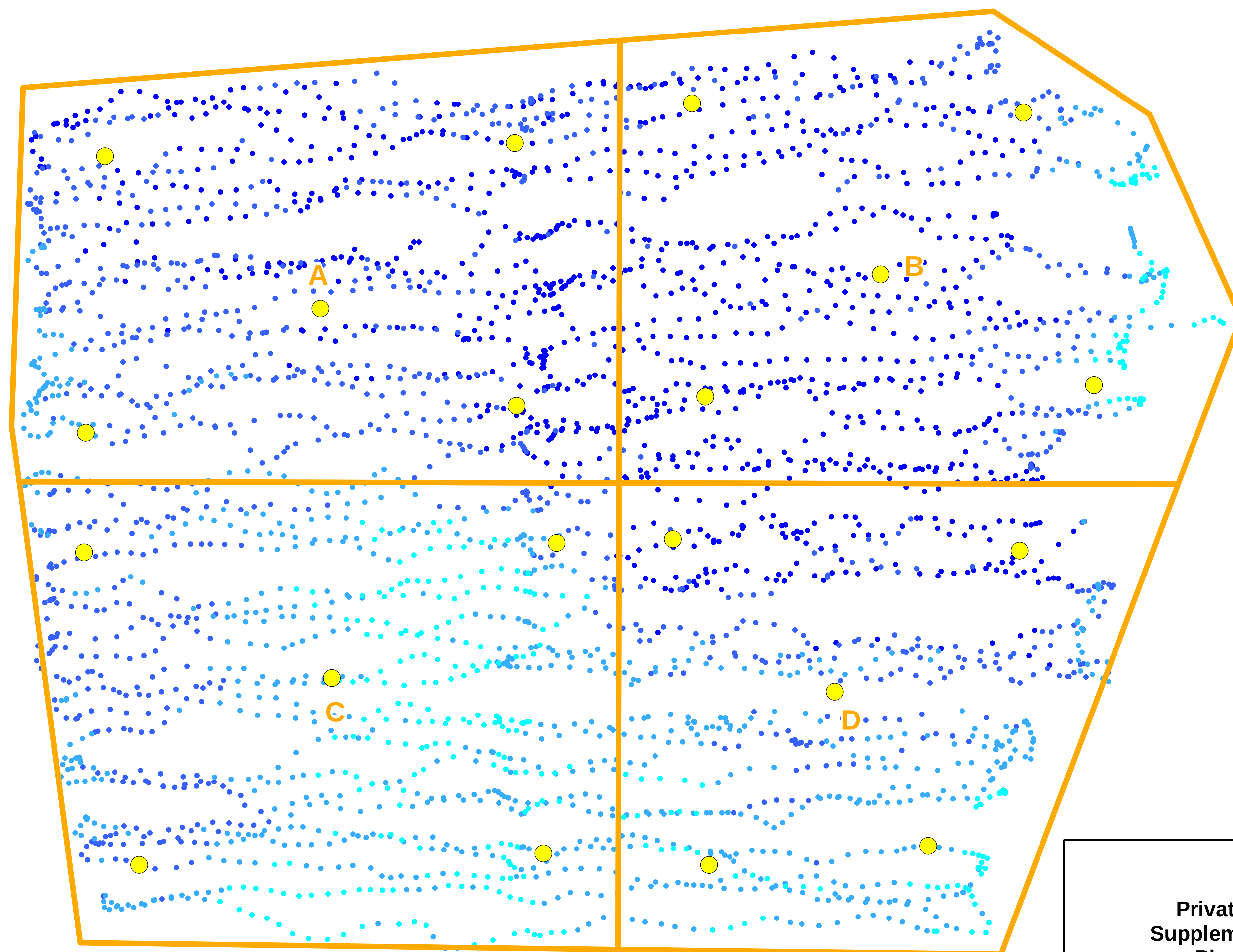
Sampling Quadrant

Sampling Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000

19,453 cpm Approximating background + 5 pCi/g



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-4
Property 24
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

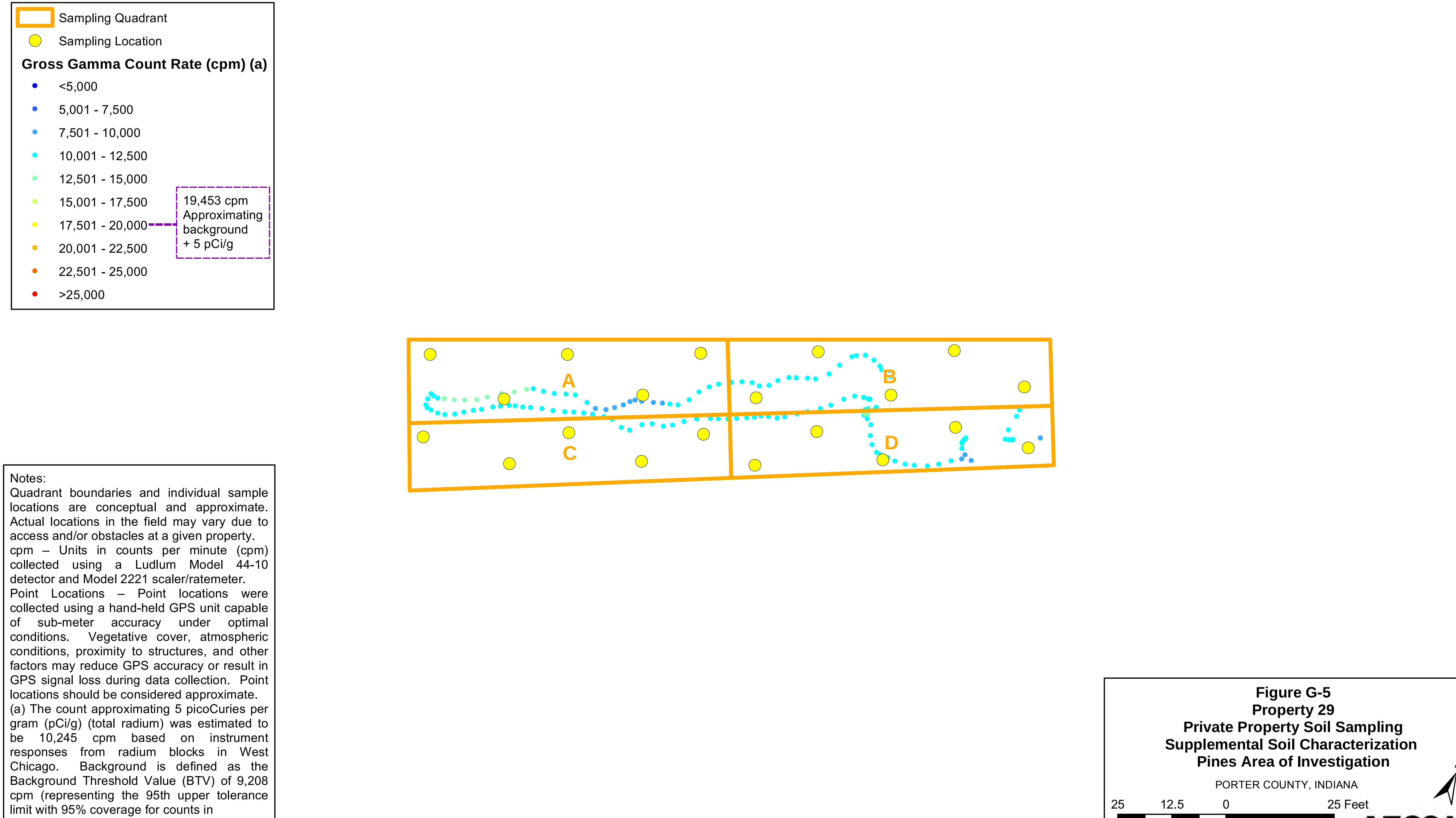
PORTER COUNTY, INDIANA

20 10 0 20 Feet

N

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

AECOM



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-5
Property 29
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

AECOM

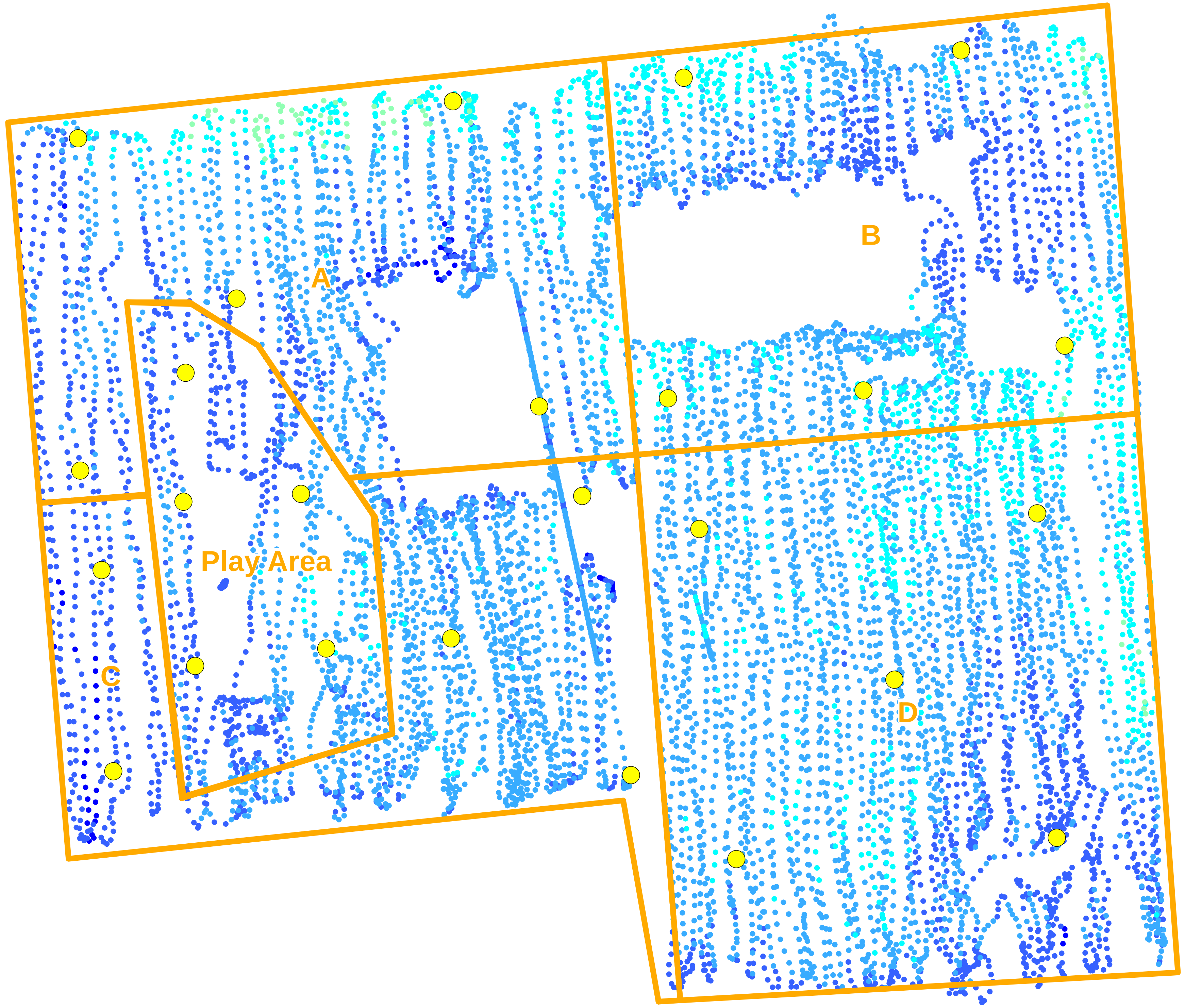
Sampling Quadrant

Sampling Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000

19,453 cpm Approximating background + 5 pCi/g



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-6
Property 34
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

40 20 0 40 Feet

N

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

AECOM

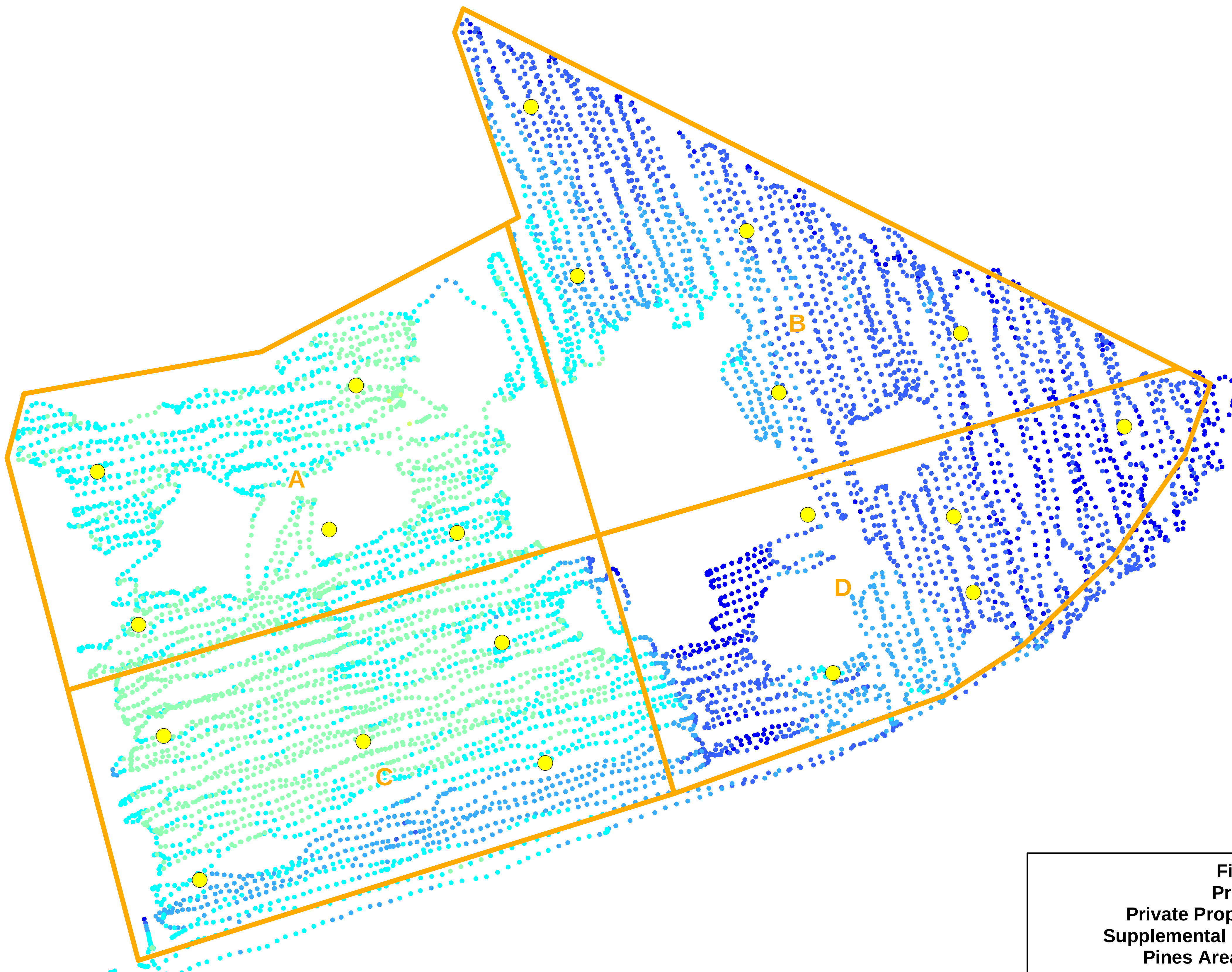
Sample Quadrant

Sample Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000

19,453 cpm Approximating background + 5 pCi/g



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-7
Property 35
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

40 20 0 40 Feet

N

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

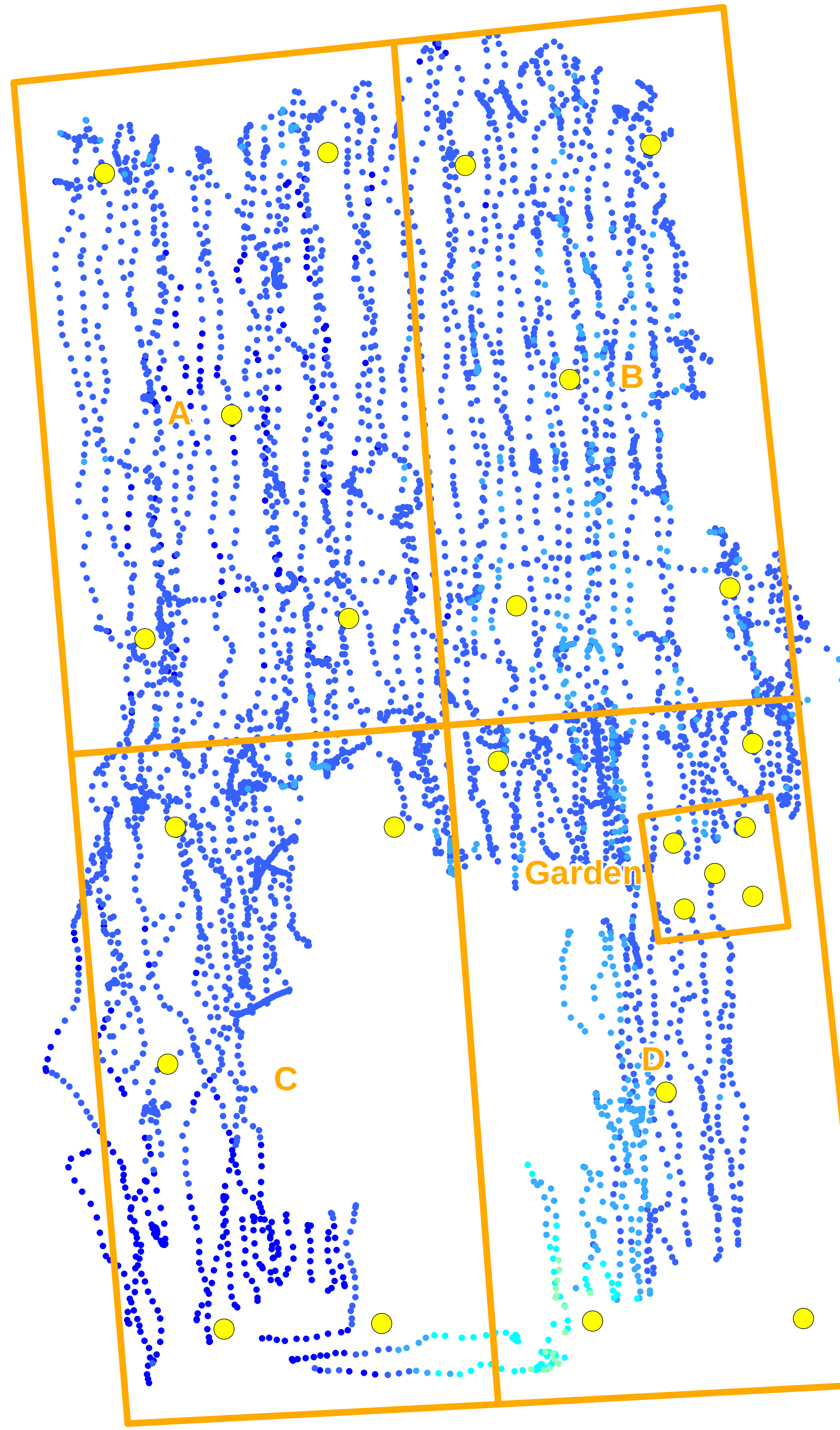
AECOM

Sampling Quadrant
Sampling Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000

19,453 cpm Approximating background + 5 pCi/g



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-8
Property 37
Private Property Soil Sampling
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

30 15 0 30 Feet

N

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

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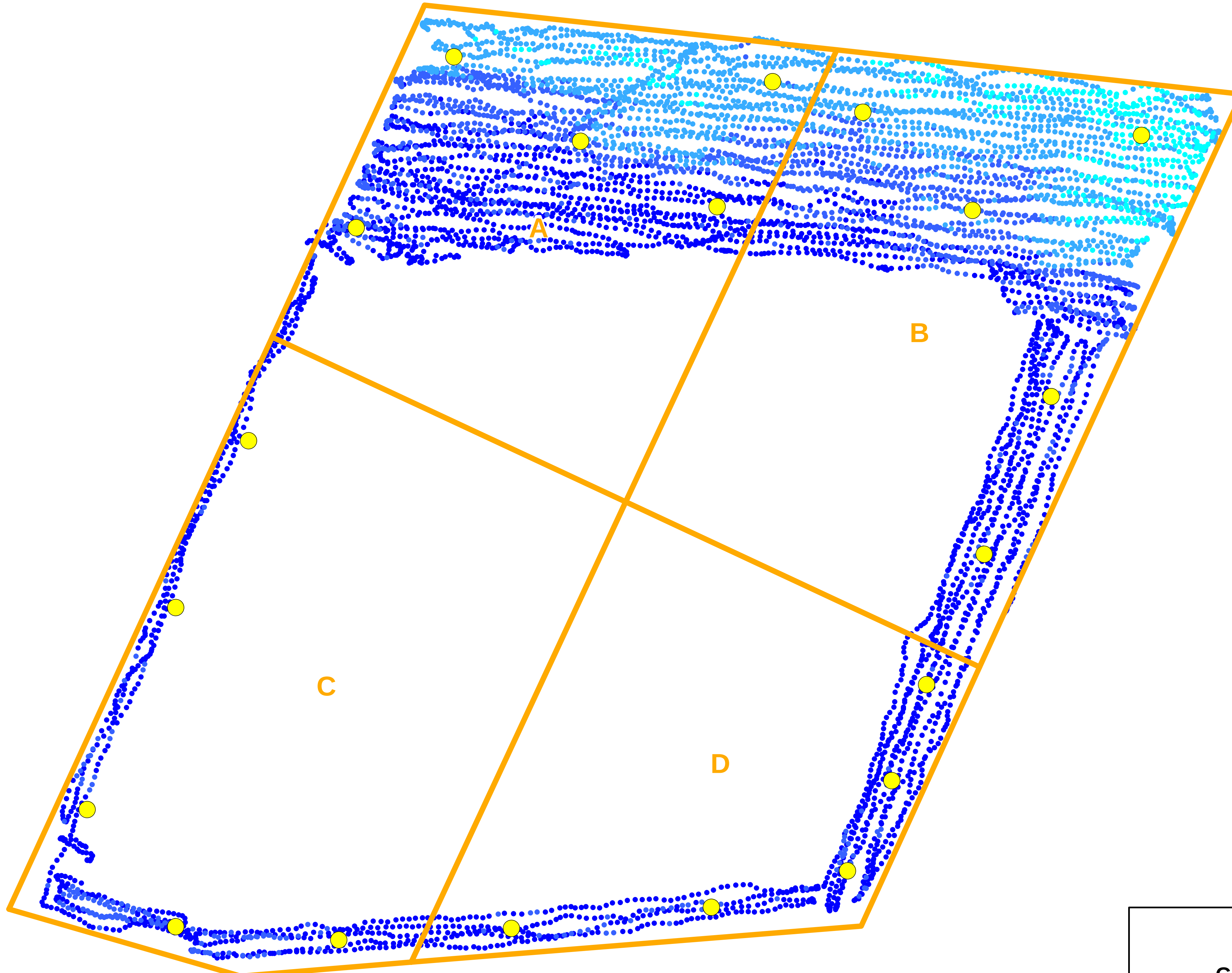
Sampling Quadrant
Sampling Location

Gross Gamma Count Rate (cpm) (a)

- <5,000
- 5,001 - 7,500
- 7,501 - 10,000
- 10,001 - 12,500
- 12,501 - 15,000
- 15,001 - 17,500
- 17,501 - 20,000 — 19,453 cpm Approximating background + 5 pCi/g
- 20,001 - 22,500
- 22,501 - 25,000
- >25,000



Notes:
Quadrant boundaries and individual sample locations are conceptual and approximate. Actual locations in the field may vary due to access and/or obstacles at a given property.
cpm – Units in counts per minute (cpm) collected using a Ludlum Model 44-10 detector and Model 2221 scaler/ratemeter.
Point Locations – Point locations were collected using a hand-held GPS unit capable of sub-meter accuracy under optimal conditions. Vegetative cover, atmospheric conditions, proximity to structures, and other factors may reduce GPS accuracy or result in GPS signal loss during data collection. Point locations should be considered approximate.
(a) The count approximating 5 picoCuries per gram (pCi/g) (total radium) was estimated to be 10,245 cpm based on instrument responses from radium blocks in West Chicago. Background is defined as the Background Threshold Value (BTV) of 9,208 cpm (representing the 95th upper tolerance limit with 95% coverage for counts in

Figure G-9
Property 38
Gamma Count Rate Survey Results
Supplemental Soil Characterization
Pines Area of Investigation

PORTER COUNTY, INDIANA

50 25 0 50 Feet

Source:
Flown on March 13, 2004
Basemap prepared by Air Maps Inc.

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About AECOM

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AECOM (NYSE: ACM) is a global provider of professional technical and management support services to a broad range of markets, including transportation, facilities, environmental, energy, water and government. With approximately 45,000 employees around the world, AECOM is a leader in all of the key markets that it serves. AECOM provides a blend of global reach, local knowledge, innovation, and collaborative technical excellence in delivering solutions that enhance and sustain the world's built, natural, and social environments. A *Fortune 500* company, AECOM serves clients in more than 130 countries and has annual revenue in excess of $8.0 billion.

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