UPPER COLUMBIA RIVER

Final
Quality Assurance Project Plan for the Bossburg Flat Beach Refined Sediment and Soil Study Amendment No. 1

Prepared for

Teck American Incorporated
P.O. Box 3087
Spokane, WA 99220-3087

Prepared by

1200 MacArthur Boulevard
Mahwah, NJ 07430

In Association and Consultation with:

Exponent, Inc.
ENVIRON
Parametrix, Inc.

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SECTION A: PROJECT MANAGEMENT

A1 TITLE AND APPROVAL SHEET

QUALITY ASSURANCE PROJECT PLAN FOR THE BOSSBURG FLAT BEACH REFINED SEDIMENT AND SOIL STUDY
AMENDMENT NO.1

Approvals

EPA Project Coordinator:	Matt Wilkening		Date: 3/25/15
EPA Quality Assurance (QA) Manager:	Ginna Grepo-Grove		Date: 03/24/2015
Teck Project Coordinator:	Kris McCaig		Date: 3/24/15
Task QA Coordinator:	Rock Vitale		Date: 3/24/15

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ACRONYMS AND ABBREVIATIONS

Agreement	June 2, 2006, Settlement Agreement
CEC	cation exchange capacity
DU	decision unit
EPA	U.S. Environmental Protection Agency
ICS	incremental composite sampling
IVBA	*in vitro* bioaccessibility assay
MQO	measurement quality objective
MS	matrix spike
MSD	matrix spike duplicate
QA	quality assurance
QA/QC	quality assurance and quality control
QAPP	quality assurance project plan
QC	quality control
RPD	relative percent difference
SDG	sample delivery group
SOP	standard operating procedure
TAI	Teck American Incorporated
TAL	target analyte list
TOC	total organic carbon
XRF	X-ray fluorescence

UNITS OF MEASURE

°C	degree(s) Celsius
cm	centimeter(s)
g	gram(s)
in.	inch(es)
mm	millimeter(s)
μm	micrometer(s)

A3 DISTRIBUTION LIST

EPA Project Coordinator	Matt Wilkening
EPA QA Manager	Ginna Grepo-Grove
TAI Project Coordinator	Kris McCaig
Task QA Coordinator	Rock Vitale

A4 INTRODUCTION

This amendment outlines proposed sampling plan modifications as outlined within the January 2015 Bossburg Flat Beach Refined Sediment and Soil Study quality assurance project plan (Bossburg QAPP). The modifications outlined herein are in response to the U.S. Environmental Protection Agency (EPA) Ancillary Comments on the QAPP received by Teck American Incorporated (TAI) on February 19, 2015. The modifications herein are limited to clarifications and Quality Assurance/Quality Control (QA/QC) measures detailed in the sections below.

All other aspects associated with field sampling and handling procedures and data validation activities remain unchanged from the approved QAPP (January 2015).

A4.1 Modifications to Main QAPP

This section presents modifications to sections of the main Bossburg QAPP made to address the above referenced ancillary comments from EPA.

A4.1.1 Data Quality

The text from Section A7.6.2 of the QAPP has been modified to address the above referenced ancillary comments:

"Field QC samples will include equipment rinsate blanks, field triplicate samples, field splits samples, and certified reference materials; no trip blanks will be collected (no organics to be analyzed). These QC samples will be collected or prepared by sampling personnel in the field and submitted to the laboratory as natural samples. Minimum sample volume (mass) requirements are detailed in Table B3-1 and in Appendix A.

Equipment rinsate blanks will be used to identify possible contamination from the sampling environment or from sampling equipment. These blanks will be collected by pouring deionized or distilled water over (or through) decontaminated sampling equipment and into a sample jar. Equipment rinsate blanks during the sampling event will be collected at an interval of one per day and will be analyzed for TAL metals.

Field triplicate samples will be collected to assess the precision of the sampling process. Field triplicate samples will be collected as identified in Section A7.2 above from sediment and soil DUs identified by EPA (USEPA 2013).

Field split samples will be collected to assess the homogeneity of samples collected in the field and will be prepared by collecting double the amount of soil required for primary samples. For incremental composite samples (ICS), core samples, and XRF confirmation samples the analytical laboratory will perform sample homogenization and will take two

aliquots of sample from the homogenized soil to generate the field split sample.. For all sample types field splits will be prepared from at least 10 percent of the sampling locations.

EPA split samples will be obtained by EPA representatives as part of their QA/QC program, following homogenization in the lab, from no less than 15 percent of the sediment and soil samples submitted for chemical analysis. For ICS samples, these will contain 2 grams of each sieved and homogenized fraction (i.e., < 2 mm and < 250 µm [sediment], and < 2 mm and < 150 µm [soils]) using ICS technique for subsampling. Core sample splits will be a minimum of 1 g of each sieved and homogenized fraction (i.e., < 2 mm and < 250 µm [sediment], and < 2 mm and < 150 µm [soils]). Splits of XRF confirmation samples will be a minimum of 1 g of the soil or sediment after being homogenized by the lab (sieving to < 2 mm will have been conducted in the field).

Experimental blanks will be used to identify possible contamination from the laboratory and will be collected according to laboratory protocols. An experimental blank will be generated for equipment used in the sieving process and will be collected once per incremental sampling event in the laboratory.

A matrix spike/matrix spike duplicate (MS/MSD) will be performed in the laboratory to assess the accuracy of the analyses. The MS/MSD will be performed according to the laboratory protocols and will occur at a frequency of once every 20 samples. MS/MSD splits will also be provided at the same frequency for the EPA split samples. This requires a total of 4 separate jars each with 2 grams of soil in each aliquot. Where the project specific evaluation criteria are fairly high for the main elements of concern, the lab should be spiking the QC samples (MS/MSD) at these criteria/action levels since those are the concentrations with which EPA needs to have confidence in the data. Otherwise the spikes are not likely to be evaluated in high concentration samples near these levels of concern.

Laboratory duplicates will be performed to evaluate the reproducibility between individual measurements of the same property (i.e., analytical precision). Precision will be evaluated using the results of laboratory duplicates and will be generated at a rate of one per 20 samples or one per sample delivery group (SDG) whichever is greater.

One sand blank study will be conducted only once during the project. EPA recommends analyzing the sand blank acid washed only, and acid washed with ICS processing (exposed to all procedures and equipment). The difference between the two will quantify any contamination and identify potential positive bias that may have been introduced

during sample processing. If the lab can show no increase within their analytical errors, then there is control of any potential contamination and thus evidence to document that."

A4.1.2 Design and Rationale for Field Sampling and Analytical Program

Section B1.2 incorrectly stated the depth of sediment and soil subsurface layers and the text has been corrected as follows:

"Sediment and soil cores will include intervals from surface (15 cm) and one or more subsurface layers (e.g., 15 to 30 cm and 30 to 45 cm) to support evaluation of the vertical extent of contamination."

A4.1.3 Minimum Sample Size for Metals

Section B3 references Table B3-1 which contains among other requirements, minimum sample mass for metals analysis. Table footnotes f through h have been updated to provide clarification for generating aliquots for field split samples as follows:

"Mass represents the amount of <2 mm sieved material. For ICS split samples (field splits and EPA splits) 2 grams of the <2 mm sieved fraction will be generated using ICS technique for subsampling.

Mass represents the amount of <250 μm sieved material. For ICS split samples (field splits and EPA splits) 2 grams of the <250 μm sieved fraction will be generated using ICS technique for subsampling.

Mass represents the amount of <150 μm sieved material. For ICS split samples (field splits and EPA splits) 2 grams of the <150 μm sieved fraction will be generated using ICS technique for subsampling."

A4.1.4 Field Quality Control

Section B5 does not contain field quality control requirements however; these requirements were discussed in Appendix A, Section 2.5 of the QAPP. Reference Section A.4.2.2 below for modifications to Appendix A, Section 2.5 regarding field quality control.

A4.1.5 Data Validation and Usability

Section D1 Data Review, Verification, and Validation of the Bossburg QAPP contained an inaccurate reference to the National Functional Guidelines and the reference has been corrected as follows:

"Data verification and validation will be completed according to methods described in the following EPA guidance documents for data validation:

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review (EPA 540-R-10-011, January 2010)"

"Results for other QC procedures will be qualified if they do not meet control limits outlined in EPA's functional guidelines and SOPs for data validation (USEPA 1995, 1996, 1999, 2010)."

"No guidelines are available for validation of data for TOC. These data will be validated using procedures described in the functional guidelines for inorganic data review (USEPA 2010), as applicable."

"Equipment rinse blanks and experimental blanks generated during the sieving and ICS processes including the sand blank) will be evaluated and data qualifiers applied in the same manner as method blanks, described in the functional guidelines for data review (USEPA 1995, 1996, 1999, 2010). Data will be rejected if control limits for acceptance of data are not met, as described in USEPA (1995, 1996, 1999, 2010)."

To address EPA's comments: 1) Section B5.2 of the QAPP is missing a relative percent difference (RPD) equation and language regarding field triplicates; 2) Section D1 of the QAPP should specify criteria and frequency for any splits and if exceedances will result in data qualification; and 3) Section D1 is missing a discussion of sieve blanks and ICS sand processing blank with, text from Section D1 of the QAPP has been modified as follows:

"Results for field triplicate and laboratory split samples will be evaluated using control limits of 35 percent. Data will not be qualified as estimated if the MQOs are exceeded, but RPD results will be tabulated and any exceedances will be discussed in the data summary report.

Equipment rinse blanks and experimental blanks generated during the sieving and ICS processes (including the sand blank) will be evaluated and data qualifiers applied in the same manner as method blanks, described in the functional guidelines for data review (USEPA 1995, 1996, 1999, 2010). Data will be rejected if control limits for acceptance of data are not met, as described in USEPA (1995, 1996, 1999, 2010)."

Section D2 Verification and Validation Methods of the Bossburg QAPP also contained an inaccurate reference to the National Functional Guidelines and the reference has been corrected as follows:

"Procedures for verification and validation of laboratory data and field QC samples will be completed as described in the functional guidelines and SOPs for data validation (USEPA 1995, 1996, 1999, 2010) and summarized…"

A4.2 Modifications to Appendix A (Field Sampling Plan)

This section presents modifications to Appendix A of the Bossburg QAPP in response to the above referenced ancillary comments.

A4.2.1 Core Samples

Section 2.3.2.2 stated the metric units for core sampling depths incorrectly and the text has been corrected as follows:

"Up to three surface and subsurface intervals will be collected: 0 to 15 cm (0 to 6 in.), 15 to 30 cm (6 to 12 in.), 30 to 45 cm (12 to 18 in.)."

A4.2.2 Field Quality Control Samples

Section 2.5 did not reference field splits and therefore text from this sections has been modified as follows:

"Field QC samples include the collection of triplicate ICS samples, equipment rinsate blanks and field splits. These samples will be submitted to and analyzed by the analytical chemistry laboratory.

Field split samples will be collected to assess the homogeneity of samples collected in the field and will be prepared by collecting double the amount of soil required for primary samples. For incremental composite samples (ICS), core samples, and XRF confirmation samples, the analytical laboratory will perform sample homogenization and will take two aliquots of sample from the homogenized soil to generate the field split sample. For all sample types field splits will be prepared from at least 10 percent of the sampling locations.

EPA split samples will be obtained by EPA representatives as part of their QA/QC program, following homogenization in the lab, from no less than 15 percent of the sediment and soil samples submitted for chemical analysis. For ICS samples, these will contain 2 grams of each sieved and homogenized fraction (i.e., < 2 mm and < 250 µm [sediment] and < 2 mm and < 150 µm [soils]) using ICS technique for subsampling. Core sample splits will be a minimum of 1 g of each sieved and homogenized fraction (i.e., < 2 mm and < 250 µm [sediment], and < 2 mm and < 150 µm [soils]). Splits of XRF confirmation samples will be a minimum of 1 g of the soil or sediment after being homogenized by the lab (sieving to < 2 mm will have been conducted in the field)."

A4.2.3 Individual Sample Labeling

Section 2.6 stated the metric units for core sampling depths incorrectly and the text has been corrected as follows:

"• Core interval: ### = interval number for a core sample (001 = 0 to 15 cm; 002 = 15 to 30 cm; 003 = 30 to 45 cm)"

Section 2.6 of the QAPP did not include an adequate procedure for labeling field split samples and the following text has been modified as follows:

Field split samples for ICS samples, core samples, and XRF confirmations samples will generated by the laboratory from the parent sample collected in the field. The field crew will identify on the chain of custody which samples are to be split in the laboratory using a riffle splitter. The ICS split samples will be labeled by the laboratory using unique fictitious identifiers (e.g., BOSS-###)."

A4.2.4 Appendix A Standard Operating Procedure 3

Appendix A Standard Operating Procedure (SOP) 3 stated the metric units for core sampling depths incorrectly and the text has been corrected as follows:

"Up to three surface and subsurface intervals will be collected: 0 to 15 cm (0 to 6 in.), 15 to 30 cm (6 to 12 in.), and 30 to 45 cm (12 to 18 in.)."

A4.3 Modifications to Appendix C (ALS Environmental Quality Assurance Manual)

Appendix C to the QAPP contained a list of Laboratory Standard Operating Procedures (in Appendix F), however the actual SOPs were not included in Appendix C. At the request of EPA the laboratory SOPs are provided in Attachment A to this amendment.

SECTION B: REFERENCES

USEPA (U.S. Environmental Protection Agency). 1995. SOP for the validation of Method 1668 toxic, dioxin-like PCB data. U.S. Environmental Protection Agency, Region 10, Environmental Services Division, Seattle, WA.

USEPA. 1996. SOP for the validation of polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) data. U.S. Environmental Protection Agency, Region 10, Environmental Services Division, Seattle, WA.

USEPA. 1999. USEPA contract laboratory program national functional guidelines for organic data review. EPA-540/R-99-008. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC.

USEPA. 2010. USEPA Contract Laboratory Program national functional guidelines for inorganic Superfund data review. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, DC. EPA 540-R-10-011. January 2010.

USEPA. 2013. Draft quality assurance plan for the Bossburg Flat Beach refined sediment study, Upper Columbia River Project. Letter from Matt Wilkening, EPA Project Coordinator, dated July 3.

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Table B3-1. Sampling Containers, Preservation, and Holding Time Requirements for Sediment and Soil Chemistry

Analysis	Container		Preservation	Holding Time	Minimum Laboratory Sample Size	Total Minimum Sample Size Needed [a, b]
	Type	Size				
Whole Sediment	Plastic	2 gallon	4 ± 2ºC			
Grain size				6 months	100 g	100 g
Sediment < 2 mm size fraction						51 g[f]
TAL metals						
EPA 6020A metals [c]				6 months	10 g	
EPA 6010C metals [d]				6 months	10 g	
Percent moisture				6 months	10 g	
pH				7 days	20 g	
Total organic carbon				28 days	1 g	
Sediment < 250 µm size fraction						22 g[g]
TAL metals						
EPA 6020A metals [c]				6 months	10 g	
EPA 6010C metals [d]				6 months	10 g	
IVBA [e]				6 months	2 g	
Whole Soil	Plastic	2 gallon	4 ± 2ºC			
Grain size				6 months	100 g	100 g
Soil < 2 mm size fraction						151 g[f]
TAL metals						
EPA 6020A metals [c]				6 months	10 g	
EPA 6010C metals [d]				6 months	10 g	
Percent moisture				6 months	10 g	
pH				7 days	20 g	
Total organic carbon				28 days	1 g	
CEC				14 days	100g	
Soil < 150 µm size fraction						22 g[h]
TAL metals						
EPA 6020A metals [c]				6 months	10 g	
EPA 6010C metals [d]				6 months	10 g	
IVBA [e]				6 months	2 g	

Notes:

[a] Total sample size does not include additional sample volumes needed for laboratory quality control or field duplicate samples.

[b] Project field triplicate samples should be collected for 10 percent of all analytical sediment and soil samples and submitted blind to the analytical laboratory.

[c] TAL metals—aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, selenium, silver, thallium, vanadium, and zinc.

[d] TAL metals—calcium, iron, magnesium, potassium, and sodium.

[e] Samples will be sieved by the analytical laboratory.

[f] Mass represents the amount of <2 mm sieved material. For ICS split samples (field splits and EPA splits) 2 grams of the <2 mm sieved fraction will be generated using ICS technique for subsampling.

[g] Mass represents the amount of <250 µm sieved material. For ICS split samples (field splits and EPA splits) 2 grams of the <250 µm sieved fraction will be generated using ICS technique for subsampling.

[h] Mass represents the amount of <150 µm sieved material. For ICS split samples (field splits and EPA splits) 2 grams of the <150 µm sieved fraction will be generated using ICS technique for subsampling.

CEC - cation exchange capacity

TAL - target analyte list

IVBA - *in vitro* bio-accessibility assay (lead and arsenic only)

ATTACHMENT A

ALS ENVIRONMENTAL LABORATORY STANDARD OPERATING PROCEDURES

ALS Standard Operating Procedure

DOCUMENT TITLE:	TOTAL SOLIDS
REFERENCED METHOD:	SM 2540 B/EPA 160.3
SOP ID:	GEN-160.3
REVISION NUMBER:	14
EFFECTIVE DATE:	04/01/2015

TOTAL SOLIDS

ALS-KELSO

SOP ID:	GEN-160.3	Rev. Number:	14	Effective Date:	04/01/2015

Approved By: _____ Date: 3/11/15
Department Supervisor/Technical Director – Harvey Jacky

Approved By: _____ Date: 3/11/15
QA Manager – Lee Wolf

Approved By: _____ Date: 3/11/15
Laboratory Director – Jeff Grindstaff

Issue Date: _____ Doc Control ID#: _____ Issued To: _____

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

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TOTAL SOLIDS

1. SCOPE AND APPLICATION

1.1. This procedure is used to determine total solids using Standard Methods 2540 B-1997 and EPA method 160.3 and is applicable to drinking, surface, and saline waters, domestic and industrial wastes. This procedure can also be used to determine percent dry solids in soil, sediment, and solids. Total solids for Puget Sound Estuary Program analyses can also be determined using this procedure.

1.2. The practical range of the determination is from 5mg/L to 20,000mg/L in water. The Method Detection Limit (MDL) is 5mg/L using 200mL of sample.

1.3. For other sample matrices treated on a weight/weight basis, the working range can be as low as 2 - 100% dry solids. However, samples with less than 5-10 % solids are generally treated as water samples.

2. METHOD SUMMARY

2.1. A well-mixed aliquot of the sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105ºC, or a project specific temperature. Results are reported in mg/L for water. For non-aqueous samples, a nominal 10g portion of the sample is used. Results are reported in Percent (%) solids for soils, sediments, or solids.

3. DEFINITIONS

3.1. Total residue is defined as the sum of the homogenous suspended and dissolved materials in a sample.

3.2. Dry solids are defined as the amount of solid remaining after evaporating off all liquid contained within the sample.

4. INTERFERENCES

4.1. For water samples, non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. However, for other matrices, these particles may be included if they are considered representative of the material undergoing other associated analyses.

4.2. Samples containing HF will react with the porcelain crucibles causing a significant weight loss and artificially high results. When analyzing samples containing HF, special Teflon™ crucibles should be used and samples should be evaporated in a ventilation hood to dryness.

4.3. Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

5. SAFETY

5.1. 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.

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

5.3. Since this is often the first test performed on solid samples, the analyst should use caution in opening containers. For non-routine matrices, based on the appearance of the sample, the analyst should immediately determine if a potential hazard exists.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Sample bottles should be plastic and must be thoroughly cleaned and rinsed prior to use. Soil samples may be collected in glass jars, sleeves, or other suitable container.

6.2. A minimum of 100mL of sample should be collected for water samples. For soil samples, a minimum of 10g is required. Collecting 8 oz. jars of soil improves subsampling homogeneity.

6.3. Samples must be stored refrigerated at 4 ± 2ºC and analyzed within 7 days from date of sample collection for water samples. There is no holding time established for soils or solids.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. N/A

8. APPARATUS AND EQUIPMENT

8.1. Evaporating dishes: dishes of 100ml capacity made of porcelain.

8.2. Evaporating pans, aluminum

8.3. Desiccators, containing desiccant.

8.4. Drying oven, for operation at 103-105ºC.

8.4.1. Oven temperature may be monitored by using a thermometer or by using the oven digital readout. If a thermometer is used, it is immersed in sand, or other suitable solid material, in a flask in the oven.

8.4.2. The calibration of liquid in glass thermometers is done annually, and oven readouts are verified semi-annually.

8.5. Analytical balance capable of weighing to 0.1mg.

8.6. Glass cylinders.

8.7. Balance calibration verification weights, ASTM Class 1; 1g, 10g, 100g.

9. PREVENTIVE MAINTENANCE

9.1. The multi-point balance calibration checks are performed daily for each day analyses are performed. The results of these checks are recorded in the appropriate QA metrological logbook.

9.2. Periodic balance service is performed by an outside service provider and is coordinated by the QA section.

9.3. Analytical balances should be kept clean and free of debris. The balance bubble indicator should be checked to ensure the unit is level.

9.4. Desiccant should be changed as needed.

10. RESPONSIBILITIES

10.1. 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.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the determinative method, is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. Water samples

11.1.1. Heat the clean evaporating dish to 103-105ºC for a minimum of one hour. Cool, and desiccate. Weigh and store in desiccator until ready for use.

11.1.2. Transfer a measured aliquot of sample to the pre-weighed dish and evaporate to dryness on a steam bath or in a drying oven. Wide-bore pipette tips must be used.

11.1.3. Choose an aliquot of sample sufficient to contain a residue of at least 25mg. To obtain a measurable residue, successive aliquots of sample may be added to the same dish.

11.1.4. If evaporation is performed in a drying oven, the temperature should be lowered to approximately 98ºC to prevent boiling and splattering of the sample.

11.1.5. Dry the evaporated sample for at least 1 hour at 103-105ºC. Cool in a desiccator and weigh. Repeat the cycle of drying at 103-105ºC, cooling, desiccating and weighing until a constant weight is obtained or until loss of weight is less than 4% of the previous weight, or 0.5mg, whichever is less. Report the results of this weighing.

11.2. Soils, sediments, and solids

11.2.1. Pre-dry the aluminum pans prior to use by heating at 103-105ºC for one hour. Allow to cool. Label the pans with numbers corresponding to the sample I.D.s analyzed.

11.2.2. After opening the sample jar, mix the sample to achieve a homogenous sample.

11.2.3. Determine the tare (dry pan) weight, then weigh 10grams of sample into the pan.

11.2.4. Place in a drying oven overnight at 103-105ºC.

11.2.5. Remove from the oven and let cool. Since percent level determinations are being made on solid samples, cooling in a desiccator is not necessary. Weigh and record the dry (pan+sample) weight.

12. QA/QC REQUIREMENTS

12.1. Prior to, and after each analysis batch, balance calibration verification is performed using weights bracketing the sample weights (sample + pan). Balance calibration verification measured weights must be ± 0.5% of the true value.

12.2. QC Samples Required

12.2.1. For water samples, run a laboratory control sample (LCS) per batch of 20 (or fewer) samples. For the LCS, a certified quality control standard is purchased from APG as a solid material. Add the standard to DI water in a 1L volumetric flack and dilute to volume (for APG, add all of the material provided). The LCS will be approximately 1000mg/L, with exact values specified by lot number. Analyze as described above. The LCS recovery criterion is 85-115% of the true value.

Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

12.2.2. Run one duplicate per batch of ten samples. The RPD should be $\leq$ 10%. This statistically derived acceptance limit is subject to change as limits are updated. For Puget Sound Estuary Program protocols, perform a triplicate analysis per batch of 10 samples. The RSD should be $\leq$20%.

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1= Higher Result
R2= Lower Result

12.2.3. For water samples, run a method blank every twenty samples or one per desiccator.

13. DATA REDUCTION, REVIEW, AND REPORTING

13.1. For water samples, calculate total residue as follows:

$$Total\ residue,\ mg/L = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of sample + dish in mg
B = weight of dish in mg
C = volume of sample in ml

13.2. For soils, sediments, and solids, calculate % solids as follows:

(tare + dry weight) - tare = dry weight

dry weight ÷ wet weight x 100 = % solids

13.3. Record all measurements on a benchsheet or spreadsheet. For soils, sediments, and solids, a spreadsheet is available to calculate % solids.

13.4. Results are reported directly from benchsheets or spreadsheets. Use the appropriate form template in R:\WET or R:\TSOLIDS directories.

13.5. Report water results in mg/L total solids using whole numbers. The Method Reporting Limit is 5mg/L. Report non-aqueous samples as % Solids by 160.3Modified. Use up to a maximum of three significant figures.

13.6. Data review

13.6.1. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. All data will be initialed, dated and attached to required data quality worksheet.

13.6.2. The data packet for the sequence is submitted for review by supervisor or designee.

13.6.3. Refer to the SOP for *Laboratory Data Review Process* for general instructions for data review.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformance and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

15.1. Refer to the reference method for additional method performance data available.

15.2. The method detection limit (MDL) is established using the procedure described in the SOP for *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* (CE-QA011). Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

17. TRAINING

17.1. Refer to the SOP for Documentation of Training, ADM-TRAIN. The SOP describes the training outline and necessary documentation.

17.2. Review literature (see References section). Review the SOP. Also review safety procedures. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.3. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of 1-2 months. During this period, the analyst is expected to transition

from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.4. Independently perform Initial Demonstration of Proficiency studies and QC analyses. The data must be reviewed by a supervisor or trained analyst. Documentation is forwarded to the employee's training file.

18. METHOD MODIFICATIONS

18.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

19. REFERENCES

19.1. Total solids dried at 103-105ºC, SM 2540 B-1997.

19.2. Residue, Total, Method 160.3 EPA 600/4-79-020, Revised March 1983.

19.3. Appendix A: Benchsheet

20. CHANGES SINCE THE LAST REVISION

20.1. Reformatted to current ALS format.
20.2. Section 8.4 – revised to list both thermometer and digital readout options, and include calibration verification frequency.
20.3. Section 11.1.2 – added that wide-bore pipette tips are used.
20.4. Section 13.3 – removed computer-interfaced balance option for recording readings, no longer in use.

APPENDIX A

Benchsheet
(1 page)

Benchsheet attachments are for internal use only – not included in externally provided copies.

STANDARD OPERATING PROCEDURE

DOCUMENT TITLE:	***TOTAL CARBON IN SOIL***
REFERENCED METHOD:	***ASTM METHOD D4129-05 AND EPA 9060***
SOP ID:	***GEN-ASTM***
REV. NUMBER:	***9***
EFFECTIVE DATE:	***04/18/2014***

TOTAL CARBON IN SOIL

ASTM METHOD D4129-05 AND EPA METHOD 9060

ALS-KELSO

SOP ID:	GEN-ASTM	Rev. Number:	9	Effective Date:	04/18/2014

Approved By: _____ Date: 4/18/2014
Department Supervisor – Harvey Jacky

Approved By: _____ Date: 4/18/2014
QA Manager – Lee Wolf

Approved By: _____ Date: 4/18/2014
Laboratory Director – Jeff Grindstaff

Issue Date:	_____	Doc Control ID#:	_____	Issued To:	_____

TOTAL CARBON IN SOIL

1. SCOPE AND APPLICATION

1.1. This procedure is applicable to the determination of Total Carbon, Total Organic Carbon (TOC), and Total Inorganic Carbon using ASTM Method D4129-05 or EPA Method 9060 modified for soil and sediment matrices (Puget Sound Estuary Program and Lloyd Kahn). Total organic carbon is a measure of the total amount nonvolatile, partially volatile and particulate organic compounds in a sample. The sample should be acidified to remove inorganic carbon (carbonates, bicarbonates, free CO_2 etc.), prior to analysis. Total Carbon (TC) results are determined by analysis of an untreated, non-acidified, sample. Total Inorganic Carbon (TIC) can be determined by difference, subtracting TOC from TC.

1.2. This method is applicable to all soils and sediments and most matrices that can be dried and ground to a fine powder.

1.3. Results are reported as percent (%) carbon, and the applicable range is the MDL - 100%. The Method Reporting Limit (MRL) for TOC on soils is 0.05%, dry weight basis. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The Method Detection Limit (MDL) has been determined at 0.02%.

2. METHOD SUMMARY

2.1. Samples are combusted in an oxygen atmosphere to convert organic and inorganic forms of carbon to CO_2. The combustion temperature is selected to completely oxidize all carbon forms. The combustion product gases are swept through a barium chromate catalyst/scrubber to ensure that all of the carbon is oxidized to CO_2. Other potentially interfering product gases such as SO_2, SO_3, HX, and NO_x are removed from the gas stream in a series of chemical scrubbers. By ASTM Method D4129-05 the CO_2 is then swept to the coulometer where it is detected by automatic, coulometric titration, with coulometric end point indication. If performing EPA Method 9060, the CO_2 is determined using an infrared detector.

2.2. The coulometer cell is filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. When a gas stream passes through the solution, CO_2 is quantitatively absorbed. CO_2 reacts with the ethanolamine to form a strong titratable acid which caused the indicator to fade. The titration current automatically turns on and electrically generates base to return the solution to its original color.

3. DEFINITIONS

3.1. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.2. Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.3. Sample

3.3.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.3.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.4. Quality System Matrix - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.4.1. Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.4.2. Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.4.3. Nonaqueous Liquid - Any organic liquid with <15% settleable solids.

3.4.4. Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.4.5. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.4.6. Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.4.1 through 3.4.5. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.4.7. Miscellaneous matrices – Samples of any composition not listed in 3.4.1 – 3.4.6. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.5. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are 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 method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid point of the calibration range or at levels specified by a project analysis plan.

3.6. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.7. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.8. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.9. Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.10. Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.11. Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4. INTERFERENCES

4.1. Acidic and other gases, including SO_2, SO_3, H_2S, HCl, HBr, HI, Cl_2, and NO_x can be effectively removed using scrubbers such as KI, Ag_2SO_4, $AgNo_3$, and MnO_2.

4.2. Volatile organics may be lost in the decarbonization process.

5. SAFETY

5.1. 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.

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

5.3. Hydrochloric and/or 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.

5.4. Disconnect teflon tubing from furnace at check valve whenever system is not in use or when O_2 flow is turned off or furnace temperature is reduced. If the carbon cathode solution should be siphoned through a failed check valve into the magnesium perchlorate scrubber potentially explosive DMSO-perchlorate could be formed.

5.5. Do not attempt to combust large samples of organic or other materials that will react with pure oxygen. Such samples can cause the pyrolysis tube to explode.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Samples can be collected in glass or plastic containers.

6.2. Samples are preserved by storage at 4±2ºC. Samples are analyzed within 28 days of collection.

7. APPARATUS AND EQUIPMENT

7.1. Induction furnace, Coulometrics Incorporated.

7.2. Analytical balance, 0.1mg accuracy.

7.3. Desiccator.

7.4. Quartz combustion boats.

7.5. Sample scoop.

7.6. Porcelain dishes.

7.7. Glass ladles and miscellaneous laboratory glassware,

8. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

8.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to ADM-RTL, *Reagent/Standards Login and Tracking* for the complete procedure and documentation requirements.

8.2. Standards

8.2.1. Urea - 20% carbon. Use 10 µg.

8.2.2. Nutrients in Soil, purchased standard with a known TOC value (typically ERA #542). Use 50 mg for LCS.

8.3. Reagents

8.3.1. Hydrochloric acid, 50% and 10%.

8.3.1.1. 10%: Bring 20mL HCl to 200mL final volume
8.3.1.2. 50%: Bring 100mL HCl to 200mL final volume

8.3.2. Carbon Cathode Solution. Dimethyl Sulfoxide; DMSO. Purchased from Coulometrics Inc. as a prepared solution. Used for coulometer solution.

8.3.3. Anode Solution. Dimethyl Sulfoxide and potassium iodide. Purchased from Coulometrics Inc. as prepared solution.

8.3.4. Manganese dioxide. Gas scrubber solution.

8.3.5. Potassium Hydroxide. Gas scrubber solution.

8.3.6. Potassium Iodide. Anode chemical.

8.3.7. Magnesium Perchlorate desiccant

9. RESPONSIBILITIES

9.1. 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.

9.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in ADM-TRAIN, ALS – Kelso Training Procedure, is also the responsibility of the department supervisor/manager.

10. PREVENTIVE MAINTENANCE

10.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 10. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

Maintenance is performed as follows:

Maintenance Item	Frequency
Cell	Clean daily with methanol and water to clean frit
Mg Perchlorate Scrubber	change daily
KOH Scrubber	change monthly
NOX scrubber	change as needed
Repack Precombustion Column	as needed
Repack Combustion Column	as needed

11. PROCEDURE

11.1. Sample Preparation.

11.1.1. Turn furnace on to ≈1000ºC. Allow furnace to warm-up for about 1/2 hours. Turn on oxygen to ≈5 psi and 75 to 125 ml/min at flowmeter.

11.1.2. Clean quartz boats. Scrape out old sample and rinse boats with DI water. Place boats in crucible and muffle for at least 10-15 minutes. Remove boats and place in desiccator until ready for use.

11.1.3. Samples should be dried at 70ºC and homogenized prior to analysis. Homogenization of dried solid sample should include grinding with a mortar and pestle or shatter box. A shatter box should be used with a larger sample size (i.e. 20+ grams) if the sample exhibits a high degree of heterogeneity. Samples should be ground to a fine, homogenous, powder.

11.1.4. Ground samples must be stored in individual sealed vials. In addition, sample vials analyzed under PSEP methodology must be stored in a desiccator prior to sample analysis.

11.1.5. As a rule, the darker (or closer to black) a sample is, the more carbon it contains. Place a small portion of sample on a watch glass. Add 1 drop of 10% HCl. Watch for effervescence or bubbling. If bubbles are present, the sample contains inorganic carbon (CO_3). If sample bubbles, reduce sample size to prevent sample from bubbling out of boat. If sample is dark, wood product or sludge reduce sample volume to 5 - 10mg. Normal sample volume = 50mg. After boats are loaded with sample add 1 to 2 drops 10% HCl to each sample, LCS, and method blank. Place boats in 70ºC oven to dry. If samples bubbled when acid was added, add 1 to 2 drops more acid and dry at 70ºC. Continue acidifying and drying until samples no longer bubble. Place samples in desiccator until ready for analysis.

11.2. Apparatus Preparation.

11.2.1. Fill cell with carbon cathode solution to 100 - 125 ml, drop in stir bar. Place cell top on snug.

11.2.2. Cover bottom of anode cell with KI. About 2 small scoops.

11.2.3. Add carbon anode solution to cell such that when anode is inserted in the anode cell, the anode solution level is the same as the cathode solution level.

11.2.4. Place cell in coulometer cell holder.

11.2.5. Turn on detector lamp and stir plate. (Power on)

11.2.6. Turn adjust knob to 122 (all the way to the right) then turn back down to 100. Rotate cell until maximum transmittance is obtained.

11.2.7. With oxygen bubbling to cell and maximum transmittance obtained, turn on the current to the anode and cathode. The carbon cathode solution will begin to titrate to a blue color.

11.2.8. Change Magnesium Perchlorate desiccant daily.

11.2.9. The instrument is now ready to run.

11.3. Calibration and Standardization.

11.3.1. Burn both ladles for five minutes each to remove any residual TOC.

11.3.2. Establish baseline.

11.3.2.1. After placing ladles in sample inlet, allow system to purge for 1 minute.

11.3.2.2. Burn three empty boats five minutes each. The average of the three runs is the baseline.

11.4. Analysis.

11.4.1. Place one platinum or quartz boat in a ladle. Place the ladle in the sample inlet and purge for 1 minute. Simultaneously insert the sample into the furnace, press the reset button on the coulometer and start the timer for five minutes.

11.4.2. After five minutes, obtain a reading from the instrument. Remove the ladle from the furnace. (Occasionally, a high sample may require longer than 5 minutes to complete the titration).

11.4.3. Load the other ladle with the next platinum (or quartz) boat. Remove the ladle in use from the inlet port and insert the next ladle.

11.4.4. Repeat steps 11.4.1 through 11.4.3 until all samples are analyzed.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

The precision and accuracy of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS's are prepared and analyzed. The RSD should be <20% and average recovery must be within LCS recovery limits (see laboratory DQO Tables).

12.2. Method Detection Limits and Method Reporting Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Analyze a minimum of seven spiked blank replicates at a level near the MRL. Follow the procedures starting in Section 11 to analyze the samples. Refer to CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.* The MDL study must be performed or verified periodically, as required by the CE-QA011 SOP.

12.2.2. Calculate the average concentration found (x) in the *sample concentration*, and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates.

12.2.3. Limits of Quantification (LOQ)

12.2.3.1. The laboratory establishes a LOQ for each analyte as the lowest reliable laboratory reporting concentration or in most cases the lowest point in the calibration curve which is less than or equal to the desired regulatory action levels, based on the stated project requirements. Analysis of a standard or extract prepared at the lowest point calibration standard provides confirmation of the established sensitivity of the method. The LOQ recoveries should be within 75-125% of the true values to verify the data reporting limit. Refer to CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.*

12.2.4. The Method Reporting Limits (MRLs) used at ALS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which ALS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DoD ELAP must follow requirements defined in the DoD *Quality Systems Manual for Environmental Laboratories.* General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management (ADM-DOD).*

12.4. The QC criteria discussed in the following sections are summarized in Table 1.

12.4.1. LCS - An LCS must be analyzed with each batch of 20 or fewer samples. Analyze 50mg of the purchased standard (see 8.1.2) is used. The acceptance criteria for the LCS are listed in Table 1.

12.4.2. Method Blank – Analyze one method blank per batch of 20 or fewer samples. Add one to two drops of 10% HCl to an empty boat and place the boat in a 70ºC oven to dry. Method Blank must be <0.05% carbon.

12.4.3. CCV (Continuing Calibration Verification) - A CCV must be analyzed every tenth analysis. Analyze ~10mg urea. The CCV must be 18.0% - 22.0% carbon.

12.4.4. CCB (Continuing Calibration Blank) - A CCB must be analyzed following every CCV.

12.4.5. Sample duplicate – ASTM D 4129: One duplicate sample per batch of 20 or fewer samples must be analyzed in duplicate. TOC analysis by PSEP methodology requires one sample to be analyzed in triplicate per batch of 20 or fewer samples. Samples analyzed under Lloyd Kahn methodology must all be analyzed in duplicate. All duplicates and triplicates, regardless of the method cited, should be within 20% RPD, if > five times the MRL.

12.4.6. Matrix Spike - One spike must be analyzed with each batch of 20 or fewer samples. The acidified sample will be spiked with a known amount of urea.

12.4.7. See Table 1 for a summary of acceptance criteria and corrective actions.

13. DATA REDUCTION AND REPORTING

13.1. Calculate % carbon as follows:

$$\%Carbon = \frac{(Gross\ reading\ -\ baseline\ \mu g)(0.1)}{mg\ sample\ analyzed}$$

13.1.1. Total organic carbon is reported as % carbon, normally on a dry weight basis. Results may be reported on an as received basis.

13.2. For duplicate analyses, calculate relative percent difference as follows:

$$RPD = \frac{S_1 - S_2}{Avg} * 100$$

where S1 = Sample with higher value
S2 = Sample with lower value
Avg = Average of the two sample values

13.3. Calculate percent recovery as follows:

$$\%R = \frac{X - X1}{TV} \times 100$$

where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte

TV = True value of amount spiked

13.4. Data Review and Assessment

13.4.1. Following primary data interpretation and calculations, all data is reviewed by a secondary analyst. Following generation of the report, the report is also reviewed. Refer to the *SOP for Laboratory Data Review Process (ADM-DREV)* for details. The person responsible for final review of the data report and/or data package should assess the overall validity and quality of the results and provide any appropriate comments and information to the Project Chemist to inclusion in the report narrative. All data will be initialed, dated and attached to required data quality worksheet.

13.5. Reporting

13.5.1. Refer to ADM-RG, *Data Reporting and Report Generation* for reporting guidelines.

13.5.2. For final reports, the method is reported as ASTM Method D4129-05 Modified or EPA Method 9060 Modified.

13.5.3. Results are reported as The analyst enters data directly into LIMS templates. An Analytical Results Summary is generated for that analytical batch showing all QC and sample results. After primary and secondary review, final reports are generated in LIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). The forms generated may be ALS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.5.4. As an alternative, reports are generated using Excel© templates located in R:\WET. The analyst should choose the appropriate form and QC pages to correspond to required tier level and deliverables requirements. The results are then transferred, by hand or electronically, to the templates.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Non Conformance and Corrective Action (CE-QA008)* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision

- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

15.1. This method is validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available. The method detection limit (MDL) is established using the procedure described in CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.*

15.2. Method Reporting Limits are established for this method *based on MDL studies and as specified in* CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.*

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

16.3. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS EH&S Manual for details.

16.4. This method uses a base. Waste base is hazardous to the sewer system and to the environment. All waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS EH&S Manual for details.

17. METHOD MODIFICATIONS

17.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

18. REFERENCES

18.1. Coulometrics Inc. Instruction Manual, Model 5020.

18.2. Total Organic Carbon (TOC), Conventional Sediment Variables, Puget Sound Estuary Program, March 1986.

18.3. Determination of Total Organic Carbon in Sediment, Lloyd and Kahn, U.S.E.P.A Region II, July 1988.

18.4. ASTM Method D4129-05.

18.5. Total Organic Carbon (TOC) in Soil: EPA SW-846 Method 9060

19. CHANGES SINCE THE LAST REVISION

19.1. Reformatted SOP to current ALS format
19.2. Changed title of SOP
19.3. Updated corporate SOP references as necessary.
19.4. Section 1.1 – Revised to add further explanation of procedure options
19.5. Section 2.1 – Revised to add further explanation of detection procedures
19.6. Section 12.2.1 – Minor revision to reference SOP for MDL frequency.
19.7. Section 13.5.2 – New section
19.8. Section 18 – Added EPA 9060 reference (18.5).

TABLE 1
Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
ASTM D4129 PSEP Lloyd Kahn	CCV	Verify calibration by analyzing prior to samples, after every 10 analysis and after the last sample	±10%	Re-analyze all samples affected.
ASTM D4129 PSEP Lloyd Kahn	LCS	Include with each analysis batch (up to 20 samples)	See DQO Tables	Re-analyze all samples affected.
ASTM D4129 PSEP Lloyd Kahn	Method Blank	Include with each analysis batch (up to 20 samples)	< 0.05%	If target exceeds 0.05%, clean boats and re-analyze.
ASTM D4129 PSEP Lloyd Kahn	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO Tables	Evaluate data to determine if the there is a matrix effect or analytical error
ASTM D4129 PSEP Lloyd Kahn	Sample Duplicates	Include with each analysis batch (up to 20 samples)	≤ 20 % RPD	Re-homogenize and re-analyze if result is > 5 X the MRL
ASTM D4129 PSEP Lloyd Kahn	Sample Triplicate	Include with each analysis batch (up to 20 samples)	≤ 20 % RSD	Re-homogenize and re-analyze if result is > 5 X the MRL
ASTM D4129 PSEP Lloyd Kahn	Sample Duplicates	All samples in each analysis batch	≤ 20 % RPD	Re-homogenize and re-analyze if result is > 5 X the MRL

APPENDIX I

BENCHSHEETS

ALS Environmental

DOCUMENT TITLE:	***PH IN SOIL AND SOLIDS***
REFERENCED METHOD:	***EPA METHOD 9045D***
SOP ID:	***GEN-PHS***
REV. NUMBER:	***13***
EFFECTIVE DATE:	***04/30/2013***

PH IN SOIL AND SOLIDS

EPA METHOD 9045D

ALS-KELSO

SOPID:	GEN-PHS	Rev. Number:	13	Effective Date:	04/30/201313

Approved By: _____ Date: 4/18/13
Department Supervisor - Harvey Jacky

Approved By: _____ Date: 4/18/13
QA Manager - Suzanne LeMay

Approved By: _____ Date: 4/19/13
Laboratory Director - Jeff Grindstaff

Issue Date: _____	Doc Control ID#: _____	Issued To: _____

STANDARD OPERATING PROCEDURE

for

pH IN SOIL AND SOLIDS

1. SCOPE AND APPLICATION

1.1. This procedure is used to determine pH in soil, solid, and certain waste samples using EPA Method 9045D.

1.2. When used to determine pH in multiphase wastes, the procedure is applicable if the aqueous phase constitutes less than 20% of the total volume of the waste.

2. METHOD SUMMARY

2.1. The pH is determined by potentiometric measurement of a soil slurry or aqueous solution using a standard combination glass pH electrode and pH meter.

2.2. The procedure uses methodology described in EPA Method 9045D, WDOE Test Method, and Oregon State Soil Methods.

3. DEFINITIONS

3.1. Analysis Batch - A sequence of samples, which are analyzed within a 24-hour period and include no more than 20 field samples.

3.2. Sample Duplicate - two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. The purpose is to verify the precision associated with the laboratory procedures.

3.3. Sample Triplicate – three aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. The purpose is to verify the precision associated with the laboratory procedures.

4. INTERFERENCES

4.1. Samples with extreme pH results may give incorrect readings on the meter. Samples with a high sodium concentration and pH > 10 can cause error. Using a “low sodium error” electrode (such as Orion 8165, 8172 or equivalent) eliminates this issue to a pH of 12. If the pH is greater than 12, the sodium content of the sample may need to be determined and the pH result may need correction. Strong acid solutions with pH < 1 may give incorrect high pH readings.

4.2. Samples containing oil may coat the electrode and cause a sluggish response or inaccurate reading. If an electrode becomes coated with a material which cannot be rinsed off, the electrode can be cleaned with an ultrasonic bath, be washed with detergent and rinsed then

placed in 1:1 HCl so that the lower third of the electrode is submerged, then rinsed thoroughly with water.

4.3. Temperature fluctuations will cause instrument errors.

5. SAFETY

5.1. 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.

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

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1. Sample bottles can either be glass or plastic and must be thoroughly cleaned and rinsed prior to use.

6.2. Samples must be stored refrigerated at 4□C (± 2ºC). Although there is no holding time established for soils, samples should be analyzed as soon as possible.

7. APPARATUS AND EQUIPMENT

7.1. Fisher Accumet pH meter, Model 25 or equivalent.

7.2. Combination electrode for pH with temperature probe (such as Orion 8165 or equivalent).

7.3. Conductivity jars, 50 ml.

7.4. Analytical balance capable of weighing 0.1 g.

7.5. Paint filters.

7.6. Erlenmeyer flasks, 250 ml.

7.7. Water bath capable of maintaining a constant temperature of 25°C. One large for all samples and buffers and one smaller bath for analyzing samples at 25°C ± 1°C.

7.8. Standard stir plate and submersible stir plate and stir bars.

7.9. Eight ounce or 16 ounce juice bottles and caps.

7.10. Wrist action shaker?

8. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

8.1. pH buffers: 1.00, 4.00, 7.00, 10.00, 12.45, (true value of buffers at 25° C).

8.2. Commercially available solutions should be validated and traceable to NIST standards and are recommended for routine use.

9. PREVENTIVE MAINTENANCE

9.1. The probe should contain filling solution past the coils to ensure accurate readings. Filling solution should be a non-AgCl containing solution.

9.2 Cleaning the probe

9.2.1 The probe should be emptied and refilled with filling solution once a week.

9.2.2 The glass bulb should be cleaned every other week, or more, by placing it in a beaker with approximately 40 ml of 0.1N HCl and allowed to sit while stirring for approximately 5 minutes. Then rinse the probe with DI water 3 times and blot with a kimwipe.

9.3 If the coils are no longer orange it means the electrode's ion reservoir is empty and it needs to be replaced.

10. 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. 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.

11. PROCEDURE

11.1. **Calibration**

11.1.1. All buffers are placed in conductivity jars, capped and stored in the large 25° C water bath. All readings need to be within 1°C of the buffer temperatures.

11.1.1.1. Buffer in conductivity jars needs to be replaced with buffer from the primary container daily.

11.1.1.2. Once a manufacture's bottle of buffer is open it's good for 3 months, because it becomes contaminated with carbon dioxide.

11.1.2. Perform calibration daily. Record calibration; buffer checks and buffer temperatures in instrument logbook or benchsheet with date and analyst's initials.

11.1.3. The slope of the calibration points should be between 95 and 105% or within the range set by the probe manufacturer. The meter displays the slope of calibration.

11.1.4. If the slope exceeds the above end points either the buffer(s) is contaminated or the probe is no longer functioning properly.

11.1.4.1. Replace buffers, rewarm and then re calibrate

11.1.4.2. Empty the probe rinse the inside 3 times with DI water, then refill with electrode filling solution and rise the outside of the probe and blot with kimwipe

11.1.5. Calibration (Fisher Accumet pH Meter 25)

11.1.5.1. Push "standardize"

11.1.5.2. Select 2

11.1.5.3. Push "standardize".

11.1.5.4. Select 1

11.1.5.5. Enter the first buffer value, 4.00. Push “enter”.

11.1.5.6. Place enough buffer solution in a conductivity jar so that the electrode is sufficiently submersed without coming into contact with the stir bar.

11.1.5.7. Rinse electrode

11.1.5.8. Immerse the electrode in the solution. Allow time to stabilize.

11.1.5.9. Push “enter”.

11.1.5.10. Record the buffer value to 0.01 pH units and the buffer temperature to the nearest °C. (4.00 and 25°C).

11.1.5.11. Repeat steps 11.2.2.1 through 11.2.2.9 for buffers 7.00 and 10.00. Also use the 12.45 and 1.00 buffers if needed.

11.1.6. Calibration (Fisher Accumet pH Meter AR25)

11.1.6.1. Calibrate according to the manufacturer’s specifications.

Note: Initial calibration is performed using the 4.00, 7.00, and 10.00 buffers. If any subsequent sample pH is outside the calibration range (greater than 10.00 or less than 4.00), the 1.00 and/or 12.45 buffers are added to the calibration and the applicable samples are reanalyzed.

11.2. **Soil samples preparation for EPA Method 9045D**.

11.2.1. Weigh out 10g of soil into a beaker. Add 10mL of reagent water, cover, and stir the suspension continuously for 5 minutes. Alternative sample volumes may be used as long as soil:water ratios remain the same. Additional dilutions may be performed if working with hygroscopic soils and salts, or other problematic matrices.

11.2.2. Let the soil suspension stand for 1 hour to allow for settling. Alternatively, filter or centrifuge off the aqueous phase for pH determination.

11.2.3. Setup electrodes in clamps so that when the electrode is lowered into the beaker, the electrode will be immersed just deep enough in the supernatant solution to establish a good electrical contact through the ground-glass joint or fiber capillary hole. Immerse the electrode in samples in this manner.

11.3. **Waste material preparation for EPA Method 9045D.**

11.3.1. Wastes may be solids, sludges, or non-aqueous liquids. For multi-phase wastes by method 9045D, a determination of the percentage of the sample that is non-

aqueous must be made. This can be calculated from a % solids determination. If the non-aqueous phase is > 20%, continue with this section. If the non-aqueous phase is < 20%, analyze the sample by EPA Method 9040C see also SOP GEN-pHW.

11.3.2. Weigh out 20g of waste sample into a beaker. Add 20mL of reagent water, cover, and stir the suspension continuously for 5 minutes. Alternative sample volumes may be used as long as solid:water ratios remain the same. Additional dilutions may be performed if working with hygroscopic soils and salts, or other problematic matrices.

11.3.3. Let the waste suspension stand for 15 minutes to allow for settling. Alternatively, filter or centrifuge off the aqueous phase for pH determination.

11.3.4. If the waste absorbs all the reagent water, begin the test again with 20g waste and 40mL of water.

11.3.5. If the supernatant is multi-phasic, decant the oily phase and perform the pH determination on the aqueous phase.

11.3.6. Setup electrodes in clamps so that when the electrode is lowered into the beaker, the electrode will be immersed just deep enough in the supernatant solution to establish a good electrical contact through the ground-glass joint or fiber capillary hole. Immerse the electrode in samples in this manner.

11.4. **Sample preparation for Washington DOE Test Method**.

11.4.1. Weigh three, 50.0g aliquots of each sample into either 3, 8-ounce or 3, 16-ounce juices bottles and add 50mL of D.I. water to each and cap tightly. Each sample is analyzed in triplicate.

11.4.2. Place all bottles on the wrist action shaker. The speed of the shaker should be adjusted so that the sample and water have maximum contact time however the shaking action should not be so vigorous as to cause absorption of CO_2 into the sample.

11.4.3. Filter the liquid through a paint filter into a clean conductivity jar for analysis.

11.5. **Oregon State Soil Methods sample preparation**

11.5.1. Weigh 20.0g of soil into a beaker and add 40mL of D.I. water.

11.5.2. Stir the suspension 2-3 times over a 30-minute period.

11.5.3. Analyze the supernatant.

11.6. **Sample Analysis**

11.6.1. Rinse and blot electrode, then immerse into the sample. Press pH and record the pH when stabilized, record the temperature to the nearest °C. Remove electrodes from sample after each measurement and rinse 3 times with D.I. water.

11.6.2. Regardless of the method employed, all pH readings must be within 2°C of the temperature of the buffer solutions.

11.6.3. If the pH of the sample is ≥11.00 control the temperature of the samples to 25°C±1°C.

12. QA/QC REQUIREMENTS

12.1. A buffer check is analyzed after every 10 readings. For buffer checks, use either pH 4.00 or 10.00, choosing whichever standard brackets the majority of the previous samples with pH 7.00. The buffer check should be within 0.05 pH units of the true value.

12.2. A laboratory control sample (LCS) is analyzed at a frequency of one per 20 samples, with acceptance criteria of 85-115% of the true value. Analyze the LCS prior to the sample set. The LCS is prepared identically to associated samples and documented on the benchsheet. If the LCS is outside of these limits, recalibrate.

12.3. A duplicate sample is analyzed at a frequency of 10% of the samples, with acceptance criteria of 10% RPD between the two readings. If the duplicate is outside of these limits, the sample is reanalyzed. Duplicates are documented on the benchsheet. For duplicate analyses, calculate relative percent difference as follows:

$$RPD = \frac{S_1 - S_2}{Avg} * 100$$

Where S1 = Sample with higher value
S2 = Sample with lower value
Avg. = Average of the two sample values

12.4. For DOE/pH, all samples are analyzed in triplicate and the logarithmic average is reported.

12.5. Sum the antilog of the three pH readings obtained in section 11.5, divide by 3 then take the log.

Example:
Three pH readings obtained: 1.5 1.6 2.5

antilog(1.5) + antilog(1.6) + antilog(2.5) =
31.62 + 39.81 + 316.23 = 387.66
387.66 ÷ 3 = 129.22
log(129.22) = 2.11
pH(average) = 2.11

13. DATA REDUCTION, REVIEW, AND REPORTING

13.1. Refer to ADM-DREV, *Laboratory Data Review Process* for general guidelines for data review.

13.2. All data and corrective actions must be recorded, dated, and signed or initialed by the analyst. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified above. Average, RPD, and buffer level are entered on the benchsheet for corresponding samples. All data will be initialed, dated and attached to required data quality worksheet.

13.3. The data packet for the sequence is submitted for review by supervisor or designee.

13.4. Reporting

13.4.1. Refer to ADM-RG, *Data Reporting and Report Generation* for reporting guidelines.

13.4.2. Reports are generated in the CAS LIMS by compiling the SMO login, sample prep database, instrument date, and client-specified report requirements (when specified). The forms generated may be CAS standard reports, DOD, or client-specific reports. The compiled data from LIMS is also used to create EDDs.

13.4.3. The pH is reported as pH units. Values are reported to 0.01 pH units.

13.4.4. The benchsheets, located in Appendix A, should be in use at all times during pH analysis.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Non Conformity and Corrective Action (CE-QA008)* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

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

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

17. TRAINING

17.1. Training Outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of one week. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.1.4. Training is documented following ADM-TRAIN, *ALS-Kelso Training Procedure*.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. CHANGES SINCE THE LAST REVISION

18.1. Reformatted to ALS style.
18.2. CAS references changed to ALS
18.3. Attachment 1: Added a copy of the benchsheet.

19. REFERENCES

19.1. EPA SW-846, Test Methods For Evaluating Solid Waste, Third Edition, Update IIIIB, November 2004, Method 9045D, Revision 4.

19.2. Method 83-13, State of Washington, Department of Ecology.

19.3. Oregon State University, Methods of Soil Analysis Used in the Soil Testing Laboratory at Oregon State University.

ATTACHMENT 1
Benchsheet

COLUMBIA ANALYTICAL SERVICES, INC.

Service Request #: _____ Method: 9045D

Analysis: _____ pH Corrosivity _____ Matrix: Soil/Solid

Calibration						
Buffer	1.00	4.00	7.00	10.00	12.45	Value of Buffers at 25 °C
Reading						pH Slope:_____
Temp °C						

Sample Number	Sample Wt. (g)	Vol of Ext Sol (mLs)	pH	Time Analyzed	Temp °C	% Solids
Buffer Check	**Buffer Value:**					
LCS	--	--				
Buffer Check	**Buffer Value:**					
Buffer Check	**Buffer Value:**					

LCS: ERA **Lot #:** **ID #:** **T. V. =** **% REC. =**

pH 4.00 buffer: 12-GEN. pH-001-21_____ pH 7.00 buffer: 12-GEN. pH-001-35_____ pH 10.00 buffer: 12-GEN. pH-001-49_____

ph 1.00 buffer Cond/1-73-_____pH 12.45 buffer Cond/1-82-_____ Extraction Solution: _____

Probe ID# rcl/1-79-1 Water Bath ID# K-wb-01 Thermometer ID# L82605

Meter ID# K-pH-01

Analyst:	Date:
Reviewed By:	Date:

R: WET/Analysis/PH/Templates/SOILPH Revison: 2

SOILPH2.xls

COLUMBIA ANALYTICAL SERVICES, INC.

Service Request #: _____ Method: 9045D

Analysis: pH Corrosivity Matrix: Soil /Solid

Sample Number	Sample Wt. (g)	Vol of Ext Sol (mLs)	pH	Time Analyzed	Temp °C	% Solids
Buffer Check	**Buffer Value:**					
Buffer Check	**Buffer Value:**					
Buffer Check	**Buffer Value:**					

Comments: _____

Analyst:	Date:
Reviewed By:	Date:

SOILPH2.xls

PARTICLE SIZE DETERMINATION – ASTM PROCEDURE

ASTM D 422-63

ALS-KELSO

SOP ID:	GEN-PSASTM	Rev. Number:	2	Effective Date:	07/31/2013

Approved By: _____ Date: 7/12/13
Department Supervisor – Harvey Jacky

Approved By: _____ Date: 7/12/13
QA Manager – Suzanne LeMay

Approved By: _____ Date: 7/12/13
Laboratory Director – Jeff Grindstaff

Issue Date:	_____	Doc Control ID#:	_____	Issued To:	_____

Standard Operating Procedure

For

PARTICLE SIZE DETERMINATION – ASTM PROCEDURE

1. SCOPE AND APPLICATION

1.1. This procedure covers the quantitative determination of the distribution of particle sizes in soils as described in ASTM D 422-63. The distribution of particle sizes larger than 75 μm is determined by sieving, while the distribution of particle sizes smaller than 75 μm is determined by a sedimentation process, using a hydrometer to obtain the necessary data.

1.2. Detection limits are determined from accuracy of analytical balances. Samples are weighed to the nearest 0.01g and results are reported to the nearest 0.01 percent.

1.3. The pre-preparation of the samples employs ASTM Method D421-85.

2. METHOD SUMMARY

Particle size is used to characterize the physical characteristics of sediments. Because particle size influences both chemical and biological variables, it can be used to normalize chemical concentrations according to sediment characteristics and to account for some of the variability found in biological assemblages. Particle size is also an important variable for marine engineering purposes.

3. DEFINITIONS

3.1. Particle size – The size of various solid components making up sediment, as named in the applicable method reference (gravel, sand, silt, clay, etc.).

3.2. Dispersing agent – A solution introduced into the soil suspension to disperse the small sediment fractions and reduce flocculation, allowing more accurate determination of particle sizes using a hydrometer.

3.3. Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample.

4. INTERFERENCES

4.1. Depending on the required particle size distribution, organic material can be interference.

5. SAFETY

5.1. 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.

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

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1. Samples can be collected in glass or plastic containers. A minimum sample size of 300-2000g is recommended. If unrepresentative material is to be removed from the sample, it should be removed in the field under the supervision of the chief scientist and noted on the field log sheet.

6.2. Samples should be stored at 4 ± 2°C, and can be held for up to 6 months before analysis. Samples must not be frozen or dried prior to analysis, as either process may change the particle size distribution.

7. APPARATUS AND EQUIPMENT

7.1. Sieve shaker – Ro-Tap or equivalent

7.2. Drying oven

7.3. Mortar and rubber covered pestle

7.4. Thermometer accurate to 0.5 °C

7.5. Analytical balance – 0.1mg accuracy

7.6. Desiccator

7.7. Clock – with second hand

7.8. Standard sieves – Appropriate mesh sizes, sieve pan and top, sieve brush.

7.9. Funnel

7.10. Graduated cylinders

7.11. 250-mL beakers

7.12. Hydrometer – An ASTM hydrometer, graduated to read specific gravity and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100.

7.13. Stirring apparatus as described in ASTM D422-63 Section 3.2.1.

7.14. Water pique or squirt bottle

7.15. Glossy paper

8. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

8.1. Dispersant - 4 percent sodium hexamethaphosphate. To prepare, weigh 40.0g sodium hexamethaphosphate and dilute to 1.0L in DIW. Expires 3 months from preparation date.

8.2. Distilled water

9. PREVENTIVE MAINTENANCE

9.1. No specific maintenance steps are needed for sieves other than normal cleaning and inspection.

9.2. Balance calibration checks are performed daily.

9.3. Color-indicating desiccant is recommended so that spent desiccant can be detected easily. Also, the seal on the desiccator should be checked periodically, and, if necessary, the ground glass rims should be greased or the "0" rings should be replaced.

10. RESPONSIBILITIES

10.1. 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.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Training and proficiency is documented in accordance with ADM-TRAIN, *ALS-Kelso Training Procedure*.

11. PROCEDURE

11.1. Sample Preparation (from ASTM D421-85)

11.1.1. As received samples shall be air-dried at room temperature until thoroughly dried.

11.1.2. A portion of the as received sample shall be used to determine the specific gravity of the sample for later use on the report.

11.1.3. Air-dried samples shall be broken up into the individual aggregates using a mortar and rubber covered pestle. Analyst will take care not to reduce the size of individual particles, but only de-aggregate clumps of dried material.

11.1.4. After de-aggregation, select approximately 10-15g for hygroscopic moisture content. Moisture content is to be measured by drying the sub sample at 110 ± 5 °C.

11.2. Analysis

11.2.1. Select a portion of the air-dried sample for the purpose of testing. Separate the test sample by sieving with a No. 10 sieve. Grind the fraction retained on the No. 10

sieve with a mortar and rubber covered pestle until the aggregations of soil particles are broken up into separate grains and re-sieve that portion.

11.2.2. Wash the fraction retained on the No. 10 sieve free of all fine material, dry at 110 ± 5 °C, and weigh. Record this mass as the mass of course material.

11.2.3. Separate the portion retained on the No. 10 sieve into a series of fractions using the 3/4, 3/8 in, No. 4 (4.75 mm) and No. 10 (2.00 mm) sieves and a Ro-Tap shaker.

11.2.4. Determine the mass of each fraction using a balance accurate to 0.1mg and record on the benchsheet.

11.2.5. Thoroughly mix together the fractions passing the No. 10 sieve in both sieving operations, and by the method of quartering, select a portion weighing approximately 115g for sandy soils and 65g for silt and clay soils.

11.2.6. Take 10 to 15g of the sample passing the No. 10 sieve, dry it at 110 ± 5 °C, and record the weight. Enter these weights on the benchsheet under hygroscopic moisture.

11.2.7. Weight a portion of the remaining sample passing the No. 10 sieve. Use approximately 50g when the sample is mostly silt and/or clay and approximately 100g when the sample is mostly sand. Place this portion in a 250 mL beaker and cover with 125 mL of sodium hexametaphosphate solution and stir until thoroughly wetted. Allow to soak for at least 16 hours.

11.2.8. After the 16 hour soaking period, move wetted sample into a stirring apparatus as described in ASTM D422-63 Section 3.2.1. Stir sample for a period of one minute and transfer slurry into a sedimentation cylinder. Bring the final volume up to 1 L.

11.2.9. Determine the correction factor for each hydrometer by placing 125 mL sodium hexametaphosphate solution in a sedimentation cylinder, and diluting to 1 L with de-ionized water. Place the hydrometers in the cylinder and take a reading. This number will be subtracted from each reading taken. It is important to note that the readings should be taken at the top of the meniscus as it is nearly impossible to see the bottom of the meniscus when soil particles are present in the suspension.

11.2.10. Cap the sedimentation cylinder with Parafilm and turn the cylinder upside down and back for a period of one minute. At the end of the one minute, set the cylinder on the counter, uncap, and take hydrometer readings of the suspension at the following intervals: 2, 5, 15, 30, 60, 250, and1440 minutes. When a hydrometer reading is taken, carefully insert the hydrometer into the suspension 20 to 25 seconds before the desired reading to allow the hydrometer to settle. After the reading is taken, carefully remove the hydrometer from the suspension and place it with a spinning motion in a graduate of clean de-ionized water. Record the temperature of the suspension after each hydrometer reading.

11.2.11. After the last hydrometer reading is taken, transfer the suspension to a No. 200 (75 μm) sieve and wash with tap water until the wash water is clear. Transfer the material to a suitable weighed container and dry to a constant weight in an oven at

110 ± 5 °C, record dried sample weight, and make a sieve analysis of the portion retained using the No. 20, No. 40, No. 60, No. 140, and No. 200 sieves and a pan.

11.2.12. Determine the specific gravity of the sample (ASTM D854) by accurately weighing 10 to 15 grams (on analytical balance). Record weight. Transfer to a 100 ml volumetric flask. Tare flask with sample on analytical balance. Fill with DI water to almost full, attach a vacuum hose to the flask and pull a slight vacuum to remove any air bubbles fill to mark and reweigh (W_b). Transfer the contents (water and sample) to a beaker and evaporate the water to obtain dried material (W_o). Weigh a 100 ml volumetric flask with water alone (W_a). Calculate the specific gravity using the formula:

$$\textbf{Specific Gravity} = W_o / [W_o + (W_a - W_b)]$$

12. QA/QC REQUIREMENTS

For ASTM D422-63 one duplicate analysis shall be conducted on one of every 20 samples, or one sample per batch if fewer than 20 samples are analyzed. The duplicate control limit is RPD≤20.

Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1= Higher Result
R2= Lower Result

13. DATA REDUCTION, REVIEW, AND REPORTING

13.1. The data is entered into a spreadsheet and results determined using the appropriate equations. Refer to Appendix A.

13.2. Reporting and review

13.2.1. The weight of each sediment fraction should be reported to the nearest 0.0001g dry weight. The laboratory should report the results of all samples analyzed (including QA replicates) and should note any problems that may have influenced data quality.

13.2.2. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified for samples (above). These results are then used to calculate QC determinations

13.2.3. The results are entered directly onto the appropriate EDD forms located in the ALS network directory R:\WET\WIP. Refer to Appendix A. Once the results are transferred, the data and report are reviewed.

13.2.4. Refer to the SOP for Laboratory Data Review Process for general instructions for data review.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Non Conformance and Corrective Action (CE-QA008)* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

Refer to the reference method for method performance data available.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Independently perform the analyses. For Initial Demonstration of Capability the data must be reviewed by a supervisor and the supervisor must document that the analyst is trained.

17.2. Training is documented following the SOP for Documentation of Training.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

19. REFERENCES

19.1. ASTM Procedure D422.

20. CHANGES SINCE LAST REVISION

20.1. Reformatted SOP per ALS branding
20.2. Replaced “CAS” references with “ALS”.
20.3. Updated SOP references.
20.4. Sec. 8.1: Added expiration.
20.5. Sec. 11.2.12: Added calculation of specific gravity.
20.6. Sec.12: Added duplicate acceptance criterion.

Appendix A

Benchsheets and Spreadsheets
(6 pages)

Sample Name :	sample 1	Service Request:	0
Lab Code:	-001	Method:	D421 / D422
Client:	0	Date Collected:	01/00/00
Project:	0	Date Received:	01/00/00
Sample Matrix:	0	Date Analyzed:	01/00/00
Time Started:	0000		

Sample Preparation (ASTM D421-85)

(1) Mass of total test sample. (g) (6.1) _____

(3) Mass retained on the No. 4 sieve. (g) (6.2) _____

(2) Coarse Material (6.2)

Coarse material + Tare. (g) _____

Tare weight. (g) _____

(4) Selected portion of fine material. (g) (7.1) _____

Particle Analysis (ASTM D422-63)

Sieve Analysis Of Coarse Material. (6.1)

Gravel 19.0 mm	3/4"	
Gravel 9.50 mm	3/8"	
Gravel 4.75 mm	4	
Gravel 2.00 mm	10	

Sieve Analysis Of Fine Material. (11.1)

Gravel 0.850 mm	20	
Gravel 0.425 mm	40	
Gravel 0.250 mm	60	
Gravel 0.106 mm	140	
Gravel 0.075 mm	200	
Pan	-	

Analysis of fine material.

Hydrometer corrections. (7.3)

	Hydro 1	Hydro 2
Reading:		

Hygroscopic moisture. (8.1)

Air dried (g)	
Tare (g)	
Oven dried + Tare	

Weight of Fine material

Dry wt.+Tare (g)	
Tare (g)	
Fine material (g)	

Determination of Silt/Clay Fraction. (10.2) (10.3) (10.4)

(10.2) T (Min)	(10.2) Hydro Reading	(7.3) Corr. Fact.	(10.4) Temp °C	Specific Gravity		Table 1 a		Table 3 K		
2										
5										
15										
30										
60										
250										
1440										

Analyst : _____ Date : _____

Reviewed by : _____ Date : _____

Client:	0	Service Request:	
Project:	0	Date Collected:	
Sample Matrix:	0	Date Received:	
		Date Analyzed:	

ASTM Method D422 Particle Size

Sample Name: sample 1 Lab Code: -001

Initial Weight of air-dried sample. (6.1)	
Mass retained on the No. 4 sieve. (6.2)	
Air-dried portion of fine material. (7.1)	

Course Sieving ASTM D421 (6.2)

Mass of coarse material (g)	
Percent Recovered	

Coarse sieving (6.1)		Sieve #	Weight (g)	% Passing	Mass Passing
Gravel	19.0 mm	3/4"			
Gravel	9.50 mm	3/8"			
Medium Gravel	4.75 mm	4			
Fine Gravel	2.00 mm	10			
Fine sieving (11.1)					
V.C. Sand	0.850 mm	20			
C. Sand	0.425 mm	40			
M. Sand	0.250 mm	60			
F. Sand	0.106 mm	140			
V.F. Sand	0.075 mm	200			(16.2)

Calculated amount retained on the # 10 sieve. (16.1)	

Total Recovered (g)	
Total Recovered (%)	

(W) (14.2)	

Hygroscopic Moisture (8.1)

Air-dried sample (g)	
Oven dried sample (g)	
Hygroscopic Moisture (13.1)	

Oven-Dried Sample used in hydrometer analysis. (g) (14.1)	

Determination of Silt/Clay Fraction

(10.2) T (Min)	(10.2) Hydro Reading	(7.3) Corr. Fact.	(10.4) Temp °C	Table 1 Specific Gravity	H (Net)	(14.3) a	Table 2 L Eff. Depth	Table 3 K	(14.3) % Passing = H/Wa * 100	(15.1) Dia-meter
2										
5										
15										
30										
60										
250										
1440										

Comments:

Analyzed By:	Date:
Reviewed By:	Date:

	X	Y		
	arithmetic	logarithmic	Convert Y	Value of Y
	Percent Passing	Particle Diameter	mm to nm	Log form
Sieve	(%)	(mm)	(nm)	(log)
3/4"		19.0	19000000	7.279
3/8"		9.5	9500000	6.978
4		4.75	4750000	6.677
10		2.00	2000000	6.301
20		0.850	850000	5.929
40		0.425	425000	5.628
60		0.250	250000	5.398
140		0.106	106000	5.025
200		0.0750	75000	4.875
2			#VALUE!	#VALUE!
5			#VALUE!	#VALUE!
15			#VALUE!	#VALUE!
30			#VALUE!	#VALUE!
60			#VALUE!	#VALUE!
250			#VALUE!	#VALUE!
1440			#VALUE!	#VALUE!

determined hydrometer			
mm	mm to nm	log hyd x	% Passing
0.074	74000	4.87	#VALUE!
0.005	5000	3.70	#VALUE!
0.001	1000	3.00	#VALUE!

COLUMBIA ANALYTICAL SERVICES, INC.

Analytical Report

Client: 0
Project: 0
Sample Matrix: 0

Service Request: 0
Date Collected:
Date Received:
Date Analyzed:

Particle Size Determination
ASTM Method D 422

Sample Name: sample 1
Lab Code: -001

Gravel and Sand
(Sieve Analysis)

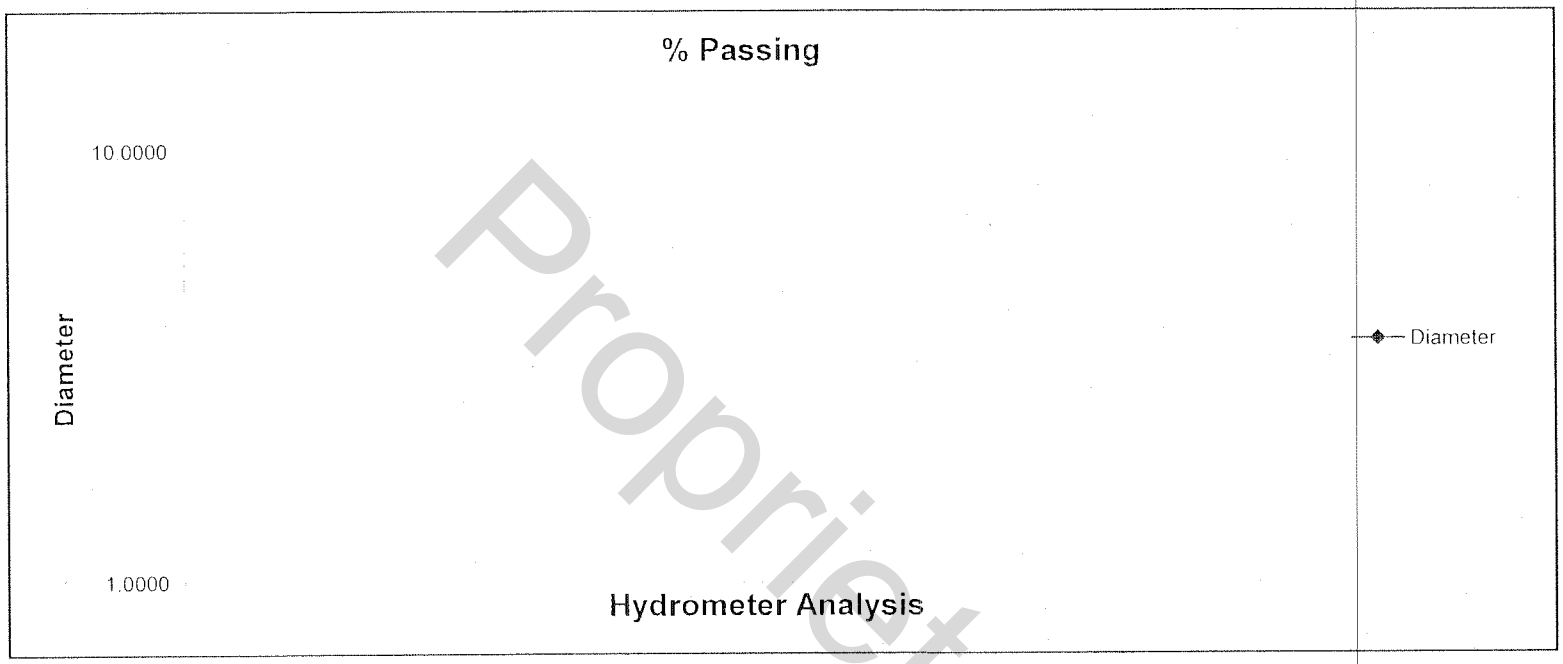
Description	Sieve Size	Weight (g)	Percent Passing
Gravel	No.3/4"(19.0 mm)		
Gravel	No.3/8"(9.50 mm)		
Gravel, Medium	No.4 (4.75 mm)		
Gravel, Fine	No.10 (2.00 mm)		
Sand, Very Coarse	No.20 (0.850 mm)		
Sand, Coarse	No.40 (0.425 mm)		
Sand, Medium	No.60 (0.250 mm)		
Sand, Fine	No.140 (0.106 mm)		
Sand, Very Fine	No.200 (0.0750 mm)		

Silt and Clay
(Hydrometer Analysis)

Particle Diameter	Percent Passing
0.074 mm	#VALUE!
0.005 mm	#VALUE!
0.001 mm	#VALUE!

Approved By: _____ Date: _____
1A/102094

Sample Name: sample 1
Lab Code: -001



HYDROMETER SHAKE SHEET

	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
	7:59 8:00	8:03 8:04	8:09 8:10	8:13 8:14	8:19 8:20	8:23 8:24	9:59 10:00	10:03 10:04	10:09 10:10	10:13 10:14	10:19 10:20	10:23 10:24	1159 1200	1203 1204	1209 1210	1213 1214	1219 1220	1223 1224
MIN																		
2	8:02	8:06	8:12	8:16	8:22	8:26	10:02	10:06	10:12	10:16	10:22	10:26	1202	1206	1212	1216	1222	1226
5	8:05	8:09	***8:15***	***8:19***	***8:25***	***8:29***	10:05	10:09	***10:15***	***10:19***	***10:25***	***10:29***	1205	1209	***1215***	***1219***	***1225***	***1229***
15	***8:15***	***8:19***	***8:25***	***8:29***	8:35	8:39	***10:15***	***10:19***	***10:25***	***10:29***	10:35	10:39	***1215***	***1219***	***1225***	***1229***	1235	1239
30	8:30	8:34	8:40	8:44	8:50	8:54	10:30	10:34	10:40	10:44	10:50	10:54	1230	1234	1240	1244	1250	1254
60	9:00	9:04	9:10	9:14	9:20	9:24	11:00	11:04	11:10	11:14	11:20	11:24	100	104	110	114	120	124
250	12:10	12:14	12:20	12:24	12:30	12:34	2:10	2:14	2:20	2:24	2:30	2:34	410	414	420	424	430	434
1440	8:00	8:04	8:10	8:14	8:20	8:24	10:00	10:04	10:10	10:14	10:20	10:24	1200	1204	1210	1214	1220	1224

ALS Standard Operating Procedure

DOCUMENT TITLE:	SUBSAMPLING AND COMPOSITING OF SAMPLES
REFERENCED METHOD:	N/A
SOP ID:	GEN-SUBS
REVISION NUMBER:	6
EFFECTIVE DATE:	04/01/2015

SUBSAMPLING AND COMPOSITING OF SAMPLES

ALS-KELSO

SOP ID:	GEN-SUBS	Rev. Number:	6	Effective Date:	04/01/2015

Approved By: _____ Date: 2/20/15
Department Supervisor/Technical Director – Harvey Jacky

Approved By: _____ Date: 2/20/15
QA Manager – Lee Wolf

Approved By: _____ Date: 2/24/15
Laboratory Director – Jeff Grindstaff

Issue Date: _____	Doc Control ID#: _____	Issued To: _____

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

TABLE OF CONTENTS

SUBSAMPLING AND COMPOSITING OF SAMPLES

1. SCOPE AND APPLICATION

1.1. This standard operating procedure describes procedures for obtaining subsamples used for laboratory analysis. The procedure also describes general practices for making composite samples from multiple individual samples. Procedures are given for aqueous, soil, sediment, vegetation and miscellaneous matrices. The SOP does not apply to tissue samples. Procedures for tissue samples are described in the GEN-TISP and MET-TDIG SOPs.

1.2. The SOP describes routine, or default, procedures for samples that do not require VOC analyses. Handling of VOC samples is described in SOP VOC-5035. Program or project-specific requirements may differ from those described in the SOP. Samples analyzed by EPA CLP procedures are specifically excluded from this procedure, and will be handled according to the applicable SOW.

1.3. Multi-increment samples require special handling and subsampling procedures. In addition to routine procedures, this SOP also includes instructions for handling and sampling from multi-increment samples submitted to the laboratory.

1.4. This procedure does not apply to situations where the entire sample (container) is used for the analysis.

2. METHOD SUMMARY

2.1. Obtaining a representative analytical subsample from the field sample submitted is essential to providing meaningful data. The subsample must be taken to most closely reflect the predominant composition of the sample. For aqueous and liquid samples, this is usually accomplished by shaking or inverting the sample. For soil, sediment, powders, and other solids the procedures are more involved. Procedures for subsampling are based on the information given in the references listed.

2.2. Some projects may employ multi-increment (MI) sampling in the field. The primary objective of MI sampling is to control the certain statistical errors associated with discrete sampling. Some studies have shown that MI sampling, using 30+ sample increments within a decision unit (a defined field sampling area) may provide a more representative view of contaminant concentrations than traditional discrete sampling approaches. References listed provide additional background on MI sampling. When this approach is taken it is important that laboratory procedures are consistent with field procedures when taking samples.

2.3. Unique sample matrices such as vegetation, wood and wood chips, mechanical parts and filters, etc. pose additional challenges to obtaining representative samples. For these samples the laboratory staff should consult with the Project Manager to determine the subsampling strategy. These special situations will be handled on a case-by-case basis. Service requests should list any specific sample preparation required.

3. DEFINITIONS

3.1. Sample – A portion of material taken from a larger quantity for the purpose of estimating properties or composition of the larger quantity (ASTM).

3.2. Subsample – A portion of a sample taken for the purpose of estimating properties or composition of the whole sample (ASTM).

3.3. Composite sample – A mixture of multiple samples or subsamples produced to result in one sample representative of multiple field samples.

3.4. Representative subsample – A subsample collected in such a manner that it reflects one or more characteristics of interest (a defined by the project objectives) of the laboratory sample from which it was collected (ASTM).

3.5. Multilayered sample – A sample consisting of two or more clearly differentiated components (ASTM).

3.6. Multi-increment sample (MIS) – A field sample consisting of multiple bulk containers from one decision unit (defined in a MIS sampling plan) submitted to the lab for subsampling into a representative sample for analysis. Also known as Incremental Sampling Methodology (ISM).

4. INTERFERENCES

4.1. When obtaining subsamples it is important to minimize any chances for sample contamination or cross-contamination between samples. Work should be performed in an organized and neat manner. Spilling of samples (from overfilled containers, etc.) should be minimized and spills cleaned up. Equipment and laboratory tools used with samples should be cleaned between samples to prevent cross-contamination.

4.2. Analysis-specific interferences are described in the applicable analytical SOP.

5. SAFETY

5.1. 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.

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

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Refer to the analytical SOP for sample collection preservation and storage of samples. Subsamples and composite samples held for later analysis should be preserved and stored in the same manner as specified for field samples.

6.2. MIS Projects

6.2.1. Projects for MI samples may include additional instructions not found in the analytical SOP. The analyst should consult with the Project Manager, or refer to the Project Manager's instructions, prior to working with these samples.

6.2.2. LIMS test codes are used to specify which MIS-analytical tests are needed (e.g. ISM-PAH). These test codes will have holding times associated with them that will ensure the completion of the MIS work before the initial analytical holding times (e.g. sample extraction) lapse.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. Dichloromethane, acetone, and acetonitrile may be used during the noted procedures for cleaning and decontamination of equipment.

8. APPARATUS AND EQUIPMENT

8.1. Laboratory balance capable of weighing the desired sample mass. There are various makes and models of balances available for use, with each department having balances appropriate for its use. For weighing solids and non-aqueous liquids (wastes), use a top-loader balance. Ensure that the mass (sample + container) to be placed on the pan is within the calibration-verified range of the balance.

8.2. Wiley laboratory mill, Model 4. Operate the Wiley mill following the manufacturer's recommendations.

8.3. Sieve shakers.

8.4. Shatter box.

8.5. Mechanical mixer and/or shaker.

8.6. Stainless steel or Glass mixing bowl.

8.7. Metal or disposable spoons and spatulas.

8.8. Aluminum foil.

8.9. Weighing boats, plastic or aluminum

8.10. Clean sample containers and lids (various sizes) as specified in the applicable test SOP.

8.11. Common laboratory glassware/apparatus (beakers, flasks, pipets, syringes, etc.).

8.12. Multi-Increment Samples

8.12.1. Flat spatula, modified to create sides perpendicular to the flat surface used to scoop.

8.12.2. Flat stainless steel masons trowel

8.12.3. Volatile sample containers.

8.12.3.1. 250-500 milliliter (ml) narrow mouth, amber bottles (recommended)

8.12.3.2. 4-8 ounce (oz.) amber jars with Teflon lined septum lids

8.12.4. Large stainless steel spoon or scoop

8.12.5. Large clean containers (a large stainless steel or glass bowl, Ziploc bags, or 5-gallon bucket)

8.12.6. #10 (2mm) sieve

8.12.7. Stainless steel cookie sheet or other tray.

9. PREVENTIVE MAINTENANCE

9.1. No preventive maintenance is required other than normal glassware and apparatus cleaning.

10. RESPONSIBILITIES

10.1. 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.

10.2. It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in ADM-TRAIN, *ALS-Kelso Training Procedure*.

11. PROCEDURE

11.1. Aqueous samples - Subsampling

11.1.1. Examine the sample. Thoroughly mix all samples by vigorous shaking. Immediately open the container and obtain the subsample. Additional filtering of the subsample may be required by the analytical SOP.

11.1.2. If the sample is multi-layered (a water layer with a sand/sediment layer that cannot be mixed or non-aqueous liquid layer) the Project Manager should be consulted on how to proceed with the sample. Additional analyses or sample preparations may be necessary depending on the client's data needs. Document the condition of the sample and decision made on subsampling.

11.2. Aqueous samples - Compositing

11.2.1. The customer may require compositing based on flow rates to create a flow proportional composite. The compositing instructions are included with the Form V or other project specification. Equal volume compositing is assumed if there are no specific instructions provided for compositing ratios.

11.2.2. Setup the necessary glassware and/or sample container receiving the composite sample. Ensure that proper measuring glassware is used, typically a graduated cylinder or volumetric flask for larger volumes and pipet or syringe for smaller volumes.

11.2.3. Working quickly, mix the individual samples (as described above), open the container(s) and obtain the composite aliquot. Add each aliquot to the composite container and cap between samples.

11.2.4. Once all composite aliquots are obtained, cap and mix the composite sample. Label the container appropriately. Complete all documentation necessary to describe the compositing procedure, including samples used, aliquot taken, etc.

11.3. General considerations – Non-liquid samples

11.3.1. The analyst must first understand what the sample matrix of interest is. The project information should be consulted. If the sample appears to be homogeneous (other than extraneous materials described below) particle size reduction is not necessary. Particle size reduction should is performed only when required by the project QAPP, project specifications, or client request. If particle size reduction is required, use the appropriate apparatus (Wiley mill, shatter box, etc.) to perform crushing, grinding, milling, or sieving, and document. Refer to ASTM D6323 for guidelines on performing particle size reduction.

11.3.2. Once the matrix of interest is known, examine the sample for presence of extraneous material. The default procedure is to remove these items, or not include in the representative subsample. However, the presence of these materials should be documented in lab records and the Project Manager should be consulted prior to subsampling. Some examples are given below.

- Soil, solid, and sediment samples may include such material as larger rocks, sticks, leaves, pieces of metal, man-made materials, etc.
- Wood or bark samples may include chunks of soil, mud, rocks, etc.
- Vegetation samples may include chunks of soil, mud, rocks, sticks (not of the sample type, etc.).
- Sediment samples may include rocks, twigs, vegetation, organisms, etc.
- Sediment/marine projects, organisms are typically analyzed under separate sampling and analysis plans.
- Mechanical parts, filters, etc., may include chunks of soil, mud, rocks, sticks, etc.

11.3.3. Examine soil samples to determine if the sample contains significant amounts of water. If the amount of water is greater than approximately 30%, treat the sample as a sediment sample.

11.3.4. Samples which are especially heterogeneous, as well as various special matrices, may require additional preparation. These will be handled on a case-by-case basis after consultation with the appropriate supervisors and Project Manager. Unique matrices for TCLP and other leaching procedures should be handled according to the applicable SOP or reference method.

11.4. Soil/solid Samples

11.4.1. Subsampling samples in jars

11.4.1.1. Using a spatula or other utensil made of an inert material, thoroughly mix and homogenize the sample, making sure to loosen sample from the sides of the container, and continue mixing the entire contents, breaking up soil clumps, etc., until there is no visible segregation of the sample by layer, grain size, color, etc. The sample should appear uniform in color and texture.

11.4.1.2. Once mixed, remove the desired mass of sample for the analysis and document accordingly. Recap the jar and return to storage.

11.4.2. Subsampling samples in sleeves (core samples) and large bulk containers.

11.4.2.1. Empty samples in sleeves into a metal or glass homogenizing container and thoroughly stir using a spatula or other utensil. When homogenized the appropriate sample portions are placed in jars. Perform additional drying and grinding only when specified for the project. Client specifications for drying and grinding will be communicated by the Project Manager.

11.4.2.2. When working with sleeves and resulting homogenized samples or subsamples, always double-check the sample ID on the sleeve against the sample numbers on the samples.

11.4.3. Compositing soil/solid samples

11.4.3.1. Thoroughly mix each individual sample as described above.

11.4.3.2. Combine equal masses from each of the individual samples into a clean stainless steel mixing bowl. The amount used will depend upon the number of analyses to be performed on the composite and/or the amount available. The analyst preparing the composite will document the mass of each individual sample used for the composite, the date and time of compositing, and any other pertinent observations.

11.4.3.3. Thoroughly homogenize the sample using a spatula or other utensil and returned to clean glass jars. The sample container is labeled as a composite and with the sample identification, dated, and initialed.

11.4.3.4. Return the composite sample and remaining individual samples to storage.

11.5. Sediment Samples - Subsampling

11.5.1. Standard procedure calls for mixing overlying water into the sample. EPA SW-846 methods for organic extractions specify to decant and discard overlying water. However, the Puget Sound Protocols and others have options for decanting and discarding this water, decanting and performing a separate water analysis, or mixing the water into the sample. The analyst should confirm which option is to be used on the sample. For projects not within the scope of the Puget Sound Protocols or similar project plans, the overlying water should be decanted and discarded for organics analysis. For metals and inorganics, mix the overlying water into the sample.

Note: If water is decanted and discarded and percent solids is to be applied or determined, a separate solids determination must be made on the decanted sample.

11.5.2. Thoroughly mix and homogenize the sample, making sure to mix the entire contents of the jar. Additional steps may be needed to homogenize the sample (break up soil clumps, etc.). The sample should be mixed so there is a uniform color and texture. See section 11.4.1.1.

Note: Sediment samples may contain considerable amounts of organics matter. Ensure that samples and thoroughly mixed. Document the presence of substantial organic matter, shells, etc.

11.5.3. Once mixed, remove the desired mass of sample for the analysis and document accordingly. Recap the jar and return to storage.

11.5.4. The subsample is transferred to an appropriate, labeled container. The sample container is stored in the appropriate refrigerator in sample receiving and any empty sleeve can be stored at room temperature.

11.6. Sediment Samples - Compositing

11.6.1. Thoroughly mix each individual sample as described above.

11.6.2. Combine equal masses from each of the individual samples into a clean stainless steel mixing bowl. The amount used will depend upon the number of analyses to be performed on the composite and/or the amount available. The analyst preparing the composite will document the mass of each individual sample used for the composite, the date and time of compositing, and any other pertinent observations.

Note: Equal masses are used unless otherwise instructed. It may be required to use the entire jar or other measure.

11.6.3. The sample is thoroughly homogenized using a spatula or other utensil and returned to clean glass jars. The sample container is labeled as a composite and with the sample identification, dated, and initialed.

11.6.4. The composite sample and remaining individual samples are returned to storage.

11.6.5. Samples should be received prepared from the field as sample increments. Although unlikely, in cases where proper preparation of increments from large bulk samples does not occur in the field, the following steps will be taken.

11.6.5.1. When obtaining sample increments from a large bulk container (bucket, large jar, large bag, etc.) be sure to sample from the center and remove the soil 1-2 inches deep. Using the large spoon or scoop, collect the sample increment according to the work plan. Scoop approximately 30-60 grams into a large, clean container and move on to the next sample increment location. Be cautious of oversize material, which means more mass may need to be taken from each increment to end with the 30–50 g sub-sample after sieving (a 5 kg field sample may not be uncommon). Increments can be sieved directly into the bucket, or they can be bagged and sieved later.

11.7. Multi-Incremental Sampling (or Incremental Sampling Methodology (ISM)) – When laboratory subsampling using MIS/ISM is to be used to produce the analytical subsample(s), the following procedures are used.

NOTE: Section 11.7.1 lists the default procedure that is to be used when no other client or project specifications or modifications are given. This section refers to two tables – one specifying default increment amounts for analytical and one listing a "large mass" option that is to be used only when project specified. Section 11.7.2 describes the procedures to be used when the State of Hawaii DOH protocol is specified. Section 11.7.3 describes procedures for analysis method 8330B.

If, after reviewing the project and Service Request information, the analyst has any uncertainty of the MIS approach to take, they must confirm with the Project Manager the protocol to be used.

11.7.1. Default procedure

11.7.1.1. After the 30-50 sample increments have been field collected into a container (a 5 kg field sample may not be uncommon) air dry the entire sample (all received containers) in aluminum pans pre-rinsed 3 times with DCM (dichloromethane/methylene chloride). Note, if Aluminum is a target analyte of interest then substitute the aluminum pans for glass or stainless steel. Air drying may take 2-4 days with occasional stirring.

11.7.1.2. The intent of air drying is to convert the sample to a more manageable form prior to sieving. The sample is considered air-dried when the material appears dry enough to enable disaggregation and sieving. Due to high variability of laboratory samples, sample dryness should be confirmed by a senior analyst or supervisor prior to going further with the procedure.

11.7.1.3. Rinse all utensils and equipment with DCM three times prior to use (stainless steel tray, mortar & pestle, 2mm sieve & catch pan, trowel, ISM spatula).

11.7.1.4. Lightly grind the air dried sample with a mortar & pestle in order to break up dirt and clay chunks (do not size reduce rocks or vegetation) and pass sample through a 2mm sieve.

11.7.1.5. Weigh the remaining +2mm fraction in an appropriate sized jar and record the weight on the ISM bench sheet. Describe the +2mm fraction on the bench sheet (size of rocks, type of any vegetation, etc.).

11.7.1.6. Weigh and record the weight of the -2mm fraction.

11.7.1.7. Mix the sample, dump on a DCM-rinsed stainless steel pan, and spread the sample out with a trowel, forming a rectangle no more than 1cm deep.

11.7.1.8. Divide the sample into a minimum of 30 equal sections (30 to 50 sections is recommended) using the trowel blade. Note that the entire sample should be included in the grid and amount of sample 'outside' the grid outer edges

minimized (however, do not overly manipulate the sample in an attempt to create a perfect grid).

11.7.1.8.1. Collect an equal (approximate) amount of sample from each of the sections based on the applicable table (Table 1 or Table 2) and place into a labeled container (see Tables 1 and 2). Scrape the modified flat spatula along the bottom of the tray and pull straight up to make sure all depths and particle sizes are represented in the collection area. Avoid collecting portions from the edge of gridlines (where the slab has been disturbed). Record the exact final weight of sample for each test on the ISM bench sheet and on the jar. Metals tests should be weighed on an analytical balance. All larger amounts can be done on a 2-place balance.

11.7.1.8.2. Since the each laboratory area must analyze the entire contents of the prepared (or submitted) jar, the subsampling process must be repeated for each separate analysis to be performed on the sample. The subsampling process must be performed for each individual QC sample as well. The entire mass in the jar will be analyzed (TOC is the exception). The results may be less defensible if only a subsample or fraction of the jar contents is analyzed.

11.7.1.8.3. If sample amount is sufficient, it is recommended to repeat the process to obtain a backup sample in the event that re-analysis is required. This 'As Received' backup is placed back in the original sample jar and returned to sample management/custody.

11.7.1.9. Labeling and storage

11.7.1.9.1. Refer to Table 3 for default storage conditions, which are based on how the MIS sample was prepared and on the stability/volatility of target analytes.

11.7.1.9.2. MIS subsamples do not need to be returned to SMO for barcode labeling. Label the sub-aliquots with LIMS sample labels and deliver them to the designated storage areas for each lab section performing analysis. Document the internal custody transfer in a logbook, on the benchsheet, or similar fashion. .

11.7.1.9.3. Place any remaining -2mm sample into jars labeled as "-2mm archive." If there are multiple jars, label them as "1 of 3", "2 of 3", etc. All remaining bulk sample jars must be returned to SMO for barcode labeling and storage.

Usually, the -2mm archive and test archive (back-up samples) jars are placed in a freezer, while the +2mm archive and test jars (with QC) are placed on the room temperature shelves.

11.7.2. Procedure for ISM following State of Hawaii DOH Protocol (see references)

11.7.2.1. Samples requesting the Hawaii DOH procedure require wet and/or dry sieving depending on the test/analytes for which subsamples are being

prepared. Refer to a copy of the Hawaii DOH procedure and/or the Project Manager for details before beginning.

11.7.2.2. Obtain instructions from the Project Manager or Service Request for increment amounts and test subsample amounts. Also refer to the *Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan*, November 12, 2008, Section 4.2.2 for guidance on increment/sample amounts.

11.7.2.3. Subsample bulk MI samples to be tested for SVOCs, including TPH-D, some PAHs, and Mercury, unstable pesticides, should be subsampled without drying or sieving in order to minimize chemical loss or alteration and meet holding times for analysis. Refer to Table 2a. of *Technical Guidance Manual Notes: Decision Unit and Multi-Increment Sample Investigations* , March 2011, State of Hawaii, Department of Health, Reference document number 2011-143-RB.

11.7.2.4. If both SVOC and non-volatile PAHs are targeted contaminants of interest then include testing for both in laboratory subsamples collected from the multi-Increment sample prior to drying and sieving.

11.7.2.5. For wet ISM aliquots, organic tests (SVG/SVM) require a larger aliquot size to accommodate for the extra water content. In most cases, low-level organic tests will require a 40g wet aliquot (max weight capacity for most tests) and normal level tests will require a 20g wet aliquot (double the target dry weight).

11.7.2.6. Use a separate sample from the wet material and test for soil moisture in order to convert analytical results to dry-weight basis.

11.7.2.7. Not all samples from Hawaii require the State of Hawaii DOH procedure. See service request and/or verify with the Project Manager.

11.7.3. Procedure for ISM on 8330B Explosives

11.7.3.1. Samples from Ammunition Depots and anywhere except Firing Ranges (not DOD)

11.7.3.1.1. Follow the basic ISM procedure, except all utensils/pans need rinsed 3 times with Acetonitrile (instead of DCM). Collect a 10.00g aliquot and place in a 4oz amber jar (explosives are sunlight sensitive).

11.7.3.2. Samples from Firing Ranges

11.7.3.2.1. Grinding: For firing ranges, the entire -2mm portion collected from the sieving procedure must be ground to a powder in the shatter box.

11.7.3.3. Method 8330B DOD samples

11.7.3.3.1. Grinding: For DOD work, the entire -2mm portion collected from the sieving procedure must be ground to a powder in the shatter box prior to proceeding. Note: high-speed milling, such as in the shatter box, can elevate sample temperature due to friction. The thermal stability of the target analytes should be considered when performing this grinding procedure. Method 8330 B specifies a 2-minute (or longer) cool down period between five 60-second grinding intervals to maintain acceptable temperatures and minimize loss of volatile energetic contaminants.

11.7.3.3.2. An SRM (supplied by the Organic LC instrument lab) must be taken through the grinding and ISM procedure (already dry so doesn't need to be air dried or sieved). Shatter box 50g to 100g of the well-mixed SRM, and then make a 10g aliquot after grinding. Place the aliquot in 4oz amber jar. Archive the remaining SRM in an amber jar.

11.7.3.3.3. Grinding Blank: Matrix sand blanks (use baked sand) must be ground in the shatter box between each sample and aliquoted following the ISM procedure. The blanks can be ground in equal portions and then recombined at the end to make one sample requiring one ISM aliquot procedure. (Example: To ISM a 200g portion for use in making the final 10g aliquot, divide 200g by the number of samples needing shatter box and grind that amount of matrix sand between each sample. Recombine all ground matrix sand at the end and ISM one 10g aliquot from the 200g of ground matrix sand.) Archive the remaining matrix sand in an amber jar.

11.8. Analyte-Specific Considerations

11.8.1. Metals

11.8.1.1. It has been proven that grinding can greatly improve the reproducibility for metals analyses. However, erosion of the metals surfaces used in grinding may contribute to a high bias in the samples. It is recommended that the tungsten carbide grinding mill is used when grinding soils in the shatter box thereby limiting the amount of potential bias in the prepared samples.

11.8.1.2. When grinding soil samples that may potentially contain ores of malleable metals (e.g. Lead, Copper, Tin) be aware that the malleable particles may tend to smear during grinding, and may be lost from the samples to equipment surfaces. This anomaly may bias sample results low, decontamination of equipment surfaces may be difficult and could result in high bias in subsequent samples from carry over.

11.8.1.3. Reproducibility for Lead analyses in unground, incrementally sampled (IS) samples from small arms firing ranges may have an unacceptable large variability. The large variability for Lead may be due to single particles of Lead between one and two millimeters in diameter being present in only some of the replicate splits. If the end data is to assess risk of accidental ingestion of Lead, precision for the concentration of lead contained in larger particles may be of less interest then the Lead contained in the finer, less than 0.25 mm, fraction. Using a finer mesh sieve (0.25 mm rather than 2

mm) may improve precision and reproducibility. However, sieving unground samples through sieves finer than two millimeters is not appropriate if analyzing for high explosives or propellants. Typical mass sizes for energetic analytes are in particles sizes greater than 0.59 millimeters.

11.8.1.4. MI samples collected for Arsenic analyses that contain greater than 20 mg/K total Arsenic should be tested for bioaccessible Arsenic. This should be discussed with the project manager. If deemed appropriate, the entire <2mm fraction of the respective samples should be sieved to a ≤0.25 mm, representatively sub-sampled and analyzed for bioaccessible Arsenic using SBRC methodology, 1-2 grams are required.

11.8.2. Polycyclic Aromatic Hydrocarbons (PAHs)

Currently there is little information in published procedures specific to the laboratory processing of ISM samples for PAHs. The default procedure above is used, but the 8330B procedure is an acceptable option if specified.

11.8.3. Perchlorate

11.8.3.1. Currently there is little information in published procedures specific to the laboratory processing of ISM samples for Perchlorate. Laboratory processing of samples per EPA Method 8330B as described in Section 11.7.3 is recommended. A 10 gram sample is required for propellants and explosives. It is recommended that a 10 gram ISM sample should be extracted with 100mL of DI water for Perchlorate analysis by EPA Method 314.0.

11.9. Vegetation samples

Since vegetation samples often are not amenable to standard mixing and homogenization techniques, or because specific sections of the vegetation are targeted, these are handled on a case-by-case basis with instructions from the Project Manager. The PM will obtain sample-specific instructions from the client, and then communicate the specifications to the lab personnel using the ALS Form V or similar project specification document for the project. If the client makes reference to specific procedures, methods, or technical references, the PM will make the document(s) available to the laboratory personnel.

11.10. Paperboard samples

11.10.1. In general, prepare paperboard samples as described below. Project-specific instructions may replace these.

11.10.2. Review the Service Request and determine the jars you will need. In general, the jars needed are as follows:

Metals = 8 oz. jar.
Voa = 8 oz jar.
Dioxins = 8 oz jar.
SVG = 32 oz jar.
SVM = 32 oz jar.
PHC (8315) = 8 oz jar.
Gen Chem (not Biology) = 8 oz jar.

11.10.3. Make sample labels according to test and put on appropriate jar.

11.10.4. If FDA Ext is on the Service Request for PHC you will need a 16 oz jar per sample. Do Not Composite into one sample. Each sample is a separate sample.

11.10.5. Prepare the FDA Ext first.

- Cut the sheet of paper into one 10" x 10" square.
- Cut the 10" x 10" into strips at the cut lines 7 ½, 5, and 2 ½.
- Cut the strips at the cut lines 7 ½, 5, and 2 ½. This will make 16 2" squares.
- Put each sample into its own jar and label accordingly. i.e. (1, 2 3, etc.); PHC will composite in the lab.

11.10.6. Put one sheet of paper into shredder, run the shredder back and forth to get the entire sample out. Use tongs to remove any remaining sample in bottom of shredder (make sure to turn off before you do this)

11.10.7. Shred equal amounts of each sample (1 or more sheets) to create the composite sample. Homogenize sample thoroughly and aliquot into each jar needed for analysis. Put sample storage on lid of jar.

11.10.8. Dioxins are sent out to Houston. Label the lid "Out".

11.10.9. Take all composites to Sample Management for ALS labeling and shelving.

11.10.10. Update composites as being done….Open Starlims, double click on Ad Hoc by Test (Under Results entry), highlight samples composited and click the Update to Done button at the top of page. Do not add jars when asked. Just click the X on the right hand corner.

12. QA/QC REQUIREMENTS

12.1. Ongoing QC Samples required for each sample batch (20 or fewer samples) are described in the SOP for Sample Batches and in the determinative SOPs.

13. DATA REDUCTION AND REPORTING

13.1. All compositing and subsampling data must be recorded into the bench records by the analyst. In addition to sample volumes and masses, sample identifications, etc., this should include descriptions of unique samples or sample components. Figure 1 shows the current MIS benchsheet template used to record MIS subsampling. Other project-specific benchsheets may apply.

13.2. It is the supervisor's responsibility to ensure that analytical data is reviewed and to ensure that all quality control requirements have been met.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for corrective action procedures. Personnel at all levels and positions in the laboratory are to be alert to

identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example. Table 4 lists typical actions taken.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

15.1. Not applicable.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. 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 ALS EH&S Manual.

16.2. It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements. Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

16.3. This method uses non-halogenated solvents and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and disposed of in accordance with Federal and State regulations.

16.4. This method uses Dichloromethane and any waste generated from this solvent must be placed in the collection cans in the lab. The solvent will then be added to the hazardous waste storage area and recycled off site.

17. TRAINING

17.1. Training outline – Training Plan

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of time. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.2. Training is documented following the SOP for *Documentation of Training*.

17.2.1. When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. Not applicable.

19. REFERENCES

19.1. Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, U.S. Environmental Protection Agency, EPA/600/R-03/027, November 2003.

19.2. Standard Guide for Laboratory Subsampling of Media Related to Waste Management Activities, ASTM D 6323, Annual Book of ASTM Standards, 1999.

19.3. Test Methods for Evaluating Solid Waste, EPA SW-846, Final Update III, December 1996.

19.4. Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound, January, 1996.

19.5. Draft Guidance on Multi-Increment Soil Sampling State of Alaska, Department of Environmental Conservation, March 2007.

19.6. Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan, November 12, 2008.

19.7. Technical Guidance Manual Notes: Decision Unit and Multi-Increment Sample Investigations, March 2011, State of Hawaii, Department of Health, 2011-143-RB.

19.8. Standard operating Procedure, In Vitro Method for Determination of Lead and Arsenic Bioavailability; Solubility/Bioavailability Research Consortium, Document 8601-102.011-0601-1099-RN01.

19.9. Figure 1: Multi Incremental Sampling Worksheet.

20. CHANGES SINCE THE LAST REVISION

20.1. Updated entire SOP to current ALS format and sections.
20.2. Corrected various typographical and grammatical errors, and similar minor changes made to improve readability.
20.3. Changed Project Manager to Project Manager throughout.
20.4. Section 3.6 – updated MIS definition to include ISM.
20.5. Section 6.2 – revised to add MIS holding time discussion.
20.6. Section 8.12.1 – revised to specify modified spatula with perpendicular sides.
20.7. Section 10.2 – New (default language added).
20.8. Section 11 – much of the section is reorganized with previous content to improve the relationship of topics and reading flow.
20.9. Section 11.7 – beginning note is new.
20.10. Section 11.7.1.2 – revised language on air drying completeness.
20.11. Section 11.7.1.8 – significant revision to improve association of topics and provide not detailed instructions. Moved Table from section to end of SOP.
20.12. Section 11.7.1.8 and 11.7.1.8.1 – revised to add detail to increment sampling technique.
20.13. Sections 11.7.1.9 – revised to implement new processes.
20.14. Section 11.7.2 – added note to see references.
20.15. Section 11.8.2 – revised to indicate default procedure.
20.16. Section 13 – updated to refer to MIS benchsheet in Figure 1 and use of other MIS sheets.
20.17. Section 14 – New (default format).
20.18. Section 15 – New (default format).
20.19. Section 16 – New (default format).
20.20. Section 17 – updated with default language.
20.21. Section 18 – New (default format).
20.22. Section 19 – Updated references to Hawaii DOH documents.
20.23. Table 1 – added default basis and container columns.
20.24. Table 2 – new table.
20.25. Table 3 – new table.
20.26. Figure 1 – updated.

TABLE 1
Default Multi-Incremental Sampling Information

Test	Subsample Basis	Aliquot	Approximate Amount per Increment	Container	QC Requirement
Total Solids	Air Dried	15.00 g	0.50 g	2 oz. soil jar	DUP per 10
200.7 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 10
6010 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 20
200.8 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 10
6020 Metals	Air Dried	1.0000 g	0.0333 g	Metals digestion tube	DUP/MS per 20
Mercury	Air Dried	0.5000 g	0.0167 g	Mercury digestion cup	DUP/MS per 20
8081 PEST	As Received	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8081 PEST-LL	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB-LL	Air Dried	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8151	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270 LL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH ULL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
8290/Dioxin	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8330B*	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
Diesel or Residual Range Organics (DRO, RRO)**	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
TOC	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	None
Backup Sample	As Received	30.00 g	1.00 g	Back into original jar	N/A

* For DOD projects refer to the DOD 8330B protocols.
** Alaska Methods AK102 and AK103 call for the extraction of from 10-30 g of sample material (soil). For MIS purposes, the minimum required amount of material per analysis is 30 g.

TABLE 2
"Large Mass" Multi-Incremental Sampling Information

Test	Subsample Basis	Aliquot	Approximate Amount per Increment	Container	QC Requirement
Total Solids	Air Dried	15.00 g	0.50 g	2 oz. soil jar	DUP per 10
200.7 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 10
6010 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 20
200.8 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 10
6020 Metals	Air Dried	10.00 g	0.333 g	Metals digestion tube	DUP/MS per 20
Mercury	Air Dried	5.00 g	0.167 g	Mercury digestion cup or 2 oz. soil jar	DUP/MS per 20
8081 PEST	As Received	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8081 PEST-LL	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8082 PCB-LL	Air Dried	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8151	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
8270 LL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
PAH ULL	As Received	20.00 g	0.67 g	2 or 4 oz. soil jar	MS/DMS per 20
8290/Dioxin	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	MS/DMS per 20
8330B*	As Received	10.00 g	0.33 g	2 or 4 oz. soil jar	MS/DMS per 20
Diesel or Residual Range Organics (DRO, RRO)**	As Received	30.00 g	1.00 g	2 or 4 oz. soil jar	MS/DMS per 20
TOC	Air Dried	15.00 g	0.50 g	2 or 4 oz. soil jar	None
Backup Sample	As Received	30.00 g	1.00 g	Back into original jar	N/A

* For DOD projects refer to the DOD 8330B protocols.
** Alaska Methods AK102 and AK103 call for the extraction of from 10-30 g of sample material (soil). For MIS purposes, the minimum required amount of material per analysis is 30 g.

TABLE 3
Storage of Multi-Incremental Subsamples

Test	Storage
Total Solids	Room Temperature
200.7 Metals	Room Temperature
6010 Metals	Room Temperature
200.8 Metals	Room Temperature
6020 Metals	Room Temperature
Mercury	Room Temperature
8081 PEST	4 ± 2˚C
8081 PEST-LL	4 ± 2˚C
8082 PCB	Room Temperature
8082 PCB-LL	Room Temperature
8151	4 ± 2˚C
8270	4 ± 2˚C
8270 LL	4 ± 2˚C
PAH	4 ± 2˚C
PAH ULL	4 ± 2˚C
8290/Dioxin	Room Temperature
8330B*	4 ± 2˚C
Diesel or Residual Range Organics (DRO, RRO)*	4 ± 2˚C
TOC	Room Temperature
Backup Sample	4 ± 2˚C

* For DOD projects refer to the DOD 8330B protocols.

FIGURE 1

Multi-Incremental Sampling Benchsheet Template

Service Request #: _____

Analysis: **Multi Incrimental Sampling (MIS/ISM)**

Sample Number	+2mm Fraction Air Dried Weight (g)	Comments, Description of +2mm Fraction	-2mm Fraction Air Dried Weight (g)	-2mm Fraction Multi Incrimental Sample Aliquots									
				Test	Sample Wt. (g)	Test	Sample Wt. (g)	Test	Sample Wt. (g)	Test	Sample Wt. (g)	Test	Sample Wt. (g)

Comments:

Balance ID: K-BALANCE- 42

Prepared By:	**Date:**
Reviewed By:	**Date:**

ALS Standard Operating Procedure

DOCUMENT TITLE:	METALS DIGESTION
REFERENCED METHOD:	EPA 3050B
SOP ID:	MET-3050B
REVISION NUMBER:	14
EFFECTIVE DATE:	2/15/2015

METALS DIGESTION

ALS-KELSO

SOP ID:	MET-3050B	Rev. Number:	14	Effective Date:	02/15/2015

Approved By: _____ Date: 2/3/15
Department Manager/Technical Director – Jeff Coronado

Approved By: _____ Date: 2/3/15
QA Manager – Lee Wolf

Approved By: _____ Date: 2/3/15
Laboratory Director – Jeff Grindstaff

Issue Date: _____ Doc Control ID#: _____ Issued To: _____

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date

TABLE OF CONTENTS

METALS DIGESTION

1. SCOPE AND APPLICATION

1.1. This procedure uses techniques described in method 3050B for acid digestion of sediments, sludges, and soil samples designated for "Total Metals" analysis. One technique is designed for the preparation of samples for analysis by flame AA (Methods 7420-Pb, 7742-Se, and 7062-As) or ICP-OES (methods 6010 and 200.7). Another technique is given for the preparation of samples for analysis by GFAA (see SOP MET-GFAA for methods) or ICP-MS (methods 6020 and 200.8). This procedure is not a *total digestion* technique, but extracts "environmentally available" elements from the sample of interest.

2. METHOD SUMMARY

2.1. One-gram equivalent dry weight sediment, sludge, or soil samples are digested with repeated additions of nitric acid (HNO3) and hydrogen peroxide (H2O2). For GFAA and ICP-MS analysis the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL. For ICP-OES and flame AA analysis, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed prior to dilution to a final volume of 100 mL.

3. DEFINITIONS

3.1. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.2. **Preparation Batch** - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.3. **Sample**

3.3.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.3.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.4. **Quality System Matrix** - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.4.1. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.5. **Laboratory Control Sample (LCS)** - A laboratory blank that has been fortified with target analyte and used to determine that the analysis is in control.

3.6. **Matrix Spike (MS)** - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The percent recovery is calculated. The MS is used to evaluate the effects of the sample matrix on the method used for the analysis. The concentration of the spike should be at three to five times the sample result or at levels specified by a project analysis plan.

3.7. **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.

3.8. **Method Blank (MB)** - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

4. INTERFERENCES

4.1. Refer to the determinative method for a discussion of interferences.

5. SAFETY

5.1. 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.

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

5.3. Hydrochloric and/or Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield must be used while pouring concentrated 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.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Samples may be collected in plastic or glass jars. Non-aqueous samples are refrigerated at 4 ± 2˚C from receipt until analysis.

6.2. The recommended holding time is 6 months from the day of sampling.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking (ADM-RTL)* for the complete procedure and documentation requirements.

7.2. Reagent water: ASTM Type I water (resistivity ≥18 MΩ-cm, conductivity ≤0.056 uS/cm).

7.3. Concentrated Nitric Acid: J.T. Baker "Instra-analyzed", Trace Metals Grade

7.4. Concentrated Hydrochloric Acid: EMD GR ACS

7.5. Hydrogen Peroxide (30%): EMD GR ACS

7.6. Standards

7.6.1. Stock standards may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. The vendor assigned expiration date is used.

7.6.2. Metals spiking solutions: Five spiking solutions are needed to prepare the matrix spike sample; SS1, SS2, SS3, SS4, and SS5.

7.6.3. Follow the formulations laid out on the "Metals Spike Form" (see attached Table A). These solutions are prepared in acid rinsed Class A volumetric flasks using purchased custom mixed standards or 1000 ppm single analyte standards. Aliquots are made using acid rinsed Class A volumetric pipettes of the appropriate size.

7.6.4. SS1 (Al, Ag, Ba, Be, Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Sb, V, and Zn): Fill a 1000 mL volumetric flask approximately half full with reagent water, add 50 mL of nitric acid and mix. Next add 100 mL of the custom mixed standard (CAS-CAL-14) purchased from "Inorganic Ventures". In addition add 50 mL of 1000 ppm Antimony(use the Antimony standard that does not contain HCL.) Dilute to volume with reagent water, mix thoroughly and transfer to a 1000 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

7.6.5. SS2 (GFAA As, Cd, Cu, Pb, Se, Tl): Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 2.0 mL each of 1000 ppm Arsenic, Cadmium, Copper, Lead, Selenium, and Thallium. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

7.6.6. SS3 (As, Se, Tl, and Hg): Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 50 mL each of 1000 ppm Arsenic, Selenium, and Thallium. Add 6.0mL of 1000ppm Hg. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

7.6.7. SS4 (B, Mo): Fill a 500 mL volumetric flask approximately half full with reagent water, add 25 mL of nitric acid and mix. Next add 50 mL each of 1000 ppm Boron and Molybdenum. Dilute to volume with reagent water, mix thoroughly and transfer to a 500 mL Teflon bottle for storage. The solution's expiration date is determined by the earliest expiration date of any single component in the solution.

7.6.8. SS5 (K,Na,Mg,Ca): Fill a 200 mL volumetric flask approximately half full with reagent water add 10.0 mL of nitric acid and mix. Next add 20 mL each of 10,000 ppm Potassium, Sodium, Magnesium and Calcium. Dilute to volume with reagent water, mix thoroughly and transfer to a 250 mL Teflon bottle for storage. The solution's expiration date is determined by the earliest expiration date of any single component in the solution.

7.7. Metals reference material (ERA Priority PollutnT/CLP Inorganic Soil) for use as the laboratory control sample. The expiration date is assigned by the manufacturer.

7.8. Teflon beads, Teflon boiling chips, or other suitable blank material.

8. APPARATUS AND EQUIPMENT

8.1. 125 mL plastic cup beaker cup, calibrated at 50mL and 100mL

8.2. Borosilicate watch glasses

8.3. Block Digester, calibrated to maintain 95˚C ± 2˚C

8.4. Hot Plates: "Thermolyne Cimerac 3", calibrated to maintain 95˚C ± 2˚C

8.5. Laboratory balance, top-loader capable of reading 0.01g

8.6. Digestion tubes, 125 mL - Environmental Express. An accuracy and precision verification check must be made with each new vendor lot prior to use. Refer to the SOP for *Checking Volumetric Labware ADM-VOLWARE*, for further detailed instructions. Performance data must meet the accuracy and precision requirements specified in Table 1 (*ADM-VOLWARE*) for non-volumetric labware used for measuring initial and/or final digestate volumes.

8.7. USS # 10 sieve.

9. PREVENTIVE MAINTENANCE

9.1. All maintenance activities are recorded in a maintenance logbook. Pertinent information must be in the logbook. Maintenance entries should include date, symptom of problem, corrective actions, and description of maintenance, date, and name. The log should contain a reference to return to analytical control.

9.2. Maintenance for this procedure is generally limited to glassware cleaning, pipet monitoring, and hot plate calibration. Procedures for glassware washing are described in the SOP for Metals Laboratory Glassware Cleaning (MET-GC). Procedures for pipet monitoring are given in the SOP for Checking Volumetric Labware, (ADM-VOLWARE).

9.3. Each hotplate or block digester is uniquely identified and the temperature is verified with each batch of samples. To perform the verification, a certified thermometer is placed in a container half filled with mineral oil, which is then placed in the center of the hotplate or block digester. The thermometer does not touch the bottom of the container. The temperature is turned to the 95˚C setting and the mineral oil is allowed to come to temperature. The analyst will verify that the hotplate gives a temperature of 95˚C ± 2˚C. If not, the thermostat is adjusted until the thermometer reads and maintains 95˚C ± 2˚C. The thermostat is then marked to clearly

indicate the correct setting to be used during sample digestion (when using Hot Plates.). Each hot Block has an assigned calibrated thermometer. The Temperature and the correction factor of the assigned thermometer is recorded on the digestion bench sheet.

10. RESPONSIBILITIES

10.1. 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.

10.2. It is the responsibility of the department supervisor/manager to document analyst training.

11. PROCEDURE

11.1. Record all digestion and sample information on the applicable benchsheet.

11.2. Mix the sample thoroughly to achieve homogeneity. Sieve if necessary using a USS #10 sieve.

11.3. It can be difficult to obtain a representative sample with wet or damp materials. As per Method 3050B, wet samples may be dried, crushed, and ground to reduce subsample variability, however, drying is not recommended since drying may affect the extraction of the analytes of interest in the sample.

11.4. Weigh approximately 1g of sample into a 125ml plastic beaker cup and record the weight to the nearest 0.01g. For sludge's and sediments that have high moisture content, use more sample. A plastic 10.0 mL disposable pipette is used to measure 10.0 mL of sample. The volume and weight of the pipetted sample is recorded. In cases where the sludge is very thick a 10.0 mL graduated cylinder may be used. The objective is to use about 1g of dry weight sample. For analysis of Lead by Flame AA, use about 2.5g of dry wt. sample and change the final dilution volume to 50ml. This will achieve a lower detection limit needed for most projects. At this point add the appropriate spiking solutions directly onto the designated spike sample prior to addition of reagents.

11.5. Add 5ml reagent water and 5ml concentrated HNO_3. Place in a hot block, cover and reflux (without boiling) at 95ºC for 10 to 15 minutes. Allow the sample to cool. Add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat the addition of 5ml of HNO_3 and reflux over and over until no brown fumes are given off. Reduce the digestate volume to approximately 5 mL without boiling or digest for two hours maintaining a covering of solution over the bottom of the beaker at all times. If this occurs discard the digestate and begin with a new sample aliquot.

Note: The 95°C hot block temperature must be monitored and documented on a per-batch basis. The actual measured temperature, thermometer correction factor, and corrected temperature must all be recorded.

Note: All Wisconsin samples must digest for 2 hours after generation of brown fumes has ceased.

11.6. Cool the sample and add 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 in the hot block until effervescence subsides. Remove from hot block and cool the beaker.

11.7. Continue to add 30% H_2O_2 in 3ml 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. When the peroxide additions are complete cover the sample with a watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°± 5°C without boiling for 2 hours. Do not let the samples go to dryness, by ensuring the solution covers the bottom of the vessel at all times.

Note: All Wisconsin samples must digest for 2 hours after the final peroxide addition.

If the sample is being prepared for analysis by ICP-OES or Flame AA, add 10 mL of concentrated HCl. If the sample is being prepared for ICP-MS or GFAA analysis no HCl is added. Dilute the sample to 100 mL with reagent water: ASTM Type I water (resistivity $\geq$18 MΩ-cm, conductivity $\leq$0.056 uS/cm) in a 125 mL plastic beaker cup.

Note: For method 7062 and 7742 samples, the 3050B soil digestion is modified as follows: After the final peroxide addition (i.e. before the final reduction stage) add 5.0mL of concentrated hydrochloric acid and reduce the digestate volume to less than 5.0mL, but not to dryness. After cooling, dilute the digestate to 100mL with reagent water.

11.8. Cover and reflux the Flame AA and ICP samples for 15 minutes at 95°C. After cooling, the samples may be diluted to 100ml for ICP analysis, or 50ml for Flame AA analysis.

11.9. Particulates in the digestates that may clog the nebulizer are allowed to settle overnight, or the digestates may be centrifuged.

11.10. To improve the solubility for Antimony, Barium, Lead and Silver, the following modification of the digestion procedure may be used as directed by the client or project chemist.

11.10.1. Weigh (to the nearest 0.01g) 1.00 g of sample into a 125ml plastic cup. For sludges and sediments that have high moisture content, use more sample. The objective is to use about 1g of dry weight sample.

11.10.2. Add 2.5mL HNO_3 and 10mL HCl and cover with a watch glass. Reflux for 15 minutes.

11.10.3. Filter the digestate through Whatman No. 41or equivalent filter paper and collect in a 100mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5mL of hot (95°) HCl, and then with 20mL of hot (95°) reagent water. Collect washing in the same volumetric flask.

11.10.4. Remove the filter and residue from the funnel, and place them back in the beaker. Add 5mL HCl, cover and heat at 95° ± 5° until the filter paper dissolves. Remove from the heat and wash the cover and sides with reagent water.

11.10.5. Filter the residue and collect the filtrate in the same 100mL flask. Allow to cool, then dilute to volume.

11.10.6. If precipitation occurs in the flask upon cooling, do not dilute to volume. Instead, add up to 10mL of HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with water.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

12.1.1. The accuracy and precision of the procedure must be validated before analyses of samples begin, or whenever significant changes to the procedures have been made. To do this, four blank matrix samples are spiked with the LCS spike solution, then prepared and analyzed.

12.2. Monitor Hot Blocks and Hotplates on a per batch basis. Report all deficiencies to the Lab Manager. Corrective action must be taken.

12.3. Digest one laboratory control sample with each batch. Weigh 1.00 g of the current lot of Environmental Resource Associates PriorityPollutnT/CLP Inorganic Soil prepared reference material into a 150 mL beaker and digest as per the procedure.

12.4. Digest one preparation blank (method blank) per digestion batch, or per 20 samples whichever is more frequent. For the method blank, use Teflon beads, Teflon boiling chips, or other suitable solid blank material and follow the digestion procedures.

12.5. Digest one duplicate and one spiked sample with each sample matrix. Prepare one duplicate and spike sample per each digestion batch, or per twenty samples whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

12.6. Soil spikes for ICP and ICP-MS are prepared by adding 2.0 mL of SS1, and 1.0 mL of SS3, SS4 and SS5 directly to the sample aliquot, prior to the addition of any water or acid. Fill out a spiking data sheet and keep it with the digestion data sheets.

12.6.1. For GFAA digestions 2.0 mL of SS2 is added to the sample aliquot designated as the matrix spike sample. The matrix spike sample is then digested as per the procedure.

13. DATA REDUCTION AND REPORTING

13.1. Digestion data sheets including weights and volumes used and reagents/acids are completed and a prep run number or batch lot number is assigned and attached to the data sheet. The lot numbers for the reagents used are added to the digestion data sheet (see Attachments).

13.2. Spiking sheets are included (See Attachments).

13.3. Data Review and Assessment

13.3.1. Refer to the *SOP for Laboratory Data Review Process* for general instructions for data review.

13.3.2. It is the supervisor's responsibility to ensure that digestions data is reviewed to ensure that all quality control requirements have been met and documentation is complete.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

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

15.2. The method detection limit (MDL) is established using the procedure described in the SOP CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification*. Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

16.3. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS EH&S Manual for details.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2. Training is documented following the *SOP ADM-TRAIN*.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. The method uses 2 mL of water and 3 mL of H202 in step 11.6. The lab does not add the 2 mL of water. 3.0 mL aliquots of 30% H202 in lieu of 1.0 mL aliquots are added subsequently.

19. REFERENCES

19.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. EPA SW-846, 3rd Edition, Final Update III, Method 3050B, December 1996.

19.2. Table A – METALS SPIKING SOLUTIONS CONCENTRATIONS FORM

20. CHANGES SINCE THE LAST REVISION

20.1. Reformatted SOP to current ALS format and style.
20.2. Updated internal SOP references.
20.3. Few minor changes (correct typos and errors, etc.).
20.4. Section 7.6.6 – revised to include Mercury in SS3 solution.
20.5. Section 8.6 – revised to update tubes to those in use.
20.6. Section 11.5 – Added second note regarding Wisconsin samples.
20.7. Section 11.7 – Inserted first note regarding Wisconsin samples.
20.8. Section 12.6 – revised to list spiking with current solution formulations.
20.9. Section 13.3 – New section.
20.10. Section 14 – updated to current standard language for the section.
20.11. Section 15 – updated to current standard language for the section.
20.12. Section 16 – updated to current standard language for the section.
20.13. Table A – updated

TABLE A
METALS SPIKING SOLUTIONS CONCENTRATIONS FORM

Solution Name	Element	mL of 1000ppm Solution	Final Volume	Solution Conc. mg/L	Enter ml Added
	HNO3	50.0	1000ml	-	
	Al	100*	1000ml	200	
	Ag	100*	1000ml	5	
	Ba	100*	1000ml	100	
	Be	100*	1000ml	5	
	Cd	100*	1000ml	5	
	Co	100*	1000ml	50	
K-MET SS1	Cr	100*	1000ml	20	
	Cu	100*	1000ml	25	
	Fe	100*	1000ml	100	
	Pb	100*	1000ml	50	
*** Add after HNO3	Mn	100*	1000ml	50	
and before cas cal	Ni	100*	1000ml	50	
-14	Sb***	50	1000ml	50	
when making the	V	100*	1000ml	50	
solution	Zn	100*	1000ml	50	
	HNO3	25.0	500ml	-	
K-MET SS2	As	2.0	500ml	4	
	Cd	2.0	500ml	4	
	Pb	2.0	500ml	4	
	Se	2.0	500ml	4	
	Tl	2.0	500ml	4	
	Cu	2.0	500ml	4	
K-MET SS3	HNO3	25.0	500ml	-	
	As	50.0	500ml	100	
	Se	50.0	500ml	100	
	Tl	50.0	500ml	100	
	Hg	6	500ml	12	
	HNO3	25	500ml	-	
K-MET SS4	B	50	500ml	100	
	Mo	50	500ml	100	
K-MET SS5	HNO3	10.0	200ml	-	
	K**	20	200ml	1000	
	Na**	20	200ml	1000	
	Mg**	20	200ml	1000	
	Ca**	20	200ml	1000	

K-MET GFLCSW	HNO3	10.0	1000ml	-	
	As, Pb, Se, Tl	5.0	1000ml	2.5	
	Cd	-	-	1.25	
	Cu	2.5	1000ml	2.5	
K-MET QCP-CICV-1	Ca, Mg, Na, K	no dilution	-	2500	
	Al, Ba	no dilution	-	1000	
	Fe	no dilution	-	500	
	Co, Mn, Ni, V, Zn	no dilution	-	250	
	Cu, Ag	no dilution	-	125	
	Cr	no dilution	-	100	
	Be	no dilution	-	25	
K-MET QCP-CICV-2	Sb	no dilution	-	500	
K-MET QCP-CICV-3	As, Pb, Se, Tl	no dilution	-	500	
	Cd	no dilution	-	250	

* Denotes volume of mixed stock standard.
** Denotes 10,000 ppm individual stock standards.

ALS Standard Operating Procedure

DOCUMENT TITLE:	DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (METHOD 6020)
REFERENCED METHOD:	EPA 6020, 6020A
SOP ID:	MET-6020
REVISION NUMBER:	16
EFFECTIVE DATE:	1/01/2015

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (METHOD 6020)

ALS-KELSO

SOP ID:	MET-6020	Rev. Number:	16	Effective Date:	1/01/2015

Approved By: _____ Date: 12/9/14
Department Manager/Technical Director – Jeff Coronado

Approved By: _____ Date: 12/9/14
QA Manager – Lee Wolf

Approved By: _____ Date: 12/9/14
Laboratory Director – Jeff Grindstaff

Issue Date: _____ Doc Control ID#: _____ Issued To: _____

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date

TABLE OF CONTENTS

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (METHOD 6020)

1. SCOPE AND APPLICATION

1.1. This procedure is used to determine the concentrations of certain elements in water, soil, tissues, aqueous and non-aqueous wastes, and sediment samples using EPA Method 6020 or 6020A. Table 1 indicates analytes that are typically determined by this procedure and lists the standard Method Reporting Limits (MRLs) for each analyte in water and soil. Project-specific MRLs may apply, and if lower than standard MRLs, it is demonstrated through method detection limit determinations and analysis of MRL standards that the MRL is achievable. Method Detection Limits (MDLs) that have been achieved are listed in Table 1. These may change as new studies are performed.

1.2. The complexity of the technique generally requires outside study of appropriate literature as well as specialized training by a qualified spectroscopist. 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.

2. METHOD SUMMARY

2.1. Prior to analysis, samples must be digested using appropriate sample preparation methods. The digestate is analyzed for the elements of interest using ICP-mass spectrometry (ICP-MS).

2.2. Methods 6020 and 6020A describe 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.

3. DEFINITIONS

3.1. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2. Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The

sequence ends when the set of samples has been analyzed or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. **Sample**

3.2.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3. **Quality System Matrix** - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1. Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2. Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3. Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4. Nonaqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5. Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7. Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.4.1 through 3.4.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8. Miscellaneous matrices – Samples of any composition not listed in 3.4.1 – 3.4.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are 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 method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the midpoint of the calibration range or at levels specified by a project analysis plan.

3.5. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6. Surrogate - Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction and chromatography, but which are not normally found in environmental samples. The purpose of the surrogates is to evaluate the preparation and analysis of samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

3.7. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.8. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.9. Independent Verification Standard (ICV) - A pre-mixed, purchased, second-source standard analyzed after the calibration curve. This is used to verify the validity of the initial calibration standards

3.10. Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.11. Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.12. Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4. INTERFERENCES

4.1. 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.

4.2. 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 6020/A for further discussion.

5. SAFETY

5.1. 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.

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

5.3. Hydrochloric and/or 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.

5.4. 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.

5.5. 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.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Aqueous samples are typically collected in plastic containers. Aqueous samples are preserved with nitric acid (pH<2), then refrigerated at 4 ± 2°C from receipt until digestion. Soil or solid samples may be collected in plastic or glass jars. Non-aqueous samples are refrigerated at 4 ± 2°C from receipt until digestion.

6.2. Samples are prepared via procedures in SOPs MET-DIG, MET-3020A, or MET-3050 depending on matrix and project specifications.

6.3. Digestates are stored in the appropriate volumetric containers. Following analysis, digestates are stored until all results have been reviewed. Digestates are neutralized prior to disposal through the sewer system, 2 weeks after data is reviewed.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. All standards are prepared from NIST traceable standards. The expiration dates are assigned according to the EPA method and the vendor's assigned expiration dates. For example, working ICS solutions are prepared weekly in accordance with Method 6020, Section 5.6.1.

7.1.1. 1000 ppm Single Element Stock Standard Solutions: Each stock standard is store at room temperature on shelves located in room 113 of the metals lab. The manufacturer, lot number, and expiration date of each stock standard is recorded in a bound logbook also located in room 113. Additionally each stock standard is given a unique, identifying name.

7.1.2. Intermediate Standard Solutions: Intermediate mixed stock solutions are made from the individual stock standards described above. The individual component of each mixed solution is recorded in a bound logbook located in the ICP-MS laboratory and mixed solution is given a unique, identifying name. The expiration date for the intermediate standard is the earlier of any one of its stock components.

7.1.3. Calibration Standards: Calibration standards are made fresh daily from the intermediate standard solutions. Each individual intermediate standard used in the calibration standard is recorded in a bound logbook located in the ICP-MS laboratory, and the calibration standard solution is given a unique, identifying name. The calibration standards unique name is used on the raw data to link the data to the subsequent prepared standards and ultimately the original purchased stock standard.

7.2. Standards Preparation

7.2.1. Expiration of all standard solutions defaults to the earliest expiration date of an individual component unless otherwise specified.

7.2.2. Calibration Standards

The calibration standard is prepared from two intermediate stock solutions. These solutions are prepared in acid rinsed 1000 mL Class A volumetric flasks following the formulations laid out on the attached example standard sheet (see Attachments). The working calibration standard is made daily by aliquoting 2.5 mL of each of the intermediate solutions in to a 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This standard is also used as the Continuing Calibration Verification (CCV).

7.2.3. Initial Calibration Verification (ICV)

7.2.3.1. The ICV intermediate stock solution is prepared in an acid rinsed 100 mL Class A volumetric flask. The solution is prepared by adding 2.0 mL of Inorganic Ventures QCP-CICV-1, 1.0 mL each of QCP-CICV-2 and QCP-CICV-3, 0.5 mL of 1000 ppm Molybdenum stock solution, 0.5 mL of 1000 ppm Uranium stock solution, and 0.5mL of 1000ppm B, Bi, Sr, Ti solution and diluting to volume with 1% HNO3.

7.2.3.2. The working ICV solution is prepared by aliquoting 0.5 mL of the mixed ICV intermediate solution into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3.

NOTE: The ICV solution is not at the midpoint of the linear range which may be as high as 1000 µg/L for some elements. The ICV solution used is a premixed standard purchased from Inorganic Ventures and contains the elements of interest between 2.5 and 100 µg/L. This solution provides calibration confirmation at more representative levels, given that most ICP-MS analyses are quantifying analytes in the low-ppb to sub-ppb range.

7.2.4. Interference Check Solutions (ICSA and ICSAB)

7.2.4.1. The ICSA is prepared in an acid rinsed 50 mL Class B volumetric flask by aliquoting 1.0 mL of Elements ICSAm (CS-CAK02) solution and diluting to volume with 1% HNO3.

7.2.4.2. The ICSAB is prepared in an acid rinsed 50 mL Class B volumetric flask by aliquoting 1.0 mL of Elements ICSAm (CS-CAK02), 0.125 mL of Inorganic Ventures 6020ICS-9B, and 0.250 mL of 10 ppm Molybdenum solutions and diluting to volume with 1% HNO3.

7.2.5. Post-digestion spikes are performed by adding appropriate amounts of the calibration intermediate solutions to aliquots of the sample digestate. The volumes of each standard used vary based on the native concentrations found in the field samples. Refer to the post-digestion spike in Section 12 for details.

7.2.6. Refer to the appropriate digestion SOP for details of LCSW and matrix spike solution composition and preparation.

7.2.7. Tuning / Mass Calibration Solution

7.2.7.1. A 1ppm intermediate solution containing Be, Bi, Ce, Co, In, Li, Pb, Mg, and U is prepared by adding 1.0 mL of each from 1000 ppm stock standards to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid. The expiration date for the intermediate solution is the earliest of any one of its stock components.

7.2.7.2. The working solution is prepared in three ways:

- For the Agilent: a 1.0 ppb tune/mass calibration solution is prepared by adding 1.0 mL of intermediate solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid.
- For the X-Series (K-ICP-MS-03) instrument a 5.0 ppb tune/mass calibration solution is prepared by adding 5.0 mL of intermediate solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid.
- For the NexION (K-ICP-MS-04) instrument a 2.0 ppb tune/mass calibration solution is prepared by adding 2.0 mL of intermediate solution to an acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric acid.
- The expiration date for this solution is taken from the intermediate stock above.

7.3. Internal Standards Stock Solution – Prepare solutions by adding appropriate amounts of each 1000 ppm single element stock solution to a acid rinsed 1000 mL volumetric flask and diluting to volume with 1% nitric. Use this solution for addition to blanks, calibration standards

and samples at a ratio of 0.5 mL of internal standard to 100 mL of solution, or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump. The typical solutions are:

- XSeries instrument: 50ppb Li; 25ppb Sc, Ga, Y; 10ppb Rh, In, Lu, Tm, Th.
- Agilent instrument: 2ppm Li, Sc, Y, Ga, Ge, Ce, Tm, In, Lu, Th
- NexION instrument: 30ppb In, Tm, Lu, Th; 60ppb Li, Rh, Au; 75ppb Sc; 100ppb Ga,Y; 500ppb Ge

7.4. Additional Reagents

7.4.1. Reagent water, ASTM Type II

7.4.2. "OmniTrace Ultra" Concentrated Nitric Acid (EM Science # NX0408-2)

7.4.3. Argon (Airgas Industrial Grade – 99.999% pure, bulk delivered)

8. APPARATUS AND EQUIPMENT

8.1. ICP/MS instruments:

8.1.1.

Instrument:	Thermo Electron X-Series
Nebulizer:	Conikal
Spray Chamber:	VG Peltier-cooled
Cones:	Nickel Sampler (1.0 mm orifice)
	Nickel Skimmer (0.75 mm orifice)

8.1.2.

Instrument:	NexION 300D
Nebulizer:	PFA-ST MIcroflow
Spray Chamber:	Cyclonic, Peltier-cooled
Cones:	Nickel Sampler (1.0 mm orifice)
	Nickel Skimmer (0.75 mm orifice)

8.1.3.

Instrument:	Agilent 7700
Nebulizer:	MicroMist
Spray Chamber:	Double Pass quartz spray chamber
Cones:	Nickel Sampler (1.0 mm orifice)
	Nickel Skimmer (0.75 mm orifice)

9. PREVENTIVE MAINTENANCE

9.1. All maintenance is documented in the instrument logbook. ALS/Kelso 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.

9.2. Most routine maintenance and troubleshooting is performed by ALS staff. 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 and cleaning RF contact strips
- checking air filters and cleaning if necessary
- checking the oil mist 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
- replace the electron multiplier as necessary

10. RESPONSIBILITIES

10.1. 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.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the SOP for Documentation of Training, is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. Refer to method 6020 (or 6020A) and the instrument manuals for detailed instruction on implementation of the following daily procedures preceding an analytical run.

11.2. After the instrument has been placed in the "Operate" mode, begin completing the daily instrument log (see Attachments). Refer to the instrument manuals for the optimum settings for each instrument.

11.3. The following parameters are monitored to assure awareness of changes in the instrumentation that serve as signals that optimum performance is not being achieved, or as indicators of the physical condition of certain consumable components (i.e. EMT and cones).

11.3.1. Multiplier Voltages

11.3.2. Gas Flows - Coolant Ar

11.3.3. The nebulizer and auxiliary flows are adjusted later as part of the optimizing procedure.

11.4. Optimization

11.4.1. Gas Flows

11.4.1.1. Allow a period of not less than 30 minutes for the instrument to warm up.

11.4.1.2. Aspirate a mixed tune solution into the plasma and monitor the instrument output signal of In at mass 115 on the ratemeter. Adjust the nebulizer and auxiliary flows to obtain maximum signal. Adjust the tension screw on the peristaltic pump to obtain minimum noise in the analytical signal. Record flow rates and note any large variances.

Note: Significant differences in flow rates will be observed for different torches and cones.

11.4.2. Tuning

11.4.2.1. Ion Lens Setting - While monitoring the output signal of a mixed tune solution at mass 115 on the ratemeter, adjust the ion lenses to obtain maximum sensitivity. Refer to the instrument manual for details on performing the adjustments.

11.4.2.2. Mass Calibration - Aspirate the tune / mass calibration solution described in section 7.2 and perform the mass calibration using the instrument's Mass Calibration program. (Refer to the instrument manual for details pertaining to the mass calibration procedure.) The acceptance criteria for the mass calibration is <0.1 amu from the true value. If the mass calibration fails criteria re-tune the instrument and perform the mass calibration procedure again.

11.4.2.3. Resolution Check - Using the spectra created during the mass calibration procedure; perform the resolution check to assure the resolution is less than 0.9 AMU at 5% peak height. If the resolution does not pass criteria adjust the instrument's resolution settings, run a new scan of the mass calibration solution and recheck.

11.4.2.4. Stability Check - Using the tune / mass calibration solution, perform a short-term stability check as per EPA Method 6020 or 6020A. The relative standard deviations of five scans for each element in the tune solution must be < 5%. If the test does not pass criteria determine the cause (i.e. dirty cones, improper tune, etc.) correct the problem and re-run the test.

11.5. Analytical Run

11.5.1. Calibrate the instrument using a calibration blank (Standard 0), composed of reagent water and 1% nitric acid, and the working calibration standard (8.2.2). The masses typically monitored and those used for quantification are listed in Table 2. These masses are set as defaults in the instrument's analytical procedures. To begin select the correct method. Nebulize Standard 0 (Blank) into the plasma. Allow 1-2 minutes for system to equilibrate prior to establishing baseline. Follow directions on computer screen to perform standardization. Nebulize the working calibration standard into the plasma. The operator must sign and date the first page of standardization.

11.5.2. After the first CCB and before the ICS standards a CRA (MRL / LLICV / LLCCV) standard is analyzed. Method 6020 requires the detection to be > the MDL but < 2x the MRL. For 6020A, the criteria are 70-130% recovery. For DoD projects, the CRA criteria are 80-120%.

Note: For 6020A the LLCCV must also be analyzed at the end on the analytical run sequence.

11.5.3. Perform the analysis in the order listed below. A daily run log of all samples analyzed is maintained.

Initial Calibration Verification (ICV)
Continuing Calibration Verification (CCV)
Initial Calibration Blank (ICB)
Continuing Calibration Blank (CCB)
CRA (MRL / LLICV / LLCCV)
ICSA
ICSAB
Analyze 10 Samples
CCV
CCB
Analyze 10 Samples
CCV
CCB

Repeat sequence as required to complete analytical run, analyzing CCVs/CCBs every 10 analyses and at the end of the run.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery of for each analyte must be 85-115% (for water, and within the LCS limits for soils) and the RSD <20%.

12.2. Method Detection Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank matrices at a level near or below the MRL. Follow the procedures starting in Section 11 to analyze the samples. Refer to CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification* details of performing the MDL study.

12.2.2. Calculate the average concentration found (x) and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. MDL's must be verified annually or whenever there is a significant change in the background or instrument response.

12.3. For method 6020A, an LLQC sample (a CRA that is carried through the digestion) must be analyzed to verify accuracy at the MRL. The recovery must be 70-130%.

12.4. Instrument Detection Limits (IDLs) and linear ranges studies are performed quarterly. These will be calculated and made available to the ICP-MS operator. Linear range studies determine the Linear Dynamic Range (LDR) of the each instrument by analysis of a high concentration standard with results with ± 10% of the expected value. For non-DoD projects samples may be quantified between the MRL and 90% of the LDR without flagging. The Linear Calibration Range (LCR) is established by the highest calibration standard.

- **Note:** IDLs must be < LOD for DOD projects. DoD project samples with concentrations above the calibration standard must be diluted to bring results within the quantitation range. The LOQ and cal standard establish the quantitation range. The lab may report a sample result above quantitation range if the lab runs and passes a CCV that is > sample result.

12.5. The Initial Calibration Verification (ICV) standard is analyzed immediately after calibration. The results of the ICV must agree within ±10% of the expected value. If the control limits are exceeded, the problem will be identified and the instrument recalibrated.

12.6. A Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are analyzed after calibration then every 10 samples thereafter with a final CCV/CCB closing the final samples of the analytical run.

12.6.1. The results of the CCV must agree within ±10% of the expected value.

12.6.2. The CCB measured values must be less than the MRL / LOQ for each element for standard applications. Other project-specific criteria may apply (for DoD QSM projects CCB can have no analytes > the LOD).

12.6.3. If the control limits are exceeded, the problem will be identified and corrective action taken. The instrument recalibrated. The previous 10 samples must be reanalyzed.

12.7. The ICSA and ICSAB solutions are analyzed after calibration and before any field samples. The solutions are then reanalyzed every 12 hours. Results of the ICSA are used by the analyst to identify the impact of potential interferences on the quality of the data. Based on these results appropriate action should be taken when interferences are suspected in an field sample including, but not limited to, selecting and alternative isotope for quantification, manual correction of the data, elevating the MRL, selection of an alternative method (e.g. optical ICP, GFAA) or flagging the result as estimated when no other action is possible. Results for the spiked analytes in the ICSAB solution must agree with ± 20% of the expected value.

INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

	Solution A Concentrations (mg/L)	Solution B Concentrations (mg/L)
Al	20.0	20.0
Ca	60.0	60.0
Fe	50.0	50.0
Mg	20.0	20.0
Na	50.0	50.0
P	20.0	20.0
K	20.0	20.0
S	20.0	20.0
C	40.0	40.0
Cl	424	424
Mo	0.05	0.05
Ti	0.40	0.40
As	0.0	0.025
Cd	0.0	0.025
Cr	0.0	0.050
Co	0.0	0.050
Cu	0.0	0.050
Mn	0.0	0.050
Ni	0.0	0.050
Se	0.0	0.025
Ag	0.0	0.0125
V	0.0	0.050
Zn	0.0	0.025

NOTE: The concentration of interfering elements in the ICSA and ICSAB solutions are spiked at levels 5 times lower than recommended in Table 1 of Method 6020A. Running the full strength solutions as described in 6020A introduces too much material approximately 0.35 % dissolved solids into the ICP-MS system when trying to conduct low level analysis. Since the ICP-MS instrumentation is able to handle a maximum of 0.2% solids, the 6020A ICSA solution is higher in interfering components than any sample that would run through the instrument. However, the ICS solutions will be analyzed at levels that will provide approximately 0.1% dissolved solids.

12.8. Internal standards are used to correct for physical interferences. Masses used as internal standards include; ^{71}Ga, ^{115}In, ^{6}Li, ^{175}Lu, ^{103}Rh ^{45}Sc, and ^{89}Y. These internal standards are used in combination to cover the appropriate mass ranges. Internal standard correction is applied to the analytical isotopes via interpolation of the responses from nearest internal standard isotopes (Thermo instruments) or direct correlation of analyte to IS (NexION). This function is performed in real-time by the instruments operating system. Internal standards must be run within 50 AMU of the masses that are analyzed. Internal standard recoveries must fall between 30% and 125% when running method 6020, or 70-125% when running method 6020A Revision 1. If not, then the sample must be reanalyzed after a fivefold or greater dilution has been performed.

12.9. A method blank is digested and analyzed with every batch of 20 (or fewer) samples to demonstrate that there are no method interferences. If the method blank shows any hits above the MRL for standard applications, or >½ the MRL for DoD projects or > 1/10 the sample result, corrective action must be taken. The MB can only be rerun once. Corrective action includes recalculation, reanalysis, system cleaning, or re-extraction and reanalysis.

12.10. Laboratory Control Samples are analyzed at a frequency of 5% or one per batch, whichever is greater. Refer to the current ALS-Kelso DQO spreadsheets for the LCS limits. For method 6020A, the LCS recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range. Project, QAPP, or client-specific control limits may supersede the limits listed, but laboratory limits should be consistent with specified limits in order to establish that the specified limits can be achieved. If the control limits are exceeded, the associated batch of samples will be re-digested and reanalyzed.

12.11. A digested duplicate and matrix spike are analyzed at a frequency of 5% or one per batch, whichever is greater. Refer to the current ALS-Kelso DQO spreadsheets for the matrix spike limits. The matrix spike recovery and relative percent difference will be calculated while analysis is in progress. Project, QAPP, or client-specific control limits may supersede the limits listed. If the control limits are exceeded, the samples will be re-digested and reanalyzed, unless matrix interference or sample non-homogeneity is established as cause. In these instances, the data and the report will be flagged accordingly.

12.12. A Matrix Spike sample is digested one per batch, or per 20 samples (i.e. 5%). Default spike concentrations are listed in the sample digestion SOPs. Spike concentrations may be adjusted to meet project requirements. The matrix spike recovery will be calculated while the job is in progress. Where specified by project requirements, a matrix spike duplicate may be required. Matrix spike recovery criteria are derived from lab data. For method 6020A, the recovery limits are 75-125%. If statistical in-house limits are used, they must fall within the 75-125% range. In some cases, project-specific QC limits may be required. Unless specified otherwise, for DoD QSM projects the project LCS criteria will be used for evaluation of matrix spikes. If an analyte recovery is outside acceptance limits proceed with the additional quality control tests described in sections 12.13 and 12.14. Based on results of these tests, the physical nature of the sample (e.g. homogeneity), and any specific project requirements, a determination can then be made as to appropriate corrective action (e.g. re-digestion, reporting with a qualifier, alternative methodologies, etc.). If the analyte concentration is >4x the spike level the spike control limit is no longer applicable and no action is required. For specifics on the preparation and composition of matrix spike solutions refer to the appropriate digestion SOP.

Note: For DOD projects a MS/MSD is required with every extraction batch. The %RSD should be < 20%.

12.13. Post Digestion Spike Test: When analysis is conducted via 6020 a post digestion spike must be performed for each matrix and each batch of sample. The prepared sample or its dilution is spiked for each element of interest at a concentration sufficiently high to be observed. Typically 20 µL of 10,000 ppb intermediate stock is added to a 10 mL aliquot of sample. If analyte concentrations are elevated in the sample, spiking at a higher concentration may be required. The post spike should be recovered to within 75-125% of the known value or within the laboratory derived acceptance criteria. When analysis is conducted via 6020A, the post digestion spike test is performed whenever matrix spike or replicate criteria are exceeded. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. If this spike fails, then the dilution test

(Sec. 12.14) should be run on this sample. If both the matrix spike and the post digestion spike fail, then matrix effects are confirmed.

12.14. Dilution Test: When analysis is conducted via 6020, a serial dilution test must be performed for each matrix and each batch of sample. For sample concentrations that are sufficiently high (minimally, a factor of greater than 100 times the MDL), the analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. When analysis is conducted via 6020A, the dilution test is performed whenever matrix spike or replicate criteria and post digestion spike criteria are exceeded. If the dilution test fails then a chemical or physical effect should be suspected. Corrective action can include additional dilution of the sample, the use of alternate methodologies, etc. or the data can be flagged and reported. The exact course of action will be dependent on the nature of the samples and project requirements and should be discussed with the project manager.

12.15. Instrument blanks should be evaluated for potential carryover and rinse times need to bring the analyte signal to within the CCB criteria discussed above in section 12.6.2. Results from instrument blanks run after standards or control samples should be used to establish levels at which carryover in samples may occur. Samples exhibiting similar effects of carryover should be reanalyzed.

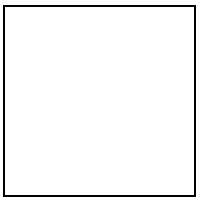
12.16. Refer to the Quality Control section of EPA Methods 6020 and 6020A for additional information describing required QA/QC. Note that the nomenclature of certain QC samples in the method differs from that of the CLP SOW, but the function of those samples is equivalent in both cases.

13. DATA REDUCTION AND REPORTING

13.1. Calculations

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.

Aqueous samples are reported in µg/L:



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

Solid samples are reported in mg/Kg:

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

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

NOTE: If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the SOP for Total Solids.

13.2. Common isobaric interferences are corrected using equations equivalent to those listed in EPA Methods 6020, 6020A, and 200.8. Monitoring of multiple isotopes for a single element provides a mechanism for identifying isobaric interferences. Refer to the Interferences section of EPA methods for additional descriptions of possible interferences and the mechanisms required for adequately compensating for their effects.

13.3. Data Review and Reporting

13.3.1. The ICP-MS operator reviews the MS data and signs and dates the Data Review Form. A qualified senior staff spectroscopist performs a secondary review of the data and the Data Review Form is signed and dated. The data is then delivered to the report generation area where it is filed in the service request file. Once all of the data for the service request is complete, a CAR is generated.

13.3.2. The data is saved on the local hard drive and is also copied to the appropriate directory on the network. The data directories are located at r:\icp\wip\data. The data is kept on the local directory for 1 month. The network files are periodically backed up on disc or network tape.

13.3.3. For "non-production" work (such as method development or research/development studies) the analyses are performed under the direction of a senior spectroscopist. All associated data is scrutinized by the senior spectroscopist. Original raw data and associated records are archived in the analytical project file.

13.3.4. The final review and approval of all data is performed by qualified spectroscopists.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformity and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels

- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

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

15.2. The method detection limit (MDL), limit of detection (LOD) and limit of quantitation (LOQ) are established using procedures described in CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.* Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS, Kelso Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

16.3. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 5-9 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS *EH&S Manual* for details.

17. TRAINING

17.1. Refer to the SOP ADM-TRAIN, *ALS-Kelso Training Procedure* for standard procedures.

17.2. A minimum of two senior level spectroscopists are to be maintained on staff at all times. Senior spectroscopists are defined as individuals with a minimum of ten years combined education and experience in, or related to atomic spectroscopy. Of those ten years, a minimum of two years of ICP-MS experience is required.

17.3. All technical staff is encouraged to attend one technical seminar per year. In addition to the technical seminars, senior spectroscopists are required to complete a one week training session offered by the instrument manufacturer.

17.4. On-the-job-training occurs daily with the senior spectroscopists providing direction to new operators. The physical operation of the equipment is relatively simple. The data reduction

and troubleshooting requires extensive experience that can only be gained by hands-on operation of the instrument and assisted evaluation of raw data.

17.5. Training outline

17.5.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.5.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.5.3. Perform initial precision and recovery (IPR) study as described above for water or soil samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.6. Training and proficiency is documented in accordance with the SOP ADM-TRAIN.

18. METHOD MODIFICATIONS

18.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

19. REFERENCES

19.1. USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update III Method 6020, Revision 0, September 1994.

19.2. USEPA, Test Methods for Evaluating Solid Waste, SW-846, Update IV, Method 6020A, Revision 1, February 2007.

19.3. Agilent and Thermo Elemental Instrument Manuals

20. CHANGES SINCE THE LAST REVISION

20.1. Reformatted SOP to current ALS format.
20.2. Minor changes (correct typos and errors, etc.) throughout SOP.
20.3. Section 1 – revised to eliminate redundant language.
20.4. Section 7.2.7.2 – updated to replace Excell with Agilent
20.5. Section 7.3 – revised to list specific internal standards and concentrations.
20.6. Section 8.1 – updated instrument information.
20.7. Section 11.4.2.3 – revised to correct peak height %.
20.8. Sections 12.10 and 12.12 – revised to refer to DQO tables for QC limits
20.9. Section 16 – revised to include default language.
20.10. Section 17 – revised to include default language and be consistent with 200.8 SOP.
20.11. Table 1 – updated.
20.12. Attachments updated.

TABLE 1
TARGET ANALYTES, MDLs, and MRLs

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL mg/kg
6020A	EPA 3050B	Aluminum	Soil	0.6	2
6020A	EPA 3050B	Antimony	Soil	0.02	0.05
6020A	EPA 3050B	Arsenic	Soil	0.2	0.5
6020A	EPA 3050B	Barium	Soil	0.02	0.05
6020A	EPA 3050B	Beryllium	Soil	0.005	0.02
6020A	EPA 3050B	Bismuth	Soil	0.02	0.05
6020A	EPA 3050B	Boron	Soil	0.05	0.5
6020A	EPA 3050B	Cadmium	Soil	0.009	0.02
6020A	EPA 3050B	Chromium	Soil	0.07	0.2
6020A	EPA 3050B	Cobalt	Soil	0.009	0.02
6020A	EPA 3050B	Copper	Soil	0.04	0.1
6020A	EPA 3050B	Lead	Soil	0.02	0.05
6020A	EPA 3050B	Manganese	Soil	0.02	0.05
6020A	EPA 3050B	Molybdenum	Soil	0.02	0.05
6020A	EPA 3050B	Nickel	Soil	0.04	0.2
6020A	EPA 3050B	Selenium	Soil	0.2	1
6020A	EPA 3050B	Silver	Soil	0.005	0.02
6020A	EPA 3050B	Thallium	Soil	0.002	0.02
6020A	EPA 3050B	Tin	Soil	0.02	0.1
6020A	EPA 3050B	Uranium	Soil	0.003	0.02
6020A	EPA 3050B	Vanadium	Soil	0.08	0.2
6020A	EPA 3050B	Zinc	Soil	0.2	0.5

TABLE 1 – continued

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL ug/L
6020A	MET-DIG (CLP)	Aluminum	Water	0.2	2
6020A	MET-DIG (CLP)	Antimony	Water	0.01	0.05
6020A	MET-DIG (CLP)	Arsenic	Water	0.05	0.5
6020A	MET-DIG (CLP)	Barium	Water	0.006	0.05
6020A	MET-DIG (CLP)	Beryllium	Water	0.008	0.02
6020A	MET-DIG (CLP)	Bismuth	Water	0.005	0.05
6020A	MET-DIG (CLP)	Boron	Water	0.07	0.5
6020A	MET-DIG (CLP)	Cadmium	Water	0.005	0.02
6020A	MET-DIG (CLP)	Chromium	Water	0.02	0.2
6020A	MET-DIG (CLP)	Cobalt	Water	0.006	0.02
6020A	MET-DIG (CLP)	Copper	Water	0.03	0.1
6020A	MET-DIG (CLP)	Iron	Water	0.3	1
6020A	MET-DIG (CLP)	Lead	Water	0.004	0.02
6020A	MET-DIG (CLP)	Manganese	Water	0.006	0.05
6020A	MET-DIG (CLP)	Molybdenum	Water	0.008	0.05
6020A	MET-DIG (CLP)	Nickel	Water	0.04	0.2
6020A	MET-DIG (CLP)	Selenium	Water	0.4	1
6020A	MET-DIG (CLP)	Silver	Water	0.005	0.02
6020A	MET-DIG (CLP)	Thallium	Water	0.005	0.02
6020A	MET-DIG (CLP)	Tin	Water	0.01	0.05
6020A	MET-DIG (CLP)	Uranium	Water	0.003	0.02
6020A	MET-DIG (CLP)	Vanadium	Water	0.05	0.2
6020A	MET-DIG (CLP)	Zinc	Water	0.09	0.5

TABLE 1 – continued

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL mg/kg
6020A	PSEP TISSUE	Aluminum	Tissue	0.2	2
6020A	PSEP TISSUE	Antimony	Tissue	0.002	0.05
6020A	PSEP TISSUE	Arsenic	Tissue	0.02	0.5
6020A	PSEP TISSUE	Barium	Tissue	0.005	0.05
6020A	PSEP TISSUE	Beryllium	Tissue	0.003	0.02
6020A	PSEP TISSUE	Bismuth	Tissue	0.003	0.05
6020A	PSEP TISSUE	Boron	Tissue	0.2	2
6020A	PSEP TISSUE	Cadmium	Tissue	0.002	0.02
6020A	PSEP TISSUE	Chromium	Tissue	0.02	0.2
6020A	PSEP TISSUE	Cobalt	Tissue	0.003	0.02
6020A	PSEP TISSUE	Copper	Tissue	0.02	0.1
6020A	PSEP TISSUE	Iron	Tissue	0.2	1
6020A	PSEP TISSUE	Lead	Tissue	0.0005	0.02
6020A	PSEP TISSUE	Manganese	Tissue	0.008	0.05
6020A	PSEP TISSUE	Molybdenum	Tissue	0.008	0.05
6020A	PSEP TISSUE	Nickel	Tissue	0.02	0.2
6020A	PSEP TISSUE	Selenium	Tissue	0.2	1
6020A	PSEP TISSUE	Silver	Tissue	0.006	0.02
6020A	PSEP TISSUE	Thallium	Tissue	0.0009	0.02
6020A	PSEP TISSUE	Tin	Tissue	0.003	0.05
6020A	PSEP TISSUE	Uranium	Tissue	0.0008	0.02
6020A	PSEP TISSUE	Vanadium	Tissue	0.007	0.2
6020A	PSEP TISSUE	Zinc	Tissue	0.06	0.5

Table 2
Target Element Masses

Analyte	ISOTOPES ANALYZED	ISOTOPE REPORTED
Aluminum	27	27
Antimony	121,123	123
Arsenic	75	75
Barium	135,137,138	137
Beryllium	9	9
Cadmium	111,112,114	111
Chromium	52,53	52
Cobalt	59	59
Copper	63,65	65
Lead	206,207,208	208
Manganese	55	55
Molybdenum	95,97,98	98
Nickel	60,61,62	60
Selenium	77,78,82	82
Silver	107,109	107
Thallium	203,205	205
Uranium	238	238
Vanadium	51	51
Zinc	66,67,68	66

ATTACHMENT A
Example Standard Sheets

SOLUTION: ICP-MS, 200.8 INTERMEDIATE STOCK
MATRIX: 2% HNO3

ELEMENT		ALIQUOT OF 1000 ppm Std./1000ml	CONCENTRATION (µg/L)
HNO3		50.0 ml.	5%
Al		1.0 ml.	1000
Sb		1.0 ml.	1000
As		1.0 ml.	1000
Ba		1.0 ml.	1000
Be		1.0 ml.	1000
Cd		1.0 ml.	1000
Cr		1.0 ml.	1000
Co		1.0 ml.	1000
Cu		1.0 ml.	1000
Fe		1.0 ml.	1000
Pb		1.0 ml.	1000
Mn		1.0 ml.	1000
Mo		1.0 ml.	1000
Ni		1.0 ml.	1000
Se		1.0 ml.	1000
Tl		1.0 ml.	1000
V		1.0 ml.	1000
U		1.0 ml.	1000
Zn		1.0 ml.	1000

SOLUTION: ICP-MS, 200.8 SILVER INTERMEDIATE STOCK
MATRIX: 5% HNO3

ELEMENT		ALIQUOT OF 1000 ppm Std./1000ml	CONCENTRATION (µg/L)
HNO3		50.0	5%
Ag		1.0	1000

SOLUTION: ICP-MS 25ppb Calibration Standard and CCV
MATRIX: As Required

SOURCE	ALIQUOT PER 100 ml.	CONCENTRATION (µg/L)
HNO3 (Ultrex)	As Required	As Required
INTERMEDIATE STOCK	2.5	25.0
SILVER INTERMEDIATE STOCK	2.5	25.0

ATTACHMENT B
Isobaric Interference Corrections

Interference Equations:

Equation Name: Default

?SW82 = I82 * 0.7
?%SE77 = ?SE82 * 0.8484163
?%ARCL77 = I77 - ?%SE77
?%ARCL75 = ?%ARCL77 * 3.0650407
?AS75 = I75 - ?%ARCL75
?%CR53 = I52 * 0.1133652
?%CLO53 = I53 - ?%CR53
?%CLO51 = ?%CLO53 * 3.0650407
?V51 = I51 - ?%CLO51
?PB208 = I208 + I207 + I206

MERCURY IN SOLID OR SEMISOLID WASTE

EPA 7471A/B

ALS-KELSO

SOP ID:	MET-7471	Rev. Number:	17	Effective Date:	1/31/2014

Approved By: _____ Date: 12/18/13
Department Supervisor - Jeff Coronado

Approved By: _____ Date: 12/17/13
QA Manager - Suzanne LeMay

Approved By: _____ Date: 12/19/13
Laboratory Director - Jeff Grindstaff

Issue Date:	_____	Doc Control ID#:	_____	Issued To:	_____

ALS-Kelso Procedure Change Form

SOP Code: MET-7471 Revision: 17 Effective Date: 1/31/2014			
SOP Section Number	**Description of Procedure Change**	**Date Procedure Change Implemented**	**Supervisor Initials & Date** Indicating Approval and Training of Staff
11.3	For 7471B analyses the criteria are “50-150%” is changed to “70-130%”	11/1/14 (from ann. review)	JDB
8.7	Additional note to section: "All acid lot numbers used must be recorded by the analyst and verified to match those in the LIMS (or added to LIMS when lot numbers change."	3/6/15	L.J.

Standard Operating Procedure

for

MERCURY IN SOLID OR SEMISOLID WASTE

1. SCOPE AND APPLICATION

1.1. This Standard Operating Procedure (SOP) describes the procedure used to determine the concentrations of Mercury in soils, sediments, freeze dried tissues, bottom deposits, and sludge-type materials using Method EPA 7471A or 7471B. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix. Method 7471 is a cold-vapor atomic absorption procedure.

1.2. The Method Reporting Limit (MRL) is 0.02 mg/kg. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The reported MRL may be adjusted if required for specific project requirements; however, the capability of achieving other reported MRLs must be demonstrated. A Method Detection Limit (MDL) of 0.002 mg/kg has been achieved using this procedure.

2. METHOD SUMMARY

2.1. A representative aliquot of sample is prepared as described in this procedure. The mercury is reduced to its elemental state and aerated from solution and measured with an atomic absorption spectrometer. The mercury vapor passes through a cell positioned in the light path of the AA where absorbance is measured as a function of mercury concentration.

3. DEFINITIONS

3.1. **Batch** – A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1. Preparation Batch – A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2. Analysis Batch – Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. **Sample**

3.2.1. Field Sample – An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2. Laboratory Sample – A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3. **Quality System Matrix** – The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1. Aqueous – Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2. Drinking water – Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3. Saline/Estuarine water – Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4. Non-aqueous Liquid – Any organic liquid with <15% settleable solids.

3.3.5. Animal tissue – Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6. Solids – Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7. Chemical waste – Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8. Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, auto fluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis – In the matrix spike analysis, predetermined quantities of target analytes are 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 method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the mid point of the calibration range or at levels specified by a project analysis plan.

3.5. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6. Method Blank (MB) – The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8. Independent Verification Standard (ICV) – A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.9. Continuing Calibration Verification Standard (CCV) – A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.10. Instrument Blank (CCB) – The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

3.11. Duplicates and Duplicate Matrix Spikes are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. Depending on the method of analysis, either a duplicate analysis (and/or a matrix spiked sample) or a matrix spiked sample and duplicate matrix spiked sample (MS/DMS) are analyzed.

3.12. Standard Reference Material (SRM) – A material with specific certification criteria and is issued with a certificate or certificate of analysis that reports the results of its characterizations and provides information regarding the appropriate use(s) of the material. An SRM is prepared and used for three main purposes: (1) to help develop accurate methods of analysis; (2) to calibrate measurement systems used to facilitate exchange of goods, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit; and (3) to ensure the long-term adequacy and integrity of measurement quality assurance programs.

4. INTERFERENCES

4.1. Potassium permanganate is added to eliminate possible interference from sulfide. Samples high in chlorides require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which absorbs radiation at 253 nm.

5. SAFETY

5.1. 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.

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

5.3. Hydrochloric and/or 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.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1. Glass, plastic, and polytetraflouroethylene (PTFE) containers are suitable in most cases.

6.2. Non-aqueous samples are stored at 4 ± 2 ºC from receipt until analysis, unless otherwise dictated by project specifications.

6.3. Samples must be analyzed within 28 days of sampling.

7. APPARATUS AND EQUIPMENT

7.1. CETAC M-6100A Mercury Analyzer. See Attachments for instrument parameters.

7.2. CPI-Modified Block (Mod Block)

7.3. Pipettors, Eppendorf and Finnpipette fixed and adjustable volume

7.4. Polypropylene graduated cylinders, 25 mL

7.5. 125 ml Digestion Vessel tubes.

7.6. Laboratory balance, top-loader capable of readings .001g (3-place). Mettler, Ohaus, or equivalent.

8. STANDARDS AND REAGENTS

8.1. Reagent grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lowering the accuracy of the determination. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking (ADM-RTL)* for the complete procedure and documentation requirements.

8.2. Mercury stock solution (1,000 mg/L). Commercially prepared certified solution stored at room temperature. The expiration date determined by manufacturer.

8.3. Mercury working standard (100µg/L). Prepared from the intermediate stock solution listed above. Store at room temperature and prepare a new standard daily.

8.4. Laboratory Control Sample – ERA Priority Pollutant/CLP Inorganic Soil reference material. Store at room temperature in the original container and use the vendor expiration date.

8.5. Matrix spike solution (1 mg/L) – Prepare by making a 1:1000 dilution of the mercury stock solution. Store at room temperature and prepare a new standard monthly.

Note: See section 11.2.2-3 for details on preparation of calibration and ICV standards. See section 12 for QC sample preparation.

8.6. Reagent water – ASTM Type II water (laboratory deionized water).

8.7. Acids – Purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the Method Reporting Limit.

8.7.1. Nitric Acid (HNO_3) 69-70% – JT Baker-Baker Instra-Analyzed® or equivalent.

8.7.2. Sulfuric Acid concentrated (H_2SO_4) – EMD-OmniTrace® or equivalent.

8.7.3. Hydrochloric Acid concentrated (HCL) – VWR – BHD-Aristar® or equivalent.

8.8. Potassium permanganate solution, 5% w/v. To prepare, add 50 g of solid reagent to 1000 mL of D.I. water and place on magnetic stir plate for approximately 30 minutes until dissolved.

8.9. Sodium chloride/hydroxylamine hydrochloride solution, 12% w/v each. To prepare, add 120g sodium chloride and 120 g of hydroxylamine hydrochloride to 1000 mL of D.I. water and place on magnetic stir plate for approximately 15 minutes until dissolved.

8.10. Stannous chloride, 10% w/v in HCl (7% v/v). To prepare, add 100g stannous chloride crystals and 70 mL of concentrated hydrochloric acid in 1000 mL of D.I. water. Seal lid on mixing bottle and shake until the stannous chloride is dissolved.

8.11. Aqua Regia – Prepare immediately before use by carefully adding 3 parts of concentrated HCL to one part of HNO_3.

9. PREVENTIVE MAINTENANCE

9.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, who performed the work, and a reference to return to analytical control.

9.2. ALS staff performs all routine maintenance and troubleshooting. Preventative maintenance activities listed below should be performed when needed as determined by instrument performance (i.e. stability, sensitivity, etc.) or by visual inspection. Repairs of an extraordinary nature may or may not require factory service, depending on the nature of the task.

9.3. Keep the instrument free of dust, deposits, and chemical spills.

9.4. Replace the peristaltic and autosampler rinse tubing.

9.5. Remove and clean the Gas-Liquid Separator.

9.6. Remove, dismantle, and clean the optical cells (sample cell and reference cell) including the sapphire windows.

9.7. Replace the Hg lamp bulb when the lamp current reaches 13 mA.

10. RESPONSIBILITIES

10.1. 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.

10.2. It is the responsibility of the department supervisor/manager to document analyst training and method proficiency, as described in the *ADM-TRAIN*.

11. PROCEDURE

11.1. Sample Preparation

11.1.1. Mix the sample thoroughly to achieve homogeneity. For soil, sediment, solids, weigh approximately 0.5g of well-homogenized sample and place in the bottom of a 125 ml digestion tube and record the weight to the nearest 0.01g. Add 5.0 mL of reagent water and 5.0 mL of aqua regia, then heat in the Mod Block for 2 minutes at 95°C.

11.1.2. Cool then add 10 mL of reagent water and 15 mL of potassium permanganate solution. If the purple color does not persist for 15 minutes add additional potassium permanganate until it does so. Any additional potassium permanganate solution must also be added to the blanks and standards in equal proportion.

Note: Spiking solution is added prior to acidification.

11.1.3. Mix thoroughly and place in the heating block for 30 minutes at 95°C. The temperature of the block is monitored with a thermometer that is calibrated monthly.

11.1.4. Cool and add 6 mL of sodium chloride-hydroxylamine hydrochloride to reduce the excess permanganate. Perform this addition under a hood as Cl_2 could be evolved.

11.1.5. Add 27 mL of reagent water and the sample is ready for analysis. (The vapor generator does the step of adding the stannous chloride solution automatically.)

11.2. Calibration

11.2.1. To prepare calibration standards a 10 ppm intermediate stock solution is first prepared by aliquoting 1.0 mL of commercially prepared 1000 ppm stock standard into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This solution must be prepared monthly. Next, a 100 ppb working solution is prepared by aliquoting 1.0 mL of the 10 ppm intermediate stock solution into an

acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO3. This solution must be prepared daily.

Note: All standard aliquots are measured using calibrated fixed or adjustable volume autopipettors or calibrated disposable 5.0 or 10.0 mL pipettes.

11.2.2. Transfer 0, 0.1, 0.25, 0.5, 2.5 and 5.0 mL aliquots of the working solution to a series of labeled 125 ml digestion tubes. Add the appropriate amount of reagent water to bring each bottle to a volume of 5mL. Add 5.0 mL of aqua regia and heat in the heating block for 2 minutes at 95°C. The final concentrations of the prepared standards are 0, 0.2, 0.5, 1.0, 5.0, 10.0 ppb.

11.2.3. The Initial Calibration Verification (ICV) is prepared by first making a 1000 ppb intermediate solution. 0.10 mL of commercially prepared 1000 ppm stock standard, from a different manufacturer and lot than the calibration standard, is aliquoted into an acid rinsed 100 mL Class A volumetric flask and diluting to volume with 1% HNO_3. This solution must be prepared monthly. Prepare the ICV standard by aliquoting 0.25 mL to a labeled 125 ml digestion tube. Add the 4.75 mL of reagent water and 5.0 ml of Aqua Regia.

11.2.4. Cool and then add 10 mL of reagent water and 15 mL of potassium permanganate solution and return the bottles to the water bath for 30 minutes.

11.2.5. Cool and add 6.0 mL of sodium chloride-hydroxylamine hydrochloride solution. Add 27 mL of reagent water and the standards are ready for analysis.

11.2.6. CETAC Calibration and Sample Analysis

11.2.6.1. Turn on the CETAC instrument, including the Hg lamp, and autosampler. After this is done turn open the operating software (Mercury Analyzer 1.5.1.1).

11.2.6.2. The rinse station for the autosampler turns on automatically, but the peristaltic pump must be started manually. Make sure all sample uptake and drain tubes are placed correctly on the pump and are secured with the appropriate tension. Place the reagent uptake tube in the stannous chloride and start the pump.

11.2.6.3. From the software's main screen select the "Worksheet" button and then the "Template" button. Select the "Kelso Mercury Program".

11.2.6.4. Go to the "Labels" tab and enter the QC and field samples to be analyzed in the appropriate order.

11.2.6.5. Transfer the solutions to be analyzed to labeled 12mL polyethylene test tubes and place them in the appropriate spaces on the autosampler trays.

11.2.6.6. Transfer the calibration blank and standards (0.2, 0.5, 1.0, 5.0, and 10 ppb) from their digestion tubes to the standard tubes located behind the autosampler trays. The calibration blank is placed in the left most tube and the other standards are placed in ascending order to the right.

11.2.6.7. Return to the software and go to the "Analysis" tab. At this point the analysis is ready to begin. Click on the start button. In the dialog box that appears be sure the following are checked:

- Calibrate before first sample.
- New output file before first sample.
- Zero before first sample.

Click start and the analysis will begin.

11.2.7. After the calibration standards have run the software will use linear regression to create a calibration curve based on the concentration and measured absorbance of each standard. The form of regression line is $y = mx + b$. If the correlation coefficient of the curve is greater than 0.995 the analysis will continue, if not the analysis will be terminated and corrective action will be needed by the analyst.

11.3. As the analysis sequence proceeds, next analyze the following QC standards.

- ICV (5.0 ppb standard prepared from a second source)
- ICB
- CCV (5.0 ppb calibration standard)
- CCB
- CRA (0.2 ppb calibration standard)

If either the ICV or CCV are different from their true values by more than 10% the software will terminate the analysis. If either the ICB or CCB is greater than the MRL the software will terminate the analysis. Method 7471A does not contain criteria for the CRA, however, the result must be a positive measured concentration. For 7471B analyses the criteria are 50-150% of the true value. Also, specific project requirements may apply.

Note: For projects falling under DoD QSM requirements, the QSM criteria for CCV standards is ±20% and for ICB and CCB standards no analytes detected > LOD. (The ICV limit is as listed above.)

11.4. Sample Analysis

11.4.1. The samples are analyzed with the CETAC analyzer in the same manner as the calibration standards. The analyzer does the step of adding the stannous chloride solution automatically. Check the baseline between samples to verify that the spectrometer reading has stabilized at the normal baseline level.

11.4.2. The analytical sequence should be set up to include all samples, QC samples, blanks, and calibration verification standards at necessary intervals. Refer to the SOP for Sample Batches.

11.4.3. Sample digestion batches are analyzed with a set of CCV and CCB standards which are run at the beginning and end of the analytical run and at a minimum every 10 samples during the run. The same criteria listed above are applied to the CCVs and CCBs and if one is found to be outside these limits the analysis is terminated.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

12.1.1. Acceptable accuracy and precision of the procedure must be demonstrated before analysis of samples begins, or whenever significant changes to the procedures have been made.

12.1.2. Accuracy and precision is demonstrated by preparing and analyzing four LCS aliquots. The average percent recovery of for each analyte must be within LCS limits and the %RSD within precision limits.

12.1.3. Initial demonstration of capability must be performed by each analyst performing sample analysis and documented in the laboratory records.

12.2. Method Detection Limits

12.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates with a MDL spiking solution near the MRL and analyze. Refer to CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation*.

12.2.2. Calculate the average concentration found (x) in the sample concentration, and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. The MDL study should be done annually. The MDL study and MDL verification check should be analyzed annually or whenever there are major changes in the instrument or procedure is implemented.

12.3. For method 7471B, an LLQC sample (a CRA that is carried through the digestion) must be analyzed to verify accuracy at the MRL. The recovery must be ±30%.

12.4. For method 7471B, Instrument Detection Limit (IDL) studies are performed quarterly. These will be calculated and made available to the analysts.

12.5. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual, in the *SOP for Sample Batches* (ADM-Batch). For this analysis, these include:

12.5.1. Prepare one method blank (MB) per digestion batch, or per 20 samples, whichever is more frequent. The MB is to be prepared as done with samples. The Method Blank should be < MRL. If the Method Blank is >MRL redigest the associated samples if sample levels are <20x the MB level.

Note: For projects falling under DoD QSM requirements, the QSM criteria for method blanks is no analytes detected > ½ MRL.

12.5.2. Prepare one Laboratory Control Sample (LCS) per digestion batch, or per 20 samples. Weigh 0.25g of the current lot of "Environmental Resource Associates Priority

Pollutant/CLP Inorganic Soil" prepared reference material in to a 125 mL Digestion vessel tube and prepare as per the procedure.

12.5.3. Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

Apply LCS recovery criteria from the DQO Table, unless project-specific or in-house limits are established. For method 7471B, the LCS recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range.

Note: For DoD QSM projects, the QSM LCS criterion is 80-120%. If the LCS fails the acceptance criteria, re-digest the batch of samples.

12.5.4. Prepare one sample duplicate and one matrix spike sample per each digestion batch, or per twenty samples, whichever is more frequent. For the matrix spike, add 0.25mL of the matrix spike solution to the designated spike sample, resulting in a spike concentration of 0.5 mg/kg. At times, specific samples will be assigned as duplicates or spikes depending on client requirements.

Note: Duplicate samples are routinely analyzed; however some projects may require a MSD. All DoD projects require a MSD. The MSD sample is prepare as described above.

12.5.5. The RPD criterion for duplicates is 20%. If not, flag the data or redigest samples. Apply matrix spike recovery criterion listed in the DQO Table, unless project-specific limits are required. For method 7471B, the recovery limits are 80-120%. If statistical in-house limits are used, they must fall within the 80-120% range. For DoD QSM work, MS recoveries are assessed using the QSM LCS control limits. If the MS (and/or MSD where applicable) recovery is outside acceptance limits proceed with the additional interference tests described in section 12.5.4. Based on results of these tests, the physical nature of the sample (e.g. homogeneity), and any specific project requirements, a determination can then be made as to appropriate corrective action (e.g. redigestion, reporting with a qualifier, alternative methodologies, etc.). If the analyte concentration is >4x the spike level the spike control limit is no longer applicable and no action is required.

Note: For DoD QSM projects, the duplicate RPD limit is 20% and MS recoveries are assessed using the QSM LCS control limits 80-120%.

12.5.5.1. Calculate percent recovery (%R) as:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

12.5.5.2.Calculate Relative Percent Difference (RPD) as:

$$\%RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1= Higher Result
R2= Lower Result

12.5.6. Interference Tests: Prepare one post spike for every batch of samples and if samples are sufficiently high (10x the MRL/LOQ) a serial dilution. The serial dilution must agree within 10% of the original sample result. Post spike recovery acceptance limits for method 7471A and 7471B are 80-120% for project falling under SW-846 Update IV. When both the post spike and dilution tests fail all of the samples in the associated preparation batch must be quantified via Method of Standard Additions (MSA).

13. CALCULATIONS, DATA REDUCTION, AND REPORTING

13.1. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12.

13.2. Record all sample weight, volumes and dilutions on an A.A. benchsheet (see Attachments).

13.3. Solution concentrations are calculated by the Mercury Analyzer software based on the linear regression calibration curve created when the calibration standards are analyzed. The absorbance measured for each sample is applied to the linear regression curve and the final solution concentration is determined and displayed as the instrument result.

13.4. 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. Solid samples are reported in mg/Kg:

$$mg/Kg\ (Sample) = C^{*} \times Post\ Digestion\ Dilution\ Factor \times \frac{Digestion\ Vol.(ml)}{Sample\ wt.(g)} \times \frac{1mg}{1000ug} \times \frac{1L}{1000ml} \times \frac{1000g}{1Kg}$$

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

NOTE: If results are to be reported on a dry weight basis as required by certain projects, the Sample Wt (g) component of the equation should be the dry-weight derived from a determination of %moisture of a separate aliquot of the sample using the SOP for Total Solids.

13.5. Record all concentrations determined at the instrument and calculate the final results in mg/Kg. Record the final results on the A.A. Benchsheet.

13.6. The data packet for the sequence is submitted for review by supervisor or designee. The results are transferred to the appropriate report form located in the ALS network directory R:\ICP\WIP. Once the results are transferred, the report is reviewed.

13.7. A daily run log of all samples analyzed is maintained. All data should be printed and stored after operator has checked for evenness of burns. A copy of this document will go with each package of Tier III or higher data run that day.

13.8. Refer to the SOP for *Laboratory Data Review Process* (ADM-DREV) for general instructions for data review.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Non Conformance and Corrective Action (CE-QA008)* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

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

15.2. The method detection limit (MDL), limit of detection (LOD), and limit of quantitation (LOQ) are established using the procedure described in CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification.* Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

16.3. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS EH&S Manual for details.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

17.2. Training is documented following the *ALS, KELSO TRAINING PROCEDURE* SOP.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. There are no known differences between the reference method and this procedure

19. REFERENCES

19.1. USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Final Update II, Method 7471A, September 1994.

19.2. USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update IV, Method 7471B, Revision 2, February 2007.

19.3. DoD Quality Systems Manual for Environmental Laboratories Version 4.1 4/22/2009.

20. CHANGES SINCE THE LAST REVISION

20.1. Sec. 3.6: Deleted.
20.2. Sec. 7.1: Corrected instrument make.
20.3. Sec. 12.3: Corrected LLQC/CRA acceptance limits.
20.4. Updated SOP references.

ATTACHMENT 1
Instrument Parameters

Analysis Parameters

Instrument M-6100 Mercury Analyzer

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	30.00	60.00	50.00	4	2.00		253.65

Instrumental Zero

Zero before first sample: No

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)
5.00	10.00		

Standby Mode

Enabled: Yes

Standby Options: gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	Yes	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of
Lower (%)	Upper (%)	Lower (%)	Upper (%)	Determination
75	125	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

ATTACHMENT 2
Benchsheets

COLUMBIA ANALYTICAL SERVICES, INC.
ANALYTICAL WORKSHEET

PRINTOUT WITH:_____

Method: (Circle One) 7470A 7471B 245.1	**Service Request # :**
Analysis For: Hg	

DATA

Pos.	SAMPLE NUMBER	Initial Sample (g) or (mL)	Initial Dilution (mL)	Dilution Factor	Measured (µg/L)	Sample Actual (mg/kg)	Sample Actual (µg/L)
1	Cal. Blk.	0.00	50	~	0.00		0.00
2	Std 0.2	*0.1	50	~	0.20		0.20
3	Std 0.5	*0.25	50	~	0.50		0.50
4	Std 1.0	*0.5	50	~	1.00		1.00
5	Std 5.0	*2.5	50	~	5.00		5.00
6	Std 10.0	*5.0	50	~	10.00		10.00
7		~	~	~			
8		~	~	~			
9		~	~	~			
10		~	~	~			
11		~	~	~			
12				~			
13				~			
14				~			
15				~			
16				~			
17				~			
18				~			
19				~			
20				~			
21				~			
22		~	~	~			
23		~	~	~			
24				~			
25				~			

Comments: Reporting Levels: **Cal. Inter. Std* (100ppb)**_____
Soil/Tissue Spike Level: **2nd Source Inter Std** (1ppm)**_____

Post Spike Level:	1.0 ppb				
Method	**Spike Level**	**MRL**	**LCS Limit**	**MS Limit**	**RPD**
7470A Water	1.0 µg/L	0.2 µg/L	83-117%	80-120%	20%
245.1 Water	1.0 µg/L	0.2 µg/L	85-115%	70-130%	20%
7470A TCLP	5.0 µg/L	1.0 µg/L	85-115%	75-125%	20%
7471A Soil LCSS	3.73 mg/kg	0.02 mg/kg	72-128%	80-120%	30%
7471A Tissue Tort	0.27 mg/kg	0.02 mg/kg	63-130%	80-120%	30%

Analyst:	**Date:**	**Page Number:** 1

[Controlled - HgWaterRunForm 7-11-11] HG1.XLS

TABLE 1

Summary of Corrective Actions

Method Reference	Control	Specification and Frequency	Acceptance Criteria	Corrective Action
EPA 7471A/B	ICAL	Prior to sample analysis	R2 ≥ 0.995	Correct problem then repeat ICAL
EPA 7471A/B	ICV	After ICAL	± 10%	Correct problem and verify second source standard; rerun second source verification. If fails, correct problem and repeat initial calibration.
EPA 7471A/B	CCV	Prior to sample analysis	± 10%	Correct problem then repeat CCV or repeat ICAL
EPA 7471A/B	Method Blank	Include with each analysis batch (up to 20 samples)	<MRL	If target exceeds MRL, reanalyze to determine if instrument was cause. If still noncompliant then: Re-extract or reanalyze samples containing contaminate, unless samples contain > 20x amount in blank.
EPA 7471A/B	Laboratory Control Sample	Include with each analysis batch (up to 20 samples)	See DQO	If exceeds limits, re-extract and re-analyze
EPA 7471A/B	Matrix Spike	Include with each analysis batch (up to 20 samples)	See DQO	Evaluate data to determine if the there is a matrix effect or analytical error
EPA 7471A/B	Sample Duplicates	Include with each analysis batch (up to 20 samples)	≤ 20 % RPD	Re-homogenize and re-analyze if result is > 5 X the MRL

DOCUMENT TITLE:	***BIOACCESSIBILITY OF METALS IN SOIL AND SOLID WASTE***
REFERENCED METHOD:	
SOP ID:	***MET-BIOACC***
REV. NUMBER:	***1***
EFFECTIVE DATE:	***07/31/2013***

ALS-Kelso Procedure Change Form

SOP Code: MET-BIOACC Revision: 1 Effective Date: 7/31/13			
SOP Section Number	**Description of Procedure Change**	**Date Procedure Change Implemented**	**Supervisor Initials & Date** Indicating Approval and Training of Staff
10.2.2	Weigh approximatly 1g of sample to the nearest 0.01g	2-3-15	L.J

BIOACCESSIBILITY OF METALS IN SOIL AND SOLID WASTE

MET-BIOACC

ALS-KELSO

SOP ID:	MET-BIOACC	Rev. Number:	1	Effective Date:	07/31/2013

Approved By: _____ Date: 7/16/13
Department Supervisor - Jeff Coronado

Approved By: _____ Date: 7/16/13
QA Manager - Suzanne LeMay

Approved By: _____ Date: 7/16/13
Laboratory Director - Jeff Grindstaff

Issue Date:	_____	Doc Control ID#:	_____	Issued To:	_____

Standard Operating Procedure

for

BIOACCESSIBILITY OF METALS IN SOIL AND SOLID WASTE

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the procedure used to determine a bioaccessibility value for Arsenic and/or Lead for soils and solid waste. This procedure describes the extraction procedure and calculations. The determinative analytical procedures are described in detail in separate SOPs.

1. METHOD SUMMARY

A soil or solid waste sample is dried and sieved to achieve a homogeneous sample. An aliquot of this homogenized sample is extracted at constant temperature for one hour then filtered to produce a final "in-vitro" aqueous extract. This extract is then analyzed for Arsenic and/or Lead by various instrumental techniques depending on target method reporting limit (MRL) and detection limit requirements. The result of the in-vitro analysis are used in conjunction with separate total metals results to calculate a bioaccessibility value.

2. DEFINITIONS

2.1. **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.

2.2. **Laboratory Control Sample** – An analyte-free matrix to which a known quantity of analytes are added. The LCS is subjected to the same processing as field samples and is carried through the entire analytical process. The percent recovery of the analyte in the LCS is used to assess analysis performance in terms of accuracy.

2.3. **Method Blank** – The method blank is a blank matrix designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

2.4. **Post-Extraction Matrix Spike** – A known amount of Arsenic and/or Lead added to an aliquot of final extract to demonstrate the analytical method is free from interference in the extraction matrix.

2.5. **Reagent Blank** – Extraction solution analyzed once per batch.

3. INTERFERENCES

3.1. When obtaining subsamples it is important to minimize any chances for sample contamination or cross-contamination between samples. Work should be performed in

an organized and neat manner. Equipment and laboratory tools used with samples should be cleaned between samples to prevent cross-contamination.

3.2. Analysis-specific interferences are described in the applicable analytical SOP.

4. SAFETY

4.1. 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.

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

4.3. Hydrochloric is used in this method. This acid is 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.

5. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

5.1. ALS laboratory staff does not collect samples. Samples are collected by field sampling staff of ALS customers using their sampling plans and procedures.

5.2. Samples may be collected in plastic or glass jars, typically 2 ounce (although larger jars may be used). Samples are refrigerated at 4 ± 2°C from receipt until analysis. Samples should be analyzed within 6 months of sampling.

6. APPARATUS AND EQUIPMENT

6.1. Aluminum drying pans

6.2. Laboratory drying oven

6.3. 60 mL Syringe – Luer-Lok (VWR # BD309653 or equivalent)

6.4. Syringe Filters – Millipore Millex-HV Hydrophilic PVDF 0.45 µm (VWR # SLHV025NK or equivalent)

6.5. pH Meter – Orion model 230A or equivalent

6.6. pH Probe – Thermo Combination pH Probe (part # 9256BN)

6.7. Modified Toxicity Characteristic Leaching Procedure (TCLP) extractor – TCLP extraction unit with tumbler assembly enclosed by oven capable of maintaining 37°C. Modified TCLP extractor located in room 108.

6.8. Water bath, capable of maintaining 37 ± 2°C

6.9. HDPE bottles, 125 mL

6.10. Evergreen disposable tubes, 50 mL. Check tubes for accuracy on a per batch basis by filling a tube to the 50 mL mark and measuring the water's mass. The measured mass must be accurate to ±3%; if not, obtain a new lot of tubes and retest. Pipettors: All-plastic pneumatic fixed-volume and variable pipettors in the range of 20 uL to 1.0 mL.

6.11. Top-loader laboratory balance capable of weighing to the nearest 0.01 g

7. STANDARDS, REAGENTS AND CONSUMABLE MATERIALS

7.1. Document all reagent and acid preparation information in a logbook, including acids and acid mixtures. Label all reagents and acids/mixtures with appropriate identification,, tracking , and expiration date information.

7.2. Reagent water: ASTM Type II deionized (DI) water

7.3. Hydrochloric Acid (12N) – EMD ACS Grade (HX0603-75)

7.4. 2.0 pH Buffer – VWR BDH5010-500mL

7.5. 4.0 pH Buffer – VWR BDH0198-2.0L

7.6. Glycine (Crystalline Granules) – J.T. Baker, Pharmaceutical Grade (0581-01)

7.7. Extraction Solution – To 1.9 L of reagent water add 60.06 g of Glycine. Place the mixture in a water bath at 37°C at allow to come to equilibrium. Standardize the pH meter using 2.0 and 4.0 pH standards which have also been brought to 37°C in the water bath. Add hydrochloric acid until the extraction solution reaches a pH of 1.50 ± 0.05. Bring the solution to a final volume of 2.0 L with reagent water.

7.8. QC Spiking solutions – Since the determinative methodology may vary, refer to the applicable determinative SOP for preparation of spiking solutions.

8. PREVENTIVE MAINTENANCE

Maintenance for this procedure is generally limited to glassware cleaning, pipet monitoring, and tumbler monitoring. Procedures for glassware washing are described in the SOP for Metals Laboratory Glassware Cleaning (MET-GC).

9. RESPONSIBILITIES

9.1. 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.

9.2. It is the responsibility of the department supervisor/manager to document analyst training and method proficiency.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Record all sample preparation and sample information on the applicable bench sheet. This includes acid mixture tracking documentation.

10.1.2. Using a spatula or other utensil, thoroughly mix and homogenize the sample, making sure to mix the entire contents of the jar. Additional steps may be needed to homogenize the sample (break up soil clumps, etc.). The sample should be mixed so there is a uniform color and texture. Since the entire jar is used, do not remove any extraneous material (this will be removed by sieving).

10.1.3. Transfer the entire mixed contents of the sample jar to an aluminum drying pan. Dry the sample in a drying oven at a temperature <40°C. The dried sample is then sieved to <250 µm. All subsequent analysis are performed on the <250 µm fraction.

10.1.4. The <250 µm sample is mixed thoroughly and placed in an appropriate sized glass jar. Subsamples are taken from this homogenized sample with a spatula or other utensil for analysis.

10.2. Leaching Procedure

10.2.1. Pre-heat the modified TCLP extractor to 37 ± 2 °C.

10.2.2. Weigh 1.00 ± 0.05 g of sample and quantitatively transfer to a 125 mL HPDE bottle. Next add 100 ± 0.5 mL of extraction solution (pre-heated to 37°C) to the bottle. Hand-tighten the cap, shake and invert to ensure there is no leakage and that no sample remains caked on the bottom of the bottle.

10.2.3. Open the door allowing access to the extractor oven then quickly place the bottles (field samples and all associated QC samples) on the tumbler and reseal the oven. Allow the temperature to return to equilibrium in the oven (usually 2 to 3 minutes) and begin the extraction.

10.2.4. Rotate the tumbler end over end at 30 ± 2 rpm for 1 hour. Record the start time of the rotation.

10.2.5. When the extraction is complete remove the bottles and arrange them on a bench top. Transfer 25-30 mL of extract to a 60 mL syringe and filter through a 0.45 µm disk filter. Capture the filtrate in 50 mL polypropylene centrifuge tubes and cap tightly. Store the filtered extracts in a refrigerator at 4 ± 2°C until they are analyzed.

10.2.6. The time each sample is filtered, and the extraction stopped, must be recorded. The elapsed time of the extraction cannot exceed 1 hour and 30 minutes. Any samples with extraction times greater than this must be re-extracted.

10.2.7. Measure the pH of the sample remaining in the extraction bottle. Standardize the pH meter using 2.0 and 4.0 pH standards which have also been brought to 37°C in the water bath. Rinse and blot electrode, then immerse into the sample. Press pH and record the pH when stabilized. Remove the electrode from samples after each measurement and rinse 3 times with D.I. water.

10.2.8. If the pH is not within ± 0.5 pH units of the starting pH then the extract must be discarded and reanalyzed using the procedure below.

10.2.8.1. Scenario 1: If the pH has dropped by more than 0.5 pH units repeat the test exactly as before. If the pH has dropped by more that 0.5 pH units again, record the pH and proceed with the analysis of the extract.

10.2.8.2. Scenario 2: If the pH has risen more than 0.5 pH units the extraction is repeated, however the extractor is stopped at 5, 10, 15, and 30 minutes and the pH adjusted down to 1.5 with dropwise additions of HCl. The pH is also adjusted upon final removal from the extractor (i.e. at 60 minutes). Note: Samples with rising pH cannot be extracted concurrently with sample being extracted with the standard procedure.

Note: All pH measurements indicated above are made by first calibrating the pH meter using 2.0 and 4.0 pH standards that have be equilibrated to 37°C in a water bath. The pH probe is acid then DI rinsed prior to making measurements is extracts and is subsequently acid then DI rinsed between samples to prevent any cross contamination.

10.3. Analysis

10.3.1. Extracts are analyzed for Arsenic and/or Lead by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), or Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) following SW-846 methodologies. Details of the instrumental analysis are described in SOPs for the specific analytical procedure and are outside the scope of this document.

11. QA/QC REQUIREMENTS

11.1. Initial Precision and Recovery Validation

The accuracy and precision of the procedure must be validated before analysis of samples begins. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery of for each analyte must be 85-115% and the RSD <20%.

11.2. Method Detection Limits

11.2.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank matrices at a level near or below the instrument limit of quantitation. Follow the procedures starting in Section 11 to analyze the samples. Refer to

CE-QA011, *Determination of Method Detection Limits and Limits of Detection* for details of performing the MDL study.

11.2.2. Calculate the average concentration found (x) and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct T value for the number of replicates. MDL's must be performed annually.

11.3. General ongoing QC Samples required for each sample batch (20 or fewer samples) are described in the ALS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. QC samples for the in vitro extraction must include the following:

11.3.1. Reagent Blank - Extraction solution analyzed once per batch. Ideally no target analytes should be detected in the reagent blank, but any detections must be <½ the MRL.

11.3.2. A method blank (bottle blank) is analyzed once per batch. A 100 mL aliquot of extraction solution is carried through the entire extraction procedure. The concentration found in the method blank must be less than the MRL for non-DoD projects and < ½ the MRL for DoD projects.

11.3.3. A Laboratory Control Sample (LCS) is analyzed once per batch using an aliquot of the extraction solution spiked at 1.0 mg/L for Arsenic and/or 10 mg/L for Lead using traceable 1000 mg/L stock solutions. Recovery for the LCS must fall between 85-115%.

11.3.4. A duplicate sample is performed at a frequency of 1 for every 10 samples. The duplicate analysis is evaluated against a control limit of ± 20% RPD.

11.3.5. A post-extraction matrix spike is analyzed once per batch. A known amount of Arsenic and/or Lead added to an aliquot of final extract to demonstrate the analytical method is free from interference in the extraction matrix. The spike concentration should be 1-5 times the native level found in the extract. The post-extraction matrix spike analysis is evaluated against a control limit of 75-125% recovery.

12. DATA REDUCTION, REVIEW, AND REPORTING

12.1. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12.

12.2. Calculations

12.2.1. Total Arsenic and/or Lead must also be determined for each sample subjected to this procedure. An additional aliquot of the homogenized <250 µm sample is digested via EPA method 3050B and analyzed by ICP, ICP-MS, or GFAA. Again, the details of the instrumental analysis are described in SOPs for the specific analytical procedure.

12.2.2. The bioaccessibility of Arsenic or Lead is calculated as follows:

$$Bioaccessibility\ value = \frac{(Concentration\ in\ in-vitro\ extract, mg/L)\ (0.1L)}{(Concentration\ in\ solid\ sample, mg/Kg)(0.001Kg)} \times 100$$

12.3. The data packet for the sequence is submitted for review by supervisor or designee. The results are transferred to the appropriate report form located in the ALS network directory R:\ICP\WIP. Once the results are transferred, the report is reviewed.

12.4. Refer to the *SOP for Laboratory Data Review Process* for general instructions for data review.

13. METHOD PERFORMANCE

13.1. This method will be validated through single laboratory studies of accuracy and precision.

13.2. The method detection limit (MDL) is established for the determinative methods using the procedure described in CE-QA011, *Determination of Method Detection Limits and Limits of Detection*.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Non Conformance and Corrective Action (CE-QA008)* for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. POLLUTION PREVENTION AND WASTE MANAGEMENT

15.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

15.2. 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 ALS Environmental Health and Safety Manual.

15.3. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS EH&S Manual for details.

16. TRAINING

16.1. Refer to ADM-TRAIN, *ALS-Kelso Training Procedure* for standard procedures.

16.2. Training outline

16.2.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

16.2.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

16.2.3. Perform initial precision and recovery (IPR) study by performing 4 replicate LCS analyses. Summaries of the IPR are reviewed and signed by the supervisor and forwarded to the employee's training file.

16.3. Training is documented following ADM-TRAIN, *ALS-Kelso Training Procedure*.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

17. METHOD MODIFICATIONS

17.1. This section is not applicable because this procedure is a laboratory developed method.

18. REFERENCES

18.1. *In Vitro Method for Determination of Lead Bioaccessibility,* Solubility/Bioavailability Research Consortium Standard Operating Procedure, Revision 8.

19. CHANGES SINCE THE LAST REVISION

19.1. Reformatted SOP to ALS branding.
19.2. Replaced “CAS” references with “ALS”.
19.3. Updated SOP references.
19.4. Sec. 17: New section.
19.5. Sec. 19: New section.
19.6. Added benchsheet as an attachment.

ATTACHMENT A
In Vitro Extraction Benchsheet
(1 page)

In Vitro Extraction

Sample ID	Sample Preparation		Extraction								Filtration	
	Weight (g)	Volume (mL)	Start Time	End Time	Elapsed Time (min)	Starting pH	Ending pH	ΔpH	Starting Temp. (°C)	Ending Temp. (°C)	Time	Time Elapsed from Extraction (min)
Acceptance Range	0.95-1.05	95.5-100.5	---	---	55-65	---	---	max = 0.5	35-39	35-39		max = 90

SRM = NIST 2711, Montana Soil Spike Solution = _____

Analyst:_____ Date:_____

Reviewer:_____ Date:_____

In Vitro Extraction

Sample ID	Sample Preparation		Extraction								Filtration	
	Weight (g)	Volume (mL)	Start Time	End Time	Elapsed Time (min)	Starting pH	Ending pH	ΔpH	Starting Temp. (°C)	Ending Temp. (°C)	Time	Time Elapsed from Extraction (min)
Acceptance Range	0.95-1.05	95.5-100.5	---	---	55-65	---	---	max = 0.5	35-39	35-39		max = 90

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Analyst:_____ Date:_____

Reviewer:_____ Date:_____

ALS Standard Operating Procedure

DOCUMENT TITLE:	DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)
REFERENCED METHOD:	EPA 200.7/6010C
SOP ID:	MET-ICP
REVISION NUMBER:	25
EFFECTIVE DATE:	01/01/2015

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

ALS-KELSO

SOP ID:	MET-ICP	Rev. Number:	25	Effective Date:	01/01/2015

Approved By: _____ Date: 12/8/14
Department Supervisor/Technical Director – Jeff Coronado

Approved By: _____ Date: 12/8/14
QA Manager – Lee Wolf

Approved By: _____ Date: 12/8/14
Laboratory Director – Jeff Grindstaff

Issue Date: _____ Doc Control ID#: _____ Issued To: _____

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature	Title	Date

TABLE OF CONTENTS

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

1. SCOPE AND APPLICATION

1.1. This procedure describes the steps taken for the analysis of soil, sludge surface water and drinking water digestates using EPA methods 6010C, 200.7, and CLP ILM04.0 for a variety of elements. The digested samples and QC standards are all diluted in a similar acid matrix. A procedure is also given for calculation of hardness by Standard Methods 2340B.

1.2. The Method Reporting Limits (MRLs) for common elements are listed in Table 1. Equivalent nomenclature for MRL includes Estimated Quantitation Limit (EQL). Therefore, MRL=EQL. The reported MRL may be adjusted if required for specific project requirements, however, the capability of achieving other reported MRLs must be demonstrated. The Method Detection Limits (MDLs) that have been achieved are listed in Table 1. The MDL and MRL may change as annual studies are performed.

1.3. In cases where there is a project-specific quality assurance plan (QAPP), the project manager identifies and communicates the QAPP-specific requirements to the laboratory. In general, project specific QAPP's supersede method specified requirements. An example of this are projects falling under DoD ELAP or project which require older versions of EPA methods (i.e. 6010B). QC requirements defined in the SOP *Department of Defense Projects – Laboratory Practices and Project Management (ADM-DOD)* may supersede the requirements defined in this SOP.

2. METHOD SUMMARY

2.1. A representative aliquot of sample is prepared as described in the applicable digestion SOP. The digestate is analyzed for the elements of interest using ICP spectrometry. The instrument measures characteristic emission spectra by optical spectrometry. The intensity of emission lines are monitored.

2.2. Final results are calculated using the digestion information and the results from the ICP analysis. Data is reported using standard ALS procedures and formats, or following project specific reporting specifications.

2.3. Deviations from the reference method(s): This SOP contains no deviations from the reference methods.

3. DEFINITIONS

3.1. **Batch** - A batch of samples is a group of environmental samples that are prepared and/or analyzed together as a unit with the same process and personnel using the same lot(s) of reagents. It is the basic unit for analytical quality control.

3.1.1. Preparation Batch - A preparation batch is composed of one to twenty field samples, all of the same matrix, and with a maximum time between the start of processing of the first and last samples in the batch to be 24 hours.

3.1.2. Analysis Batch - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc.) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. **Sample**

3.2.1. Field Sample - An environmental sample collected and delivered to the laboratory for analysis; a.k.a., client's sample.

3.2.2. Laboratory Sample - A representative portion, aliquot, or subsample of a field sample upon which laboratory analyses are made and results generated.

3.3. **Quality System Matrix** - The *matrix* of an environmental sample is distinguished by its physical and/or chemical state and by the program for which the results are intended. The following sections describe the matrix distinctions. These matrices shall be used for purpose of batch and quality control requirements.

3.3.1. Aqueous - Any groundwater sample, surface water sample, effluent sample, and TCLP or other extract. Specifically excluded are samples of the drinking water matrix and the saline/estuarine water matrix.

3.3.2. Drinking water - Any aqueous sample that has been designated a potable or potential potable water source.

3.3.3. Saline/Estuarine water - Any aqueous sample from an ocean or estuary or other salt-water source.

3.3.4. Non-aqueous Liquid - Any organic liquid with <15% settleable solids.

3.3.5. Animal tissue - Any tissue sample of an animal, invertebrate, marine organism, or other origin; such as fish tissue/organs, shellfish, worms, or animal material.

3.3.6. Solids - Any solid sample such as soil, sediment, sludge, and other materials with >15% settleable solids.

3.3.7. Chemical waste - Any sample of a product or by-product of an industrial process that results in a matrix not described in one of the matrices in Sections 3.3.1 through 3.3.6. These can be such matrices as non-aqueous liquids, solvents, oil, etc.

3.3.8. Miscellaneous matrices – Samples of any composition not listed in 3.3.1 – 3.3.7. These can be such matrices as plant material, paper/paperboard, wood, autofluff, mechanical parts, filters, wipes, etc. Such samples shall be batched/grouped according to their specific matrix.

3.4. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are 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 method used for the analysis. Duplicate samples are spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision. The concentration of the spike should be at the midpoint of the calibration range or at levels specified by a project analysis plan.

3.5. Laboratory Duplicates (DUP) – Duplicates are additional replicates of samples that are subjected to the same preparation and analytical scheme as the original sample. The relative percent difference (RPD) between the sample and its duplicate is calculated and used to assess analytical precision.

3.6. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7. Laboratory Control Samples (LCS) – The LCS is an aliquot of analyte free water or analyte free solid to which known amounts target analytes are added. The LCS is prepared and analyzed in exactly the same manner as the samples. The percent recovery is compared to established limits and assists in determining whether the batch is in control.

3.8. Laboratory fortified Blank (LFB) - A laboratory blank that has been fortified with target analyte at the method reporting limit and used to determine if the laboratory can detect contaminants at the method reporting limit.

3.9. Independent Verification Standard (ICV) - A mid-level standard injected into the instrument after the calibration curve and prepared from a different source than the initial calibration standards. This is used to verify the validity of the initial calibration standards

3.10. Continuing Calibration Verification Standard (CCV) - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.11. Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of blank reagent of composition identical to the digestates. The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

4. INTERFERENCES

4.1. Interferences from contaminated reagents must be eliminated. The purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the MRL (or above ½ the RL for DoD work).

4.2. Background emission and stray light can be compensated by background correction.

4.3. Spectral overlaps resulting in interelement contributions can be corrected for by using interelement correction factors. Interelement correction factors are established for each instrument and are maintained by the analyst at the workstation.

5. SAFETY

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

5.2. Hydrochloric, Nitric and Hydrofluoric 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. Safety glasses, lab coat and gloves should be worn while working with the solutions.

5.3. 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.

5.4. 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.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Samples are prepared using methods 3005A, 3010A, 3050, or CLPILM04.0 (ALS SOPs MET-3005A, MET-3010A, MET-3050, and MET-DIG). Samples are received in the ICP lab as completed digestates. Samples are stored in 50 mL plastic centrifuge tubes, 100 mL digestion vessels or in 100 mL volumetric flasks.

6.2. Water samples analyzed by EPA method 200.7 are preserved after arrival at the laboratory. These samples are held for a minimum of 24 hours and the pH verified to be <2 prior to digestion.

6.3. Soil samples are diluted prior to instrumental analysis by a factor of 2. This allows the method to meet the required 1 g of sample to 200 mL dilution during digestion.

6.4. Following analysis, digestates are stored until two weeks after all results have been reviewed and then brought to 3< pH<10 and disposed of through the sewer system.

7. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

7.1. Standards Preparation

7.1.1. Stock standard solutions may be purchased from a number of vendors. All reference standards, where possible, must be traceable to SI units or NIST certified reference materials. The preparation for all laboratory prepared reagents and solutions must be documented in a laboratory logbook. Refer to the SOP *Reagent/Standards Login and Tracking (ADM-RTL)* for the complete procedure and documentation requirements. Manufacturer's expiration dates are used to determine the viability of standards.

7.1.2. Calibration Standards

Calibration standards are prepared from commercially purchased single element 1000 ppm or 10,000 ppm stock standards as well as pre-mixed multi element stock standards. All standards are aliquoted using Class A volumetric pipettes, or calibrated

fixed and adjustable volume autopipetters. All dilutions are made in Class A volumetric glassware.

The standard mixes for each ICP system vary based on the requirements of each instrument. The composition of the ICAP 6500 standards are outlined in Table 2.

7.1.3. Continuing Calibration Verification (CCV) Standards

CCV standards are analyzed at the midpoint of the calibration. These standards are produced by making a two-fold dilution of each calibration standard. The CCV standards are then run in sequence during the analytical run.

7.1.4. Initial Calibration Verification (ICV) Standards

The ICV working standards are produced by direct dilution of two certified mixed stock solutions (QCP-CICV1 and QCP-CICV3 purchased from Inorganic Ventures or another qualified vendor and various single element stock solutions from sources different than the calibration standards. The composition of these standards is outlined in Table 3.

7.1.5. Interference Check Solutions (ICSA & ICSAB)

The ICSA and ICSAB working standards are produced by direct dilution of certified mixed stock solutions (CLPP-ICS-A and CLPP-ICS-B or equivalent.) Antimony is also added to the ICSAB solution from a 1000 ppm single element stock standard. The composition of these standards is outlined in Table 4.

7.1.6. CRI/Low Level Calibration Verification

The CRI, Low Level Initial Calibration Verification (LLICV), and Low Level Continuing Calibration Verification (LLCCV) are produced by diluting 1000 or 10000ppm single stock standards into a 100X intermediate standard and then diluted 1/100 to obtain the MRL level. Note: The level used is that of the normal MRL used for both instruments.

7.1.7. The solutions and materials used for the LCS and matrix spikes are described in the applicable digestion SOP.

7.1.8. Standard Log

The analyte, source, initial volume, final volume, final concentration and expiration date are recorded in a standard logbook kept in the ICP lab. The operator who prepares the standard must date and initial the entry in the standards logbook. The operator also places his initials and the date prepared on the standard container. In addition to working standards used in calibration, all other standards used in the analytical run such as ICVs, MRL standards, and other project or client specific standards shall be documented in the standard logbook.

7.2. High Purity Argon.

7.3. Capillary, rinse and peristaltic pump tubing.

7.4. 17 x 100mm polypropylene test tubes.

8. APPARATUS AND EQUIPMENT

8.1. Inductively Coupled Plasma Atomic Emission Spectrometer

8.1.1. Thermo Scientific ICAP 6500 (AES-03).
8.1.2. Thermo Scientific ICAP 6500 (AES-04).

8.2. Concentric nebulizers.

8.3. Microflow nebulizer for ICAP 6500.

8.4. Torches and injector tips for each ICP.

8.5. Cyclonic spray chambers for each instrument.

8.6. Water coolers for each ICP.

8.7. Argon Humidifiers for the ICAP 6500.

8.8. ESI SC4 DX Autosampler with Fast System for ICAP 6500.

8.9. Peristaltic Pumps for each Spectrometer.

8.10. RF Generators for each ICP (internal on the IRIS and ICAP 6500).

9. PREVENTIVE MAINTENANCE

9.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Pertinent information (serial numbers, instrument I.D., etc.) must be in the logbook. This includes the routine maintenance described in section 9. The entry in the log must include: date of event, the initials of who performed the work, and a reference to analytical control.

9.2. Torch, nebulizer, and spray chambers are cleaned as required. All instrument filters are vacuumed monthly. Dirty ICP torches and mixing chambers are soaked in aqua regia overnight, rinsed and placed in a clean dry area. The conical nebulizer is back flushed with acid or DI water as needed. The microflow nebulizer is not back flushed. Use the obstruction removal kit.

10. RESPONSIBILITIES

10.1. 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.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Training and proficiency is documented in accordance with the SOP *ADM-TRANDOC*.

11. PROCEDURE

11.1. Operating Parameters

11.1.1. For each Thermo Scientific ICAP 6500, the operating parameters are defined in the Method file. Default operating parameters are given in Tools/Options/New Method Parameters. However, each unique set of operating parameters is saved as a new file and the analyst must select and use the correct Method file for the application. Refer to the method files on the workstation for a listing of parameters for each file. The interelement correction factors to be used are established for the ICAP 6500 and are saved on the workstation also. Since these parameters change with method and correction factor updates, and due to the large amount of hardcopy printout for listing these parameters, it is not practical to include the parameters in this SOP.

11.2. Calibration/Standardization

11.2.1. ICAP 6500

11.2.1.1. Plasma is ignited and instrument is allowed to warm up for at least 30 minutes.

11.2.1.2. An internal standard is used for routine analyses on this instrument. Yttrium and Indium are used as internal standards. The internal standard solution is introduced into the analyzed solutions (standards, blanks, QC, samples, etc.) at 0.8 ug/mL for Y, and 1.6 ug/mL for In.

11.2.1.3. Run a peak check standard and adjust peaks as needed.

11.2.1.4. Standardize by running a Blank and a High Standard for each element in the analytical method. Analyst will initial and date the first page of the standardization.

11.2.2. Standardization is completed by analyzing an ICV for each analyte to be determined. For method 200.7 the result must be within ±5% of the true value. For method 6010B/C the result must be within ±10% of the true value. If the ICV fails when running method 6010C, either the calibration standards or the ICV must be prepared fresh and the instrument re-standardized. If the ICV fails when running methods 200.7 and 6010B only re-standardization is necessary.

11.2.3. Method 6010C also requires a LLICV be analyzed at the MRL level. The result must be within ±30% of the true value. The LLICV need not be made up with stock standards different than those of the calibration standards.

11.3. Analytical Run

11.3.1. Following standardization and ICV analysis, the remainder of the run is determined by what analytical method is being performed. These are listed below.

11.3.1.1. CLP ILM04.0: ICB, CCV, CCB, CRI, ICSA, ICSAB, CCV, CCB, routine samples. The CRI, ICSA, and ICSAB will be analyzed every 20 samples.

They will be labeled with an F indicating Final. Each set will be numbered in increasing order, i.e. ICSAF1, ICSAF2.

11.3.1.2. Methods 200.7 and 6010B/C: ICB, LLICV, CCV, CCB, CRI, ICSA, ICSAB, routine samples.

11.3.2. Evaluate the initial QC using the following criteria:

11.3.2.1. For methods 200.7 and 6010B/C, the following criteria apply:

- The ICB and CCB results are evaluated using method specified requirements. The following guidelines should also be used to determine acceptability:
- For 200.7, the result should be less than 3 times the standard deviation of the mean background signal.
- For method 6010B, the result should be less than the Method Detection Limit (MDL). In cases where the associated sample results are being reported to the Method Reporting Limit (MRL) the result may be greater than the MDL if the result does not adversely impact data quality.
- For method 6010C, the result should be less than the Lower Limit of Quantitation (LOQ).
- Where project specifications allow, the result may be over the MDL if the result does not adversely impact data quality.
- The CCV immediately following standardization must verify within ± 10% of the true values with a relative standard deviation of <5% from 2 replicate integrations for methods 6010B/C. For 200.7, the first CCV must verify within ± 5% with a RSD of <3% from 4 replicates. Calculate %RSD as follows:

$$\%RSD = \frac{StdDev_{CCV}}{Average_{CCV}} x\,100$$

where: StdDevccv = Standard deviation of the replicate integrations
Averageccv = Average of the replicate CCV integrations

- The LLICV or CRI is a low level standard with concentrations at the RL. For DoD projects, the LLICV standard concentrations will be equal to the project RLs. For method 6010C the CRI results should be within 30% of the true value. For 200.7 and 6010B the LLICV/CRI results should be greater than the MDL and less than 2X the MRL. For method 6010C, the LLICV results should be ± 30% of the true value.

- The ICSA is run to check the validity of the Interelement Correction Factors (IECs).

Note: DoD QSM requires this to be run at the beginning of each analytical run.

- The ICSAB must be within 20% of the expected value for the CLPP-ICS-B elements and Sb.

11.3.2.2. The ICV, LLICV, ICB, CCV, CCB, CRI, and ICSAB must meet the criteria listed. Reanalyze any elements that fail.

11.3.2.3. For CLP, refer to SOW ILM04.0 for acceptance criteria.

11.3.3. Continuing Calibration Verification

11.3.3.1. CCVs are analyzed after every 10 samples and at the end of the analytical run. They must verify within ±10% of the expected value with a RSD of <10%.

11.3.3.2. CCBs are analyzed after every 10 samples and at the end of the analytical run. CCBs are evaluated as in section 11.3.2.1.

11.3.3.3. Method 6010C requires a LLCCV be analyzed at the end of each analysis batch. The LLCCV is at the MRL level and must verify within ±30% of the true value. Reanalyze any elements to be reported at low levels that are bracketed by the LLCCV if the standard fails.

11.3.4. If the CCV or CCB solutions fail, reanalyze any elements to be reported.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery for each analyte must meet LCS criteria and the RSD< 30%.

12.2. Method Detection Limits

12.2.1. A Method Detection Limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates at a level near or below the MRL. Follow the procedures in Section 11 to analyze the samples. Refer to the SOP CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification*.

12.2.2. Calculate the average concentration found (x) and the standard deviation of the concentrations for each analyte. Calculate the MDL for each analyte using the correct

T value for the number of replicates. MDLs must be performed whenever there is a significant change in the background or instrument response.

12.2.3. A Limit of Detection (LOD) check must be performed after establishing the MDL and at least annually (quarterly if DoD) afterward. A blank is spiked with analytes at 2-4X the MDL and carried through the preparation and analytical procedure. The LOD is verified when the signal/noise ratio is > 3 for all analytes.

12.3. Limit of Quantitation Check(LOQ)/Lower Limit of Quantitation Check(LLQC)

For Method 6010C and drinking waters by method 200.7 a Lower Limit of Quantitation Check (LOQ/LLOQ) sample must be analyzed after establishing the MRL and at least annually (quarterly if DoD) afterward to demonstrate the desired detection capability. The LOQ/LLOQ sample is spiked at 1-2X the MRL and must be carried through the entire preparation and analytical procedure. Limits of quantitation are verified when all analytes are detected within 30% of their true value.

12.4. Linear Dynamic Range

The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing at least three succeeding higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% above or below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDRs are verified semi-annually or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

12.5. Instrument Detection Limit

On a quarterly basis, the instrument detection limits for all analytes are determined as per procedures outlined in ILM04.0 (Section E, paragraph 10, 12 resp.). IDLs are determined using blanks and this data is kept on file.

12.6. Interelement Correction Factors

Semi-annually, instrument interferences are calculated as per ILM04.0 (Section E, paragraph 11) and Method 6010B/C. During the course of routine work, other interferences may be found. They are verified by the operator during the analytical run and data is manually corrected. Copies of this data are kept on file. Data can be manually corrected or automatically corrected using iTEVA software.

12.7. Internal Standard

Internal standard values are tracked by the instrument software. Values should remain within 60-125% of the value found in the calibration blank. If a sample is found to have and internal standard outside this value, the sample will be diluted to bring the internal standard into range.

12.8. Ongoing QC Samples required are described in the ALS-Kelso Quality Assurance Manual and in the SOP for *Sample Batches*. Additional QC Samples may be required in project specific quality assurance plans (QAPP). For example projects managed under the DoD ELAP must follow requirements defined in the DoD *Quality Systems Manual for Environmental Laboratories*. General QA requirements for DoD QSM are defined in the laboratory SOP, Department *of Defense Projects – Laboratory Practices and Project Management (ADM-DOD).* General QC Samples are:

12.8.1. Each sample preparation batch must have a method blank associated with it. The method blank result should be < MRL. If the method blank is found to be contaminated, it may be reported if the concentration in the associated samples is at least 20 times the amount found in the method blank for methods 200.7 and 6010B, otherwise redigest the batch. For Method 6010C, the method blank may be reported if the concentration in the associated samples is at least 10 times the amount found in the method blank.A contaminated method blank (MB) may also be reported if all of the associated samples are non-detect (ND).

Note: DoD QSM requires contamination in the MB be <1/2 the RL or < 1/10 any sample amount.

12.8.2. A Laboratory Control Sample (LCS) is digested one per batch, or per 20 samples. For soil samples, the recovery must fall within the ranges specified for the reference material. For CLP, use the prescribed limits for the SOW in use. If the LCS fails the acceptance criteria, redigest the batch of samples. For specifics on the preparation and composition of LCS samples refer to the appropriate digestion SOP.

12.8.3. A Duplicate sample is digested one per batch, or per 20 samples (i.e. 5%) for 6010B/C analysis, or per 10 samples (i.e. 10%) for 200.7 analyses. If the RPD is outside acceptance limits, either redigest the sample batch or flag the data appropriately, depending on the physical nature of the samples (e.g. non-homogenous).

12.8.4. A Laboratory fortified Blank (LFB) at the MRL is digested and analyzed with every batch of drinking water samples (method 200.7). The default acceptance criteria of 50-150% are to be used until sufficient data points are acquired to calculate in-house control limits.

12.8.5. A Matrix Spike sample is digested one per batch, or per 20 samples (i.e. 5%) for 6010B/C analysis, or per 10 samples (i.e. 10%) for 200.7 analyses. Where specified by project requirements, a matrix spike duplicate may be required. If the recovery is outside acceptance limits, either redigest the sample batch or flag the data appropriately, depending on the physical nature of the samples (e.g. non-homogenous). If the sample concentration is >4x the spike level, no action is required and data is flagged accordingly. For specifics on the preparation and composition of matrix spike solutions refer to the appropriate digestion SOP.

12.8.6. Acceptance criteria

12.8.6.1. Current ALS control limits and acceptance criteria for ongoing QC analyses are listed in the current ALS-Kelso DQO tables. Criteria are subject to change as statistical data are generated. The default method criteria may be used if

statistically generated criteria are broader or insufficient points are available for accurate statistical limits.

12.8.6.2. For all QC analyses, project-specific or program-specific (e.g. DOD) acceptance criteria may supersede ALS criteria. For analyses under the CLP SOW use the prescribed limits for the SOW in use.

12.8.7. Matrix Interference

12.8.7.1. When an analyst suspects that there may be any matrix interferences present, a post digestion spike may be performed. The recovery should be ± 20%.

12.8.7.2. If the post spike fails, a 1:5 serial dilution test shall be performed. The dilution should be within ± 10% of the original result.

12.8.7.3. A 1:5 serial dilution shall be performed for all Tier III or IV deliverables.

Note: DoD QSM recovery acceptance limits are 75-125%.

12.8.7.4. Post spikes for 6010C shall be performed for Tier III and Tier 1V.

12.9. Additional QC measures include control charting and compiling of QC data for generation of control limits.

12.10. CLP analyses are performed as per the QA/QC guidelines in the most current CLP SOW.

13. DATA REDUCTION, REVIEW, AND REPORTING

13.1. 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. The wavelengths used to quantify each metal are summarized in Table 5 for the IRIS and Table 6 for the ICAP6500.

Aqueous samples are reported in ug/L:

$$\mu g/L\,(Sample) = C^{*}\ x\ Digestion\,Dilution\,Factor\ x\ Post\ Digestion\,Dilution\,Factor \times 1000\ \mu g/mg$$

Solid samples are reported in mg/Kg:

$$mg/Kg\ \ (Sample) = C^{*}\ x\ Post\ Digestion\,Dilution\,Factor\ x\ \frac{Digestion\,Vol.(ml)}{Sample\,wt.(g)}\ x\ \frac{1L}{1000ml}\ x\ \frac{1000g}{1Kg}$$

C*= Concentration of analyte as measured at the instrument in mg/L.

13.2. If total hardness is to be reported, use Calcium and Magnesium results to calculate as follows. For reporting calcium hardness, use only the calcium portion of the equation.

$$Hardness, mg\ equivalent\ CaCO_3/L = 2.497\left[Ca, mg/L\right] + 4.118\left[Mg, mg/L\right]$$

13.3. A daily run log of all samples analyzed is maintained. All CLP data should be printed and stored after operator has checked for evenness of burns. A copy of this document will go with each package of Tier III or higher data run that day.

13.4. Data Review and Reporting

13.4.1. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12. The data is then placed in a work order file until complete. When the work order is complete, a report is generated. A final review is performed and the data is delivered to the project management department.

14. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

14.1. Refer to the SOP for *Nonconformance and Corrective Action* (CE-QA008) for procedures for corrective action. Personnel at all levels and positions in the laboratory are to be alert to identifying problems and nonconformities when errors, deficiencies, or out-of-control situations are detected.

14.2. Handling out-of-control or unacceptable data

14.2.1. On-the-spot corrective actions that are routinely made by analysts and result in acceptable analyses should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, runlogs, for example.

14.2.2. Some examples when documentation of a nonconformity is required using a Nonconformity and Corrective Action Report (NCAR):

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) with target analytes above acceptable levels
- Sample holding time missed due to laboratory error or operations
- Deviations from SOPs or project requirements
- Laboratory analysis errors impacting sample or QC results
- Miscellaneous laboratory errors (spilled sample, incorrect spiking, etc.)
- Sample preservation or handling discrepancies due to laboratory or operations error

15. METHOD PERFORMANCE

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

15.2. The method detection limit (MDL) is established using the procedure described in the SOP CE-QA011, *Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantification*. Method Reporting Limits are established for this method based on MDL studies and as specified in the ALS Quality Assurance Manual.

16. POLLUTION PREVENTION AND WASTE MANAGEMENT

16.1. It is the laboratory's practice to minimize the amount of solvents, acids, and reagents used to perform this method wherever feasibly possible. 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 solvents and/or reagents used in this method can be minimized when recycled or disposed of properly.

16.2. 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 ALS Environmental Health and Safety Manual.

16.3. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 3-10 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the ALS EH&S Manual for details.

17. TRAINING

17.1. Training outline

17.1.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

17.1.2. Assist in the procedure under the guidance of an experienced analyst for approximately two weeks. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

17.1.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAP Initial Demonstration of Capability.

17.2. Training is documented following the *ALS Kelso, Training Procedure* (ADM-TRAIN) and the Corporate *Training Policy (*CE-QA003*).*

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

18. METHOD MODIFICATIONS

18.1. There are no known modifications in this laboratory standard operating procedure from the reference method.

19. REFERENCES

19.1. USEPA, Contract Laboratory Program, SOW #ILM04.0

19.2. Thermo Jarrell Ash ICAP61 Manual

19.3. USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update III, Method 6010B, Revision 2, December 1996.

19.4. USEPA, Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Update III, Method 6010C, Revision 3, February 2007.

19.5. USEPA, Methods for Determination of Metals in Environmental Samples, Supplement I, EPA/600/R-94/111, Method 200.7, Revision 4.4, May 1994.

19.6. *Hardness by Calculation, Method 2340B,* Standard Methods for the Examination of Water and Wastewater, 20th ed., 1998.

20. CHANGES SINCE THE LAST REVISION

20.1. Updated to current ALS format.
20.2. Revised internal document references from CAS to ALS
20.3. Minor typographical and format corrections.
20.4. Section 3– updated several definitions to standard definitions for SOPs.
20.5. Section 7.1.4 – corrected standard composition to reflect current practice.
20.6. Section 9.2 – revised to reflect current practice.
20.7. Section 11.3.2.1 – LL ICV criteria revised to reflect current practice.
20.8. Section 12.2.3 – LOD spike level corrected.
20.9. Section 12.4 – revised to reflect current practice (LDR semi-annual).
20.10. Sections 12.8.2. – 12.8.5 revised to remove outdated/redundant QC criteria and added new section 12.8.6.
20.11. Section 14 – updated to standard language.
20.12. Section 17 – updated to standard language.
20.13. Tables reference errors corrected and tables updated.

TABLE 1

Target Elements, Method Reporting Limits, and Method Detection Limits

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL
0.7	EPA 3050B	Aluminum	Soil	0.5	2
200.7	EPA 3050B	Antimony	Soil	2	4
200.7	EPA 3050B	Arsenic	Soil	2	4
200.7	EPA 3050B	Barium	Soil	0.3	0.8
200.7	EPA 3050B	Beryllium	Soil	0.08	0.2
200.7	EPA 3050B	Bismuth	Soil	3	8
200.7	EPA 3050B	Boron	Soil	0.7	4
200.7	EPA 3050B	Cadmium	Soil	0.09	0.2
200.7	EPA 3050B	Calcium	Soil	1	4
200.7	EPA 3050B	Chromium	Soil	0.3	0.8
200.7	EPA 3050B	Cobalt	Soil	0.2	0.4
200.7	EPA 3050B	Copper	Soil	0.4	0.8
200.7	EPA 3050B	Iron	Soil	2	4
200.7	EPA 3050B	Lead	Soil	0.7	2
200.7	EPA 3050B	Lithium	Soil	0.6	4
200.7	EPA 3050B	Magnesium	Soil	0.2	2
200.7	EPA 3050B	Manganese	Soil	0.04	0.2
200.7	EPA 3050B	Molybdenum	Soil	0.2	0.8
200.7	EPA 3050B	Nickel	Soil	0.2	0.8
200.7	EPA 3050B	Phosphorus	Soil	3	8
200.7	EPA 3050B	Potassium	Soil	10	40
200.7	EPA 3050B	Selenium	Soil	2	4
200.7	EPA 3050B	Silver	Soil	0.3	0.8
200.7	EPA 3050B	Sodium	Soil	5	40
200.7	EPA 3050B	Strontium	Soil	0.05	0.2
200.7	EPA 3050B	Sulfur	Soil	4	8
200.7	EPA 3050B	Thallium	Soil	0.8	2
200.7	EPA 3050B	Tin	Soil	0.6	4
200.7	EPA 3050B	Titanium	Soil	0.2	0.4
200.7	EPA 3050B	Vanadium	Soil	0.3	0.8
200.7	EPA 3050B	Zinc	Soil	0.2	1

TABLE 1 – continued

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL
200.7	MET-DIG (CLP)	Aluminum	Water	4	10
200.7	MET-DIG (CLP)	Antimony	Water	6	20
200.7	MET-DIG (CLP)	Arsenic	Water	5	10
200.7	MET-DIG (CLP)	Barium	Water	0.6	4
200.7	MET-DIG (CLP)	Beryllium	Water	0.5	1
200.7	MET-DIG (CLP)	Bismuth	Water	6	40
200.7	MET-DIG (CLP)	Boron	Water	4	20
200.7	MET-DIG (CLP)	Cadmium	Water	0.5	1
200.7	MET-DIG (CLP)	Calcium	Water	0.9	20
200.7	MET-DIG (CLP)	Chromium	Water	0.9	4
200.7	MET-DIG (CLP)	Cobalt	Water	1	2
200.7	MET-DIG (CLP)	Copper	Water	2	4
200.7	MET-DIG (CLP)	Iron	Water	3	20
200.7	MET-DIG (CLP)	Lead	Water	5	10
200.7	MET-DIG (CLP)	Lithium	Water	4	20
200.7	MET-DIG (CLP)	Magnesium	Water	0.3	5
200.7	MET-DIG (CLP)	Manganese	Water	0.3	1
200.7	MET-DIG (CLP)	Molybdenum	Water	0.9	4
200.7	MET-DIG (CLP)	Nickel	Water	0.6	4
200.7	MET-DIG (CLP)	Phosphorus	Water	6	40
200.7	MET-DIG (CLP)	Potassium	Water	60	200
200.7	MET-DIG (CLP)	Selenium	Water	9	20
200.7	MET-DIG (CLP)	Silicon	Water	20	200
200.7	MET-DIG (CLP)	Silver	Water	2	4
200.7	MET-DIG (CLP)	Sodium	Water	20	200
200.7	MET-DIG (CLP)	Strontium	Water	0.2	1
200.7	MET-DIG (CLP)	Sulfur	Water	20	40
200.7	MET-DIG (CLP)	Thallium	Water	4	10
200.7	MET-DIG (CLP)	Tin	Water	3	20
200.7	MET-DIG (CLP)	Titanium	Water	0.8	2
200.7	MET-DIG (CLP)	Vanadium	Water	1	4
200.7	MET-DIG (CLP)	Zinc	Water	0.6	4

TABLE 1 – continued

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL
6010C	EPA 3050B	Aluminum	Soil	0.5	2
6010C	EPA 3050B	Antimony	Soil	2	4
6010C	EPA 3050B	Arsenic	Soil	2	4
6010C	EPA 3050B	Barium	Soil	0.3	0.8
6010C	EPA 3050B	Beryllium	Soil	0.08	0.2
6010C	EPA 3050B	Bismuth	Soil	3	8
6010C	EPA 3050B	Boron	Soil	0.7	4
6010C	EPA 3050B	Cadmium	Soil	0.09	0.2
6010C	EPA 3050B	Calcium	Soil	1	4
6010C	EPA 3050B	Chromium	Soil	0.3	0.8
6010C	EPA 3050B	Cobalt	Soil	0.2	0.4
6010C	EPA 3050B	Copper	Soil	0.4	0.8
6010C	EPA 3050B	Iron	Soil	2	4
6010C	EPA 3050B	Lead	Soil	0.7	2
6010C	EPA 3050B	Lithium	Soil	0.6	4
6010C	EPA 3050B	Magnesium	Soil	0.2	2
6010C	EPA 3050B	Manganese	Soil	0.04	0.2
6010C	EPA 3050B	Molybdenum	Soil	0.2	0.8
6010C	EPA 3050B	Nickel	Soil	0.2	0.8
6010C	EPA 3050B	Phosphorus	Soil	3	8
6010C	EPA 3050B	Potassium	Soil	10	40
6010C	EPA 3050B	Selenium	Soil	2	4
6010C	EPA 3050B	Silver	Soil	0.3	0.8
6010C	EPA 3050B	Sodium	Soil	5	40
6010C	EPA 3050B	Strontium	Soil	0.05	0.2
6010C	EPA 3050B	Sulfur	Soil	4	8
6010C	EPA 3050B	Thallium	Soil	0.8	2
6010C	EPA 3050B	Tin	Soil	0.6	4
6010C	EPA 3050B	Titanium	Soil	0.2	0.4
6010C	EPA 3050B	Vanadium	Soil	0.3	0.8
6010C	EPA 3050B	Zinc	Soil	0.2	1
6010C/AVS-SEM	EPA 821/R-91-100	Antimony	Soil	0.0008	0.003
6010C/AVS-SEM	EPA 821/R-91-100	Arsenic	Soil	0.002	0.005
6010C/AVS-SEM	EPA 821/R-91-100	Cadmium	Soil	0.00007	0.0002
6010C/AVS-SEM	EPA 821/R-91-100	Chromium	Soil	0.0004	0.002
6010C/AVS-SEM	EPA 821/R-91-100	Copper	Soil	0.0005	0.002
6010C/AVS-SEM	EPA 821/R-91-100	Lead	Soil	0.0005	0.001
6010C/AVS-SEM	EPA 821/R-91-100	Nickel	Soil	0.0003	0.001
6010C/AVS-SEM	EPA 821/R-91-100	Silver	Soil	0.0003	0.001
6010C/AVS-SEM	EPA 821/R-91-100	Zinc	Soil	0.0003	0.003

TABLE 1 – continued

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL
6010C	MET-DIG (CLP)	Aluminum	Water	4	10
6010C	MET-DIG (CLP)	Antimony	Water	6	20
6010C	MET-DIG (CLP)	Arsenic	Water	5	10
6010C	MET-DIG (CLP)	Barium	Water	0.6	4
6010C	MET-DIG (CLP)	Beryllium	Water	0.5	1
6010C	MET-DIG (CLP)	Bismuth	Water	6	40
6010C	MET-DIG (CLP)	Boron	Water	4	20
6010C	MET-DIG (CLP)	Cadmium	Water	0.5	1
6010C	MET-DIG (CLP)	Calcium	Water	0.9	20
6010C	MET-DIG (CLP)	Chromium	Water	0.9	4
6010C	MET-DIG (CLP)	Cobalt	Water	1	2
6010C	MET-DIG (CLP)	Copper	Water	2	4
6010C	MET-DIG (CLP)	Iron	Water	3	20
6010C	MET-DIG (CLP)	Lead	Water	5	10
6010C	MET-DIG (CLP)	Lithium	Water	4	20
6010C	MET-DIG (CLP)	Magnesium	Water	0.3	5
6010C	MET-DIG (CLP)	Manganese	Water	0.3	1
6010C	MET-DIG (CLP)	Molybdenum	Water	0.9	4
6010C	MET-DIG (CLP)	Nickel	Water	0.6	4
6010C	MET-DIG (CLP)	Phosphorus	Water	6	40
6010C	MET-DIG (CLP)	Potassium	Water	60	200
6010C	MET-DIG (CLP)	Selenium	Water	9	20
6010C	MET-DIG (CLP)	Silicon	Water	20	200
6010C	MET-DIG (CLP)	Silver	Water	2	4
6010C	MET-DIG (CLP)	Sodium	Water	20	200
6010C	MET-DIG (CLP)	Strontium	Water	0.2	1
6010C	MET-DIG (CLP)	Sulfur	Water	20	40
6010C	MET-DIG (CLP)	Thallium	Water	4	10
6010C	MET-DIG (CLP)	Tin	Water	3	20
6010C	MET-DIG (CLP)	Titanium	Water	0.8	2
6010C	MET-DIG (CLP)	Vanadium	Water	1	4
6010C	MET-DIG (CLP)	Zinc	Water	0.6	4

TABLE 1 – continued

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL
6010C	PSEP TISSUE	Aluminum	Tissue	0.3	1
6010C	PSEP TISSUE	Antimony	Tissue	0.5	2
6010C	PSEP TISSUE	Arsenic	Tissue	0.5	1
6010C	PSEP TISSUE	Barium	Tissue	0.07	0.4
6010C	PSEP TISSUE	Beryllium	Tissue	0.05	0.1
6010C	PSEP TISSUE	Boron	Tissue	0.8	2
6010C	PSEP TISSUE	Cadmium	Tissue	0.04	0.1
6010C	PSEP TISSUE	Calcium	Tissue	2	4
6010C	PSEP TISSUE	Chromium	Tissue	0.08	0.4
6010C	PSEP TISSUE	Cobalt	Tissue	0.07	0.2
6010C	PSEP TISSUE	Copper	Tissue	0.2	0.4
6010C	PSEP TISSUE	Iron	Tissue	1	2
6010C	PSEP TISSUE	Lead	Tissue	0.3	1
6010C	PSEP TISSUE	Lithium	Tissue	0.3	2
6010C	PSEP TISSUE	Magnesium	Tissue	0.6	2
6010C	PSEP TISSUE	Manganese	Tissue	0.03	0.1
6010C	PSEP TISSUE	Molybdenum	Tissue	0.2	0.4
6010C	PSEP TISSUE	Nickel	Tissue	0.2	0.4
6010C	PSEP TISSUE	Phosphorus	Tissue	2	4
6010C	PSEP TISSUE	Potassium	Tissue	9	20
6010C	PSEP TISSUE	Selenium	Tissue	0.9	2
6010C	PSEP TISSUE	Silicon	Tissue	4	20
6010C	PSEP TISSUE	Silver	Tissue	0.2	0.4
6010C	PSEP TISSUE	Sodium	Tissue	2	20
6010C	PSEP TISSUE	Strontium	Tissue	0.04	0.1
6010C	PSEP TISSUE	Thallium	Tissue	0.4	1
6010C	PSEP TISSUE	Tin	Tissue	0.3	2
6010C	PSEP TISSUE	Titanium	Tissue	0.08	0.2
6010C	PSEP TISSUE	Vanadium	Tissue	0.2	0.4
6010C	PSEP TISSUE	Zinc	Tissue	0.2	0.4

TABLE 1 – continued

METHOD	PREP METHOD	ANALYTE	MATRIX	MDL	MRL
6010C	1311/3010A	Antimony	TCLP	0.03	0.1
6010C	1311/3010A	Arsenic	TCLP	0.025	0.05
6010C	1311/3010A	Barium	TCLP	0.5	1
6010C	1311/3010A	Beryllium	TCLP	0.001	0.005
6010C	1311/3010A	Cadmium	TCLP	0.001	0.05
6010C	1311/3010A	Chromium	TCLP	0.01	0.05
6010C	1311/3010A	Cobalt	TCLP	0.0035	0.01
6010C	1311/3010A	Copper	TCLP	0.01	0.1
6010C	1311/3010A	Lead	TCLP	0.02	0.05
6010C	1311/3010A	Manganese	TCLP	0.0025	0.005
6010C	1311/3010A	Nickel	TCLP	0.0035	0.1
6010C	1311/3010A	Selenium	TCLP	0.025	0.1
6010C	1311/3010A	Silver	TCLP	0.004	0.05
6010C	1311/3010A	Thallium	TCLP	0.1	0.25
6010C	1311/3010A	Zinc	TCLP	0.1	1

TABLE 2					
Standard A for ICAP 6500 ICP-OES					
		Source		Final	Final
Analyte	Source	Concentration	Aliquot	Volume	Concentration
		(ppm)	(mL)	(mL)	(ppm)
Antimony	(1)	100	5	1000	0.5
Beryllium	(1)	100	5	1000	0.5
Boron	(1)	100	5	1000	0.5
Cadmium	(1)	100	5	1000	0.5
Calcium	Ca stock	1000	0.5	1000	1.0*
Chromium	(1)	100	5	1000	0.5
Cobalt	(1)	100	5	1000	0.5
Copper	(1)	100	5	1000	0.5
Iron	(1)	100	5	1000	0.5
Lead	(1)	100	5	1000	0.5
Magnesium	(1)	100	5	1000	0.5
Manganese	(1)	100	5	1000	0.5
Molybdenum	(1)	100	5	1000	0.5
Nickel	(1)	100	5	1000	0.5
Selenium	(1)	100	5	1000	0.5
Silver	(1)	100	5	1000	0.5
Tin	Elemental Stock	1000	0.5	1000	0.5
Thallium	(1)	100	5	1000	0.5
Titanium	(1)	100	5	1000	0.5
Vanadium	(1)	100	5	1000	0.5
Zinc	(1)	100	5	1000	0.5
Hydrochloric Acid	-	-	50	1000	5%
Nitric Acid	-	-	10	1000	1%
(1) Mixed Standard, QCS-26 * 0.5mL 1000ppm Ca added to 5mL QCS-26(100ppm Ca), 1000mL Final Volume					

TABLE 3
ICP ICV Standards

ICV1 Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	QCP-CICV-1	1000	2.5	500	5.0
Antimony	QCP-CICV-1	1000	1.25	500	2.5
Arsenic	QCP-CICV-3	500	2.5	500	2.5
Barium	QCP-CICV-1	1000	2.5	500	5.0
Beryllium	QCP-CICV-1	25	2.5	500	0.125
Cadmium	QCP-CICV-3	250	2.5	500	1.25
Calcium	QCP-CICV-1	2500	2.5	500	12.5
Chromium	QCP-CICV-1	100	2.5	500	0.5
Cobalt	QCP-CICV-1	250	2.5	500	1.25
Copper	QCP-CICV-1	125	2.5	500	0.625
Iron	QCP-CICV-1	500	2.5	500	2.5
Lead	QCP-CICV-3	500	2.5	500	2.5
Magnesium	QCP-CICV-1	2500	2.5	500	12.5
Manganese	QCP-CICV-1	250	2.5	500	1.25
Molybdenum	Elemental Stock	1000	1.0	500	2.0
Nickel	QCP-CICV-1	250	2.5	500	1.25
Potassium	QCP-CICV-1	2500	2.5	500	12.5
Selenium	QCP-CICV-3	500	2.5	500	2.5
Silver	QCP-CICV-1	125	2.5	500	0.625
Sodium	QCP-CICV-1	2500	2.5	500	12.5
Thallium	QCP-CICV-3	500	2.5	500	2.5
Titanium	Elemental Stock	1000	1.0	500	2.0
Vanadium	QCP-CICV-1	250	2.5	500	1.25
Zinc	QCP-CICV-1	250	2.5	500	1.25
Hydrochloric Acid	-	-	25	500	5%
Nitric Acid	-	-	5	500	1%

TABLE 4
ICP Interference Check Solutions

ICSA Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	CLPP-ICS-A	5000	50	500	500
Calcium	CLPP-ICS-A	5000	50	500	500
Iron	CLPP-ICS-A	2000	50	500	200
Magnesium	CLPP-ICS-A	5000	50	500	500
Hydrochloric Acid	-	-	25	500	5%
Nitric Acid	-	-	5	500	1%

ICSAB Solution

Analyte	Source	Source Concentration (ppm)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ppm)
Aluminum	CLPP-ICS-A	5000	50	500	500
Antimony	Elemental Stock	1000	0.5	500	1
Barium	CLPP-ICS-B	50	5	500	0.5
Beryllium	CLPP-ICS-B	50	5	500	0.5
Cadmium	CLPP-ICS-B	100	5	500	1
Calcium	CLPP-ICS-A	5000	50	500	500
Chromium	CLPP-ICS-B	50	5	500	0.5
Cobalt	CLPP-ICS-B	50	5	500	0.5
Copper	CLPP-ICS-B	50	5	500	0.5
Iron	CLPP-ICS-A	2000	50	500	200
Lead	CLPP-ICS-B	100	5	500	1
Magnesium	CLPP-ICS-A	5000	50	500	500
Manganese	CLPP-ICS-B	50	5	500	0.5
Nickel	CLPP-ICS-B	100	5	500	1
Silver	CLPP-ICS-B	100	5	500	1
Vanadium	CLPP-ICS-B	50	5	500	0.5
Zinc	CLPP-ICS-B	100	5	500	1
HCl	-	-	25	500	0.05
HNO3	-	-	5	500	0.01

TABLE 5
IRIS Analytical Wavelengths

Analyte	Wavelength	
Aluminum	237.3	
Antimony	206.8	
Arsenic	189.0	
Barium	233.5	
Beryllium	313.0	
Boron	249.7	
Cadmium	226.5	
Calcium	317.9	
Calcium	211.2	High Line
Chromium	267.7	
Cobalt	228.6	
Copper	324.7	
Iron	259.9	
Iron	271.4	High Line
Lead	220.3	
Lithium	670.7	
Magnesium	279.5	
Magnesium	202.5	High Line
Manganese	257.6	
Manganese	293.9	High Line
Molybdenum	202.0	
Nickel	231.6	
Phosphorus	214.9	
Potassium	766.4	
Selenium	196.0	
Silicon	251.6	
Silver	328.0	
Sodium	589.5	
Strontium	407.7	
Thallium	190.8	
Tin	189.9	
Titanium	323.4	
Vanadium	310.2	
Zinc	206.2	

TABLE 6
ICAP 6500 Analytical Wavelengths

Analyte	Wavelength	
Aluminum	167.0	Low Line
Aluminum	394.4	
Antimony	206.8	
Antimony	217.5	Alternate
Arsenic	189.0	
Barium	455.4	
Beryllium	234.8	
Boron	249.6	
Cadmium	226.5	
Cadmium	214.4	Alternate
Calcium	315.8	
Calcium	393.3	Low Line
Chromium	267.7	
Cobalt	230.7	
Cobalt	228.6	Alternate
Copper	327.3	
Copper	224.7	Alternate
Iron	259.9	
Lead	220.3	
Lithium	670.7	
Magnesium	279.0	High Line
Magnesium	279.5	Low Line
Magnesium	285.2	
Manganese	257.6	
Manganese	260.5	High Line
Molybdenum	202.0	
Nickel	221.6	
Nickel	231.6	Alternate
Phosphorus	214.9	
Phosphorus	178.2	Alternate
Potassium	766.4	
Selenium	196.0	
Silicon	251.6	
Silver	328.0	
Sodium	588.9	Alternate
Sodium	589.5	

TABLE 6
ICAP 6500 Analytical Wavelengths, continued

Analyte	Wavelength	
Strontium	407.7	
Thallium	190.8	
Tin	189.9	
Titanium	336.1	
Vanadium	292.4	
Zinc	206.2	
Zinc	213.8	Alternate