



January 24, 2011

Mr. Dominick Orlando
 Materials Decommissioning Branch
 Division of Waste Management and Environmental Protection
 Office of Nuclear Materials Safety and Safeguard
 Two White Flint North
 11545 Rockville Pike
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Dear Mr. Orlando:

As described in Section 6.8.2 in *Field Sampling Plan (FSP) – Depleted Uranium Impact Area Site Characterization* (May 2005), the Army will conduct sequential extraction tests with soil used in the leachability tests originally collected from the Jefferson Proving Ground (JPG). This sequential extraction procedure (SEP) is useful in characterizing metal partitioning into several operationally defined geochemical fractions; therefore this SEP can predict uranium mobility in representative site soil. This letter transmits the procedure and explains some of the testing details that will be used by Materials and Chemistry Laboratory, Inc. (MCLinc)(Oak Ridge, TN) for NRC's review and approval.

The sequential extraction procedure is useful in supporting the predictions of uranium mobility in representative site soils. It cannot be used to identify the actual chemical or physical form of a given metal in soil (true speciation); however, it is useful in categorizing the metal partitioning into several operationally defined geochemical fractions. Recent studies published in technical literature have used selected sequences of extractions from soil matrices with each successive lixiviant solution (extraction reagent) increasing in its aggressiveness. The results of these sequential extractions (or "fractionation") often allow a comparison of how tenaciously different metals or radionuclides like uranium partition to different soil and sediment compositions. The partitioning of metals/radionuclides to different geochemical fractions is related to the speciation (or chemical form), as well as other physiochemical factors. Metals/radionuclides deemed least mobile in soil have a relatively small proportion of the total associated with the most readily accessible (or "exchangeable") fraction whilst having the greatest proportion associated with the most refractory (or "residual") fraction. Metals in the residual fraction are typically locked up within refractory crystalline mineral phases and are only accessible under harsher extraction conditions that are not likely to represent conditions at the site.

MCLinc has used the attached modified Tessier Sequential Extraction Procedure to evaluate low-level uranium partitioning in soils. The attached procedure is based on the original method of Tessier¹ et al. (1979), which was published in *Analytical Chemistry* (Volume 51, 1979). Subsequent work published in *Environmental Science and Technology* (1986² and 2005³) and the *Journal of Soil*

¹ Tessier, A.; Campbell, P.G.C.; Bisson, M. 1979. "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals." *Anal. Chem.* 51: 844-851.

² Rapin, F.; Tessier, A.; Campbell, P.G.C.; Carignan, R. 1986. "Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure." *Environ. Sci. Technol.* 20(8). 836-840.

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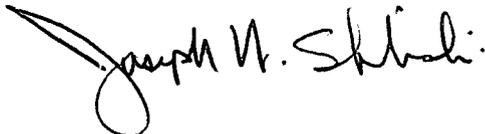
Contamination (1995⁴) has resulted in modifications that have been incorporated into the procedure proposed for use in this evaluation. MCLinc will use an aliquot of soil taken from each of the seven environmental test chambers previously used for the depleted uranium (DU) penetrator leachability tests. The methodology applies the following operationally-defined chemical treatments to selectively dissolve specific classes of macro-scale soil components:

- Fraction 1: Exchangeable Cations
- Fraction 2: Carbonate-Bound Metals
- Fraction 3: Metals Associated With Hydrated Iron- and Manganese Oxides
- Fraction 4: Bound to Organic Matter
- Fraction 5: Residual Fraction

Inductively coupled plasma optical emission spectroscopy (ICP-OES) will be used to quantify the amount of uranium present in each fraction using the attached procedures. Results will be reported in units of mg/kg (or µg/g), equivalent to parts per million (ppm).

If you have any questions, please contact Dr. David Goldblum, U.S. Army Jefferson Proving Ground (JPG) at (703) 545-2456, E-mail address: David.Goldblum@us.army.mil.

Sincerely,



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cc: Dr. David Goldblum
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SAIC Central Records Project File

³ Peltier, E.; Dahl, A.L.; Gaillard, J.-F. 2005. "Metal Speciation in Anoxic Sediments: When Sulfides can be Construed as Oxides." *Environ. Sci. Technol.* 39. 311-316.

⁴ Phillips, I.; Chapple, L. 1995. "Assessment of a Heavy Metals-Contaminated Site Using Sequential Extraction, TCLP, and Risk Assessment Techniques." *J. Soil Contam.* 4. 311-325.

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APPENDIX XX**

Code: MCL-7756
OPERATOR AIDS
Appendix XX
Effective: 12/10/2010

**MODIFIED TESSIER SEQUENTIAL EXTRACTION PROCEDURE FOR 2.5-g SOIL OR
SEDIMENT SAMPLE**

1. PURPOSE

The practical technique of choice for evaluating low-level radionuclide partitioning in soils and sediments is the sequential extraction approach.³ This methodology applies operationally-defined chemical treatments to selectively dissolve specific classes of macro-scale soil or sediment components. There is no general agreement on the solutions preferred for the extraction of various components in sediment or soils, due mostly to the matrix effects involved in heterogeneous chemical processes. The protocol below is based on the original method of Tessier et al. (1979), with minor modifications reflecting more recent literature evaluations.

2. SAMPLE RECEIPT AND PREPARATION

It is recommended that soil core samples be shipped overnight to MCLinc, packed with water ice to maintain ~ 0-4 °C (to minimize potential constituent changes due to microbial activity). If analysis cannot be initiated on the day of receipt, core samples will be placed in a deep freeze (maintained at ~ -20 °C) until testing can be performed (see, e.g., Hlavay et al., 2004). Unless specific contractual arrangements have been negotiated with the client, sample after thawing will not be excluded from exposure to the ambient atmosphere during sample processing; strict air-exclusion may minimize confounding sulfide-bound metals with their oxide-bound counterparts, and may help preserve in-situ redox conditions for anoxic sediments (Rapin et al., 1986; Peltier, 2005). If air-exclusion is specified and commissioned by the client, then sample preparation and extraction must be performed in an oxygen-free environment (e.g., within a specially maintained anoxic glove box).

Sample size is dictated by the apparent sample homogeneity. If relatively large pebbles are first removed (e.g., with use of a #10 mesh standard screen, to remove particles > 2 mm diameter), a sample size of ~ 2.5 g (dry weight equivalent) of blended soil may be used. (Record actual mass taken). If wet soil is used, the moisture content must be estimated with use of a separate sample, to permit interpretation of results expressed on a dry-weight basis.

The lack of suitable certified reference materials for use with this procedure has precluded intra-laboratory comparability of results and hence good quality control. Quality control is thus the usual controls on analytical accuracy.

³ <http://physics.nist.gov/Divisions/Div846/Gp4/Environ/speciation.html>

3. FRACTION 1: EXCHANGEABLE CATIONS (MAGNESIUM CHLORIDE, pH ~7)

Short-term (e.g., 1 h) equilibration of soil with a near-neutral solution containing a relatively high concentration (e.g., 1 mol/L) of electrolyte dissolves water-soluble salts and liberates readily exchangeable cations (by ion displacement). For the extraction of trace contaminants, Phillips and Chapple (1995) and also Tessier et al. (1979) favor use of a solution of 1 mol/L $MgCl_2$ (pH 7).

3.1 Extraction:

Reagent #1: For ~ 250-mL lixivant (extraction reagent), add 50.8-g $MgCl_2 \cdot 6H_2O$ (FW = 203.3) to ~ 200-mL de-ionized water; adjust pH value to ~ 7.0 with use of dilute NaOH or HCl solution, then adjust to final volume (~ 250-mL).

2.5 g dry soil is contacted with 20-mL of 1 mol/L $MgCl_2$ (pH 7) in a sealed 50-cc centrifuge cone for 1-h at ambient temperature. (Optimum contact is provided by tumbling the sealed vial on a TCLP rotary extractor unit). Slurry is subsequently centrifuged (4000 RPM for 12-min) and then the supernate is taken to a labeled 50-mL volumetric flask. Solid residue is rinsed in another 10-mL aliquot of lixivant, and then clarified by centrifugation. The supernate is added to the labeled volumetric flask, and the contents diluted to final volume by addition of demineralized (de-ionized) water.

4. FRACTION 2: CARBONATE-BOUND METALS (ACETATE REAGENT, pH ~ 8.2)

Following the extraction of exchangeable cations, many researchers, including Phillips and Chapple (1995), have included an extraction using 6-h contact with slightly acidic 1 mol/L sodium acetate (pH 5). This step is said to liberate the trace metal ions coprecipitated or otherwise occluded in calcite ($CaCO_3$) sediment deposits. Tessier et al (1979) prefer a variant reagent, in which the pH of the acetate solution is adjusted to 8.2; attack on silicate and sulfide minerals is said to be minimal with use of this reagent.

4.1 Extraction:

Reagent #2: For ~ 250-mL reagent, add ~ 15-g reagent grade acetic acid to ~ 200-mL de-mineralized water. Adjust pH value to ~ 8.2 by the gradual addition of sodium hydroxide, then add de-mineralized water to a final volume ~ 250-mL.

To the wet solid residue from Fraction 1, add 20-mL of ~ 1 mol/L sodium acetate (pH adjusted to a value of 8.2). Contact for 6-h at ambient temperature. The supernate is added to the labeled volumetric flask. Sample may be washed by the addition of another 10-mL aliquot of reagent, briefly re-suspending the solids, followed by centrifugation. Supernate is again added to the labeled volumetric flask and contents diluted to final volume by addition of demineralized water.

5. FRACTION 3: METALS ASSOCIATED WITH HYDROUS IRON- AND MANGANESE OXIDES (HYDROXYLAMINE-ACETATE REAGENT)

(Hydroxylamine-Acetate Reagent)

Methods for leaching iron and manganese oxides involve a combination of reagents to reduce these metals to soluble Fe^{+2} and Mn^{+2} forms, respectively, and to keep these forms in solution at relatively high concentrations. The reagent preferred by Tessier et al. (1979) consists of 0.04 mol/L $\text{NH}_4\text{OH}\cdot\text{HCl}$ in 25 % (v/v) acetic acid (pH ~ 2). The extraction of reducible iron and manganese oxides is said to be complete when soil is contacted with the reagent at 96 ± 3 °C for about 6 h with occasional agitation. The hydroxylamine reagent is said to be more effective than citrate-bicarbonate-dithionite (CBD reagent) for the dissolution of metal sulfide phases (Tessier et al., 1979).

5.1 Extraction: To the residue from Fraction 2, add 20-mL of 0.04 mol/L $\text{NH}_4\text{OH}\cdot\text{HCl}$ (FW = 71.5) in 25 % (v/v) acetic acid (pH ~ 2).

Reagent #3: For ~ 250-mL reagent: to ~ 150-mL de-ionized water add ~ 62.5-mL (~ 65.5-g) metals-grade acetic acid, and then 0.715-g $\text{NH}_4\text{OH}\cdot\text{HCl}$. Mix well and check pH value; adjust to pH ~ 2 (if necessary) with use of dilute NaOH or HCl solution. Dilute to final volume (~ 250-mL) with demineralized water.

To the residue from Fraction 2, add 20-mL of 0.04 mol/L $\text{NH}_4\text{OH}\cdot\text{HCl}$ (FW = 71.5) in 25 % (v/v) acetic acid (pH ~ 2). *Caution*: for samples containing large amounts of carbonate minerals, CO_2 gas evolution may be excessive, causing bubbling and possible spewing (with loss of sample). If vigorous bubbling is observed upon initial addition of reagent, allow several minutes for degassing in an uncapped vessel before applying heat. The centrifuge cone is then capped loosely and the soil is contacted with the reagent by placing the cone and contents in a water bath (or dry heating block) maintained at 96 ± 3 °C for about 6 h, with occasional agitation of the bottle and contents. After equilibration, the sample is centrifuged and the supernate is added to the labeled volumetric flask. Sample may be washed by the addition of another 10-mL aliquot of reagent, briefly re-suspending the solids, followed by centrifugation. Supernate is again added to the labeled volumetric flask and contents diluted to final volume by addition of demineralized water.

6. FRACTION 4: BOUND TO ORGANIC MATTER

Trace metals may be bound to various forms of organic matter: natural organic matter (notably humic and fulvic acids), microbes, detritus, coatings on mineral particles, etc. (Tessier et al., 1979). Phillips and Chapple (1995) treat the residue from Fraction 3 (above) with dilute (0.02 mol/L) nitric acid with added hydrogen peroxide solution, heating the mixture to ~ 85 C for a total of ~ 6 h.

6.1 Extraction:

Reagent #4A: Approximately 250-mL of lixivant is prepared by the addition of ~ 100-mL of 0.02 mol/L HNO₃ to ~ 150-mL of 30% hydrogen peroxide (H₂O₂). (Add dilute acid to the peroxide until the mixture pH value is adjusted to ~ 2).

Reagent #4B: Acidic ammonium acetate solution is prepared as 3.2 mol/L (247 g/L) ammonium acetate in 20% (v/v) HNO₃.

The solid residue from Fraction 3 is extracted with ~ 20 mL of acid peroxide solution (Reagent #4A). The solids are re-suspended in this solution, and the slurry heated to ~ 85 ± 2 °C for 2 h with occasional shaking. Heating is continued for a total of ~ 5-h, with additional increments of reagent added periodically as required to maintain slurry volume. The container and contents are allowed to cool to room temperature. Next, add ~ 20 mL of acidic ammonium acetate solution (Reagent #4B), and shake the bottle and contents continuously for 0.5 h at room temperature. Centrifuge and collect the supernate into a labeled 50 mL volumetric flask. Sample may be washed by the addition of another 10-mL aliquot of ammonium acetate reagent (Reagent #4B), briefly re-suspending the solids, followed by centrifugation. Supernate is again added to the labeled volumetric flask and contents diluted to final volume by addition of demineralized water.

7. RESIDUAL FRACTION

Because the residual fraction is not considered to be available for release to the environment except on a geological time scale, it may not be necessary to quantitate this fraction unless the data is needed for mass balance closure. Total digestion is relatively difficult and expensive, and seldom used in environmental analysis. More commonly used strong acid-based extractions such as EPA methods 3050 and 3051 generally recover most of the available heavy metal content, but they cannot recover metals locked within a refractory silicate matrix. The proportion of residual metal may also be roughly estimated by mass balance, if an estimate of total constituent analysis is available for the original material. Optionally (as a QC check), the residue from Fraction 5 (above) can be extracted by the same methodology used to estimate the original soil constituent or contaminant inventory; this would thus represent a direct estimate of the residual fraction.

7.1 Extraction (As Total Environmentally Available Constituent)

A separate aliquot sample of test material is extracted with use of MCLinc SOP MCL-7746 (based on EPA preparative method 3050B as defined in SW-846). This estimate for each constituent of interest will represent the total environmentally available constituent. The results for metals analysis for each of the previous sequential extractions may be compared to the available inventory, computing a percentage extracted. Mass balance closure (original inventory less constituent extracted by fractions 1 through 4) represents an indirect estimate of the residual fraction.

7. Analytical Procedures

Analysis by inductively coupled plasma spectroscopy (ICP) may require digestion to destroy excess organic reagent (e.g., acetate) and/or substantial dilution of the sample prior to analysis. Analysis will be for select dissolved metals (e.g., U and Fe, etc.) by ICP (with detection by optical emission spectroscopy, ICP-OES, MCL-7751, or mass spectroscopy, ICP-MS, MCL-7768), with appropriate analytical QA (e.g., MCL-7751, based upon NIOSH Method 7300 and USEPA SW-846 Method 6010B). Due to the very high salt and organic acid concentrations in many lixiviates used, sample digestion (MCL-7752, based on USEPA SW-846 Method 3010A) and extensive dilution will be required prior to ICP analysis. This high salt content of the digested spent lixiviant limits the sensitivity for trace elements (e.g., for U in soil, the reporting limit by ICP-OES will be ~ 0.4 µg/g for each of the extraction steps).

8. Calculations

The total mass of selected constituent extracted by each sequential leaching procedure is referenced to the original sample mass (Step 1), and is reported in units of mg/kg (or µg/g).

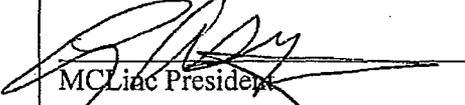
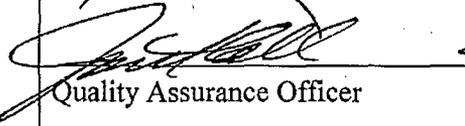
Constituent (µg/g) = (concentration, µg/L)*(V, L)/(original dry sample weight, g)

Concentration (µg/L) in the original extraction lixiviant (corrected for any dilution factors required for analysis) is estimated by the ICP instrumentation. By the procedure above, V = 50-mL = 0.05-L.

References

- Hlavay, J.; Prohaska, T.; Weisz, M.; Wenzel, W.W.; Stingeder, G.J. (2004). "Determination of Trace Elements Bound to Soils and Sediment Fractions," *Pure Appl. Chem.*, **76**(2), 415-442.
- MCL-7746, "Acid Digestion for Metals Based on EPA Method 3050B."
- MCL-7751, "Inductively Coupled Plasma – Atomic Emission Spectroscopy Metals Analysis."
- MCL-7752, "Acid Digestion of Aqueous Samples (EPA Method 3010A)."
- MCL-7768, "ICP-MS Element/Metal Sample Preparation and Analysis."
- Peltier, E.; Dahl, A.L.; Gaillard, J.-F. (2005), "Metal Speciation in Anoxic Sediments: When Sulfides can be Construed as Oxides," *Environ. Sci. Technol.*, **39**, 311-316.
- Phillips, I.; Chapple, L. (1995), "Assessment of a Heavy Metals-Contaminated Site Using Sequential Extraction, TCLP, and Risk Assessment Techniques," *J. Soil Contam.*, **4**, 311-325.
- Rapin, F.; Tessier, A.; Campbell, P.G.C.; Carignan, R. (1986), "Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure," *Environ. Sci. Technol.* ; **20**(8), 836-840.
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MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE		
Acid Digestion for Metals Based on EPA Method 3050B: Materials and Chemistry Laboratory, Inc.	Approved:  MCLinc President	8/4/10 Date
	 Quality Assurance Officer	8/4/10 Date

1.0 PURPOSE

This document provides the procedural steps and materials necessary to digest air filters, wipes, and other industrial hygiene samples, and solid samples including soils for total environmentally available metals for subsequent analysis by Flame atomic Absorption, GFAA, and Inductively Coupled Plasma

2.0 SCOPE

This procedure is based on the USEPA metals preparative Method 3050B as defined in SW-846 and NIOSH Method 7300 Elements by ICP.

3.0 ROLES AND RESPONSIBILITIES

MCLinc Analyst is responsible for following this procedure and reporting any anomalies that may occur and reviewing the results and properly documenting all elements as required in the procedure.

MCLinc Project Manager provides project oversight and is responsible to assure all users of this procedure on the project are trained and understand the procedure. The MCLinc Technical Director and QA Officer will provide support as needed.

4.0 REAGENTS/MATERIALS/EQUIPMENT

4.1 Reagents

Nitric Acid – concentrated, trace metals grade
Hydrogen peroxide – 30%
Nitric Acid Solution – 1:1 concentrated trace metals grade nitric/DI water.
Spiking Solutions
Hydrochloric Acid – concentrated, trace metals grade

4.2 Equipment

Glass beakers
Ribbed watch glasses capable of covering the beakers
Electronic Balance
Hot plate with temperature monitoring capabilities (i.e. thermometer in beaker of water)
Assorted laboratory glassware (volumetric flasks, graduated cylinders, pipets, etc.)

Funnels and Whatman # 41 filter paper or MCLinc approved equivalent.
Hot Block with temperature monitoring capability (i.e., thermometer in digestion tube of water)
50mL digestion tubes to fit hot block
50mL centrifuge tubes

4.3 Miscellaneous

Latex/nitrile gloves
Tongue depressor or metal spatulas
DI water bottle
Paper towels
Sample Prep/lot Sheet
Polyethylene bottle

5.0 PROCEDURE

Note: Clean all glassware per MCL SOP for Glassware Cleaning, MCL-7753.

5.1 Sample Preparation

1. Identify beaker and tare on the balance.
2. Transfer 2 g \pm 0.1g using a clean unused tongue depressor to the tared beaker.
3. Record the MCL Sample No. and weight on the prep/lot sheet.
4. Add 10 ml of the 1:1 nitric acid solution to the beaker mix, cover with a watch glass and reflux at 95°C \pm 5°C for a minimum of 10min without boiling.
5. Allow to cool, add 5 ml of concentrated nitric acid, replace the watch glass and reflux at 95°C \pm 5°C for a minimum of 10 min without boiling.
6. If brown fumes appear repeat step 5 until there are no more brown fumes being generated.
7. Once the generation of brown fumes has stopped allow to heat until the volume has been reduce to approximately 15-20 ml. **Do not allow to go to dryness.**
8. Allow the sample to cool, add 2 ml of DI water and 3 ml of 30% peroxide. Add the peroxide slowly being careful not to allow the sample to effervesce out of the beaker. Continue to add peroxide in 1ml aliquots until all effervescing has stopped. Do not add more than 10ml total volume of peroxide.
9. Cover the sample and reflux at 95°C \pm 5°C again reducing the volume to approximately 15-20 ml. **Do not allow to go to dryness.**
10. After cooling, filter using a funnel and Whatman #41 filter paper. Quantatively transfer the filtered sample to a 100 ml volumetric flask with DI water and bring up to volume.
11. Pour sample solution into properly labeled polyethylene sample bottle.

5.2 Sample Prep with Hot Block Digestion

1. Weigh Sample (2.0 \pm 0.1g in tared vials or carefully place air filters, wipes directly into the vials for hotblock digestion.)
2. Turn on hot block @ set point = 115 per manual (~90°C) temperature.
Check each run.

3. Weigh samples in tared vials for hot block digestion.
4. Add 10ml 8N HNO₃ and 3ml HNO₃.
5. Digest for 1 hour.
6. Remove from hot block and cool.
7. Add 3-10ml H₂O₂.
8. Digest for 30 minutes.
9. Remove from hot block and allow to cool.
10. Filter into 50mL centrifuge tube containing 5mL conc HNO₃ for ICP-OES analyses. For ICP/MS omit the 5mL conc. HNO₃.
11. Bring to volume and run on ICP.

5.3 Special Instructions – Antimony

1. This procedure is for preparation for solid sample(s) requiring antimony analysis. If sample(s) require the analysis of other metals, use this digestion procedure for the preparation for all metals.
2. Add 2.5 mL conc. HNO₃ and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample in the hot block at 95C and reflux for 15 minutes.
3. If the sample has not dissolved in the acid solution, proceed to Step 4. If the entire sample has dissolved in the digestate acid solution, filtration is not necessary. The final sample volume will be 50mL if 10 or fewer metals will be analyzed or 100mL if more than 10 metals are analyzed. Allow the digestate solution to cool. Quantitatively transfer the digestate solution to the proper size container and dilute to volume with reagent water.
4. Filter the sample/digestate solution through Whatman No. 41 filter paper or equivalent and collect filtrate in a clean 100mL volumetric flask. Wash the filter paper while still in the funnel with 5mL of hot (95±5°C) HCl, then with 5-10mL of hot reagent water. Collect the wash solutions in the same flask.
5. Remove the filter paper and residue from the funnel and place back in the digestion vessel. Add 5mL of hot HCl and place the digestion vessel back in the hot block. Heat at 95±5°C until the filter paper dissolves. Remove the tube from the hot block and rinse the watch glass and sides of tube with reagent water. Filter the residue and collect the filtrate in the same flask as in Step 4. Allow the filtrate to cool. If there is no precipitate present after cooling, dilute to volume with reagent water. If there is a precipitate present, see NOTE and proceed to Step 6.
NOTE: High Concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates in these solutions upon cooling. If precipitation occurs, do not dilute to volume.
6. If a precipitate forms, add up to 10mL HCl. After precipitate has dissolved, dilute the sample to volume with reagent water.

5.4 Special Instructions – Beryllium Oxide (BeO)

For samples requiring the analysis of BeO, prepare samples per Operator Aid UU in McLinc SOP MCL-7756.

5.5 Other Special Instructions

Radiological Screening Samples

1. Label the top of a 20 ml scintillation vial with the sample number.
2. Transfer 0.5- 2 ml of the final digestate solution from Step 10 above.
3. Proceed per MCL 7733 Section 6.6.1.11

Shipping metals digested sample

1. Label 250 ml plastic sample bottle with the MCL sample number, TM (for Total Metals) designator and Batch ID.
2. Fill bottle with final digestate solution; seal and stage for shipping

6.0 QUALITY CONTROL (QC)

Each batch of 20 or fewer samples will contain a minimum of 1 Laboratory Control Sample (LCS) and a Method Blank (MB). Matrix Spike/Matrix Spike Duplicate (MS/MSD) will be added if required by project.

6.1 LCS

Since the metal requests vary by project, select appropriate standard spiking solutions for LCS that match sample request. Spike levels should be within the calibration range of the metal.

6.2 Method Blank

1. Run with each set of samples digested.
2. Using a clean beaker begin at Step 4 above in 5.1 and process with the rest of the samples.

6.3 MS/MSD

Matrix spike (MS) and matrix spike duplicate (MSD) are project specific and are used to determine accuracy. If required, one set of MS/MSD is included with each batch of 20 or fewer samples processed.

7.0 REPORTING

All recording of information shall be done on the Metals Sample Preparation Log Sheet. An example is presented in Appendix A.

8.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Because all materials utilized in this procedure are potentially radioactive sources, all samples, waste, and standards will be appropriately labeled and handled according to MCL-7718 and MCL-7715.

The waste will be minimized by using small volumes and minimizing quantities utilized for sample preparation and standards preparation. Materials for disposal will be segregated and properly labeled. Where possible, the waste will be reduced by known treatment methodologies.

Rad waste will be measured and documented and where necessary turned over to an approved commercial handling and disposal service.

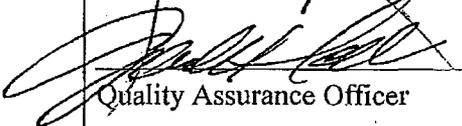
9.0 REFERENCES

USEPA SW-846 Third Edition Revision 2, December 1996 Method 3050B Acid Digestion of Sediments, Sludges, and Soils.

NIOSH Method 7300 Elements by ICP, Fourth Edition, Issue 2, August 15, 1994.

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**MATERIALS AND CHEMISTRY LABORATORY, INC.
STANDARD OPERATING PROCEDURE**

Inductively Coupled Plasma-Atomic Emission Spectrometry Metals Analysis: Materials and Chemistry Laboratory, Inc.	Approved:	
	 MCL Inc President	<u>5/15/07</u> Date
	 Quality Assurance Officer	<u>5/15/07</u> Date

1.0 PURPOSE

This document describes the procedures to determine elements/metals in properly prepared samples based upon NIOSH Method 7300 and USEPA SW-846 Method 6010B Metals using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

2.0 SCOPE AND APPLICATION

2.1 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) determines trace elements/metals, in solution. This method can be used for all elements listed in Table 1. All matrices, excluding filtered acid preserved groundwater samples; other aqueous samples, (i.e. TCLP/EP extracts; unfiltered groundwater), industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Both non-digested and digested samples must be matrix matched with the same type and concentrations of acids as found within the standards.

Table 1 lists the three analytical wavelengths to be measured per element and method detection limits for the elements. Elements other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest is demonstrated.

2.2 Users of this method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using this method for analysis.

2.3 Use of this method is restricted to chemist/qualified operators who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method. They must also have been appropriately trained on the instrumentation and its software, along with use of Attachment 1 for determining results.

3.0 RESPONSIBILITES

MCLinc Project Manager is responsible for seeing that a Total Radiological Activity Screening analysis is performed on radiochemical samples as received in a timely manner prior to ICP analysis. The Project Manager is also responsible for assuring project QA/QC is clearly defined to the ICP operator and sample preparation.

The MCLinc Analyst is responsible for routine operation, inventory of all required materials, upkeep of equipment, reviewing and reporting of results, and the housekeeping of the work area associated with the equipment.

The Operations Manager represents the first level of management and provides project oversight and is responsible for supplying the resources for proper upkeep of the required instrumentation.

4.0 SUMMARY OF METHOD

4.1 Prior to analysis, samples, except filtered and acid preserved groundwater, must be digested using appropriate sample preparation methods. This includes all total and "acid-leachable" analyses.

4.2 This method describes multi-elemental determinations by ICP-AES using a sequential optical systems and axial/radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry at the defined wavelengths. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required particularly for trace elements. A minimum of one background measurement must be measured at a wavelength adjacent to all analyte wavelengths on all samples and QA/QC during analysis. (Note two point background measurements are the preference and to be done routinely. The selection of one point is for unusual measurements.) The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In the selection of the reported wavelength the analyst should select the best representation of the measured wavelength that is determined to be as free as possible from spectral interference and appropriately compensated for background intensity. Background corrections are made as needed to compensate for excessive interferences if they occur on all three of the calibrated monitored wavelengths.

The logic for the selection of the reporting wavelength and affiliated concentration is shown in Attachment 1.

For each element - two primary and a secondary wavelength are measured. These wavelengths are predetermined (Ref. Table 1) based upon their response and the *relative absence* of spectral interferences.

5.0 DEFINITIONS

5.1 Applicable definitions are located throughout this SOP.

6.0 INTERFERENCES

6.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra, and instrumental noise (i.e. plasma flutter, pump pressure/nebulizer flutter etc.).

6.2 *Background emission and stray light can usually be compensated for by subtracting the background intensity on either side of the analyte wavelength peak. The use of multiple wavelengths for an analyte allows the selection of the wavelengths with the least amount of interference and/or background emission for reporting. The locations selected for the measurement of background intensity are determined by the complexity of the spectrum adjacent to the analyte wavelength peak. The placement of the wavelength peak baseline can be made during method set up before an analysis or during analyst data review after the analysis. The wavelength peak baseline used for routine measurement must be free of off-line spectral interference or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.*

6.2.1 The analyst in establishing the method and reviewing the resulting spectra will verify presence or absence of spectral interference by:

- Evaluating scanned wavelength on either side of the *analyte wavelength peak*
- Determining the shape of the *analyte wavelength peak of a sample compared to a calibration standard*
- Evaluating the *analyte wavelength peak* integration

6.2.2 Samples that show an elevated background emission/interferences across the range for all three defined wavelengths may be background corrected by applying the instrumental software correction program that uses algorithms to compensate and interpolate contributions from adjoining interfering spectra (i.e. interelement interference etc.). Individual spectra that show interference will be corrected only if deemed necessary due to problems with the other spectra for the affected analyte.

6.2.3 To determine the appropriate location for background correction, the user must scan the area on either side adjacent to the specified wavelength and define these areas appropriately in the establishment of the analytical methods files or during data review.

6.2.4 The potential for spectral overlaps are avoided/greatly reduced by measuring multiple wavelengths for each of the target elements.

6.2.5 Because interelement corrections vary depending upon the choice of background correction points and the complexity of the sample, multiple wavelength measurements are being used in this SOP for routine operation instead of interelement correction factors and corrections. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences that can only be compensated for by interelement manipulation, use of multiple wavelength, or software algorithms or methods of standard additions.

6.2.6 The interference effects must be evaluated when instrument parameters are changed. Intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). Even though these variables are compensated for by the calibration of each defined wavelength for each target element, the analyst is required to review the results for each wavelength. This review will determine and document per wavelength the effect of the interferences and the selection of the wavelength to be reported.

6.2.7 When the instrumental software interelement correction algorithms are applied, their accuracy should be verified, by analyzing the appropriate spectral interference check solutions.

6.2.8 When interelement corrections are used, verification of absence of interferences is required or proof that the interference is not included in the data. To demonstrate this absence of interference, an Interference Check Solution (ICS) containing similar concentrations of the major components of the interference contributing elements at > 10mg/L must be run with each new project; the resulting data must be kept on file with the sample analysis data and the affected element (those elements with > 20% variability from expected value) flagged appropriately.

6.3 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. A *Yttrium* internal standard is not used routinely but will be used if the analyst and QC deem necessary to allow for appropriate correction if physical interferences are present.

6.4 Another physical interference that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. Routine maintenance and operational awareness/data review will minimize the occurrence of this interference.

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

6.6 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and are minimized by high flow flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. If a memory interference is suspected, the sample should be reanalyzed after a rinse period of sufficient length and/or alternate rinse times and acid concentration of the rinse water may be established by the analyst based upon their DQOs

7.0 SAFETY

7.1 General laboratory protection (safety glasses, lab coat, and disposal latex/nitrile gloves) should be worn at all times when handling standards or samples.

7.2 Stock metal standards and acid solutions may pose potential health risks. Extreme care should be utilized when handling these solutions.

8.0 APPARATUS AND MATERIALS

8.1 Perkin Elmer 2000 Model Inductively Coupled Argon Plasma Atomic-Emission Spectrometer with both axial and radial measurement capability.

8.2 Sequential multiple wavelengths per analyte with affiliated computer-controlled emission spectrometer and background correction.

8.3 Radio-Frequency generator compliant with FCC regulations.

8.4 Mass flow-controller for argon nebulizer gas supply. (Geminheart nebulizer and cyclonic spray chamber)

8.5 Peristaltic pump.

8.6 Perkin Elmer Autosampler.

8.7 Argon gas supply: high-purity grade (99.99%).

8.8 Nitrogen, dry – 99% purity

9.0 REAGENTS

9.1 Acids used in the preparation of standards and for sample processing must be of high purity. Nitric acid (conc), HNO_3 , trace metals grade

9.2 Reagent water: All references to water in the method refer to reagent water which meets the electrical resistivity requirements (18Mohms.cm) of ASTM Type I water or proven to be free of target analytes, unless otherwise specified. This is also referred to as the “rinse blank” in this procedure. A 10% HNO_3 and reagent water is referred to as both the rinse and calibration blank. The rinse and calibration blank can be made in bulk amounts.

9.3 Standard stock solutions are either purchased commercially as certified standards or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity) within the lab.

Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Standards greater than 100ug/L are stable for one year from preparation date in a 10% acid solution. Standards less than 100ug/L are stable for only 6 months in a 10% acid solution. Stock standards are per manufactures expiration date and in-house at greater than 1,000mg/L are stable for 3yrs in 10% acid.

9.4 Two types of blanks are required for the analysis of samples. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample preparation processing.

9.4.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations. The calibration blank is also analyzed prior to calibration and immediately after all CCV's. The resulting spectral values for each measured wavelength are automatically subtracted from the calibration standards measurements.

9.5 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. This result is not subtracted from the samples measurements but reported as a separate QC result.

(OPTIONAL) Working ICS Solutions for checking interferences and case-by-case interference correction if required. The stock solutions for the ICS solutions will be procured certified from a commercial source.

9.7 The quality control standard is a second source standard used for Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV).

The second source solution is an independent standard near the midpoint of the calibration linear range at a concentration other than that used for instrument calibration for the majority of the calibration analytes. This standard will contain each analyte found in each of the stock solutions used to prepare the commercial standard. An independent standard is defined as a standard composed of the analytes from either a source different from those used in the standards for instrument calibration or from the same vendor but a different lot.

10.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

10.1 Sample collection procedures should address all considerations described in Quality Assurance Project Plan.

10.2 Plastic or glass containers are acceptable for use in Method 6010B.

10.3 Aqueous samples should be preserved with 1:1 HNO₃ to a pH < 2.

11.0 QUALITY CONTROL

11.1 The type and frequency of the quality control program will be define by the project. Dependant on the project defined program the following quality control data, and as defined in Table II may be included The resulting data should be maintained and be available for easy reference or inspection.

11.2 Lower Instrument Detection Limits (IDLs) in $\mu\text{g/L}$ can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined annually and kept on file. The IDL will be determined by the multiplication of the average standard deviation for each of the three days analysis measurement for each analyte wavelength by 3.14. The IDL will be defined by the least sensitive wavelength as defined in Table 1 for each measured element unless lower limits are required by the specific project.

11.3 The upper detection Limit is defined by the point where data results are not reportable due to either:

- 1) The calibration line is no longer linear
- 2) For non linear lines it is the point where the line curvation is lost and the line becomes relatively flat.

11.4 The reporting limits will be defined by the limits of the upper and lower calibration standard. All values outside the calibration range (i.e. the upper and lower reporting limit) will either be diluted to be within the calibration range or reported as estimated values. Table 1 list routine reporting limits based on least sensitive of the three wavelengths except where noted. Lower; lower reporting limits can be achieved on numerous analytes based on one or two lines if need by specific project.

11.5 A minimum three (3) point calibration curve will be developed prior to sample analysis. Two points will be the concentrations defining the upper and lower calibration limit for every wavelength being used in the analytical run (i.e. 3 wave lengths for each target analyte)

11.6 Dilution Test: This test may be applied for unusual matrices. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the method blank) an analysis of a fivefold (1+4) dilution must agree within $\pm 15\%$ of the original determination. If not, an interference effect must be suspected. One dilution test, if applicable, would be included for each twenty samples (or less) of each matrix in a batch.

11.7 Post-Digestion Spike Addition: This test may be applied for new or unusual matrices. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within $\pm 25\%$ of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.

11.8 There will be two different Laboratory Control Samples (LCS) analyzed with each batch of samples. These being:

- 1) LCSN which is a solution spiked to yield concentrations in the lower to *mid-range* of the calibration curve with all target analytes.
- 2) LCSL which is a solution spiked to yield concentrations in the 2-4X the lower calibration standard for each target analyte.

The acceptance criterion for the LCSL has yet to be defined. When sufficient data has been obtained, a decision will be made.

The acceptance criterion for the LCSN is the average of the accepted spectral lines $100 \pm 30\%$ of the known value or within the laboratory derived acceptance criteria, should that be determined.

11.9 Continuous Calibration Verification (CCV) checks the instrument calibration.

The CCV will be prepared from either a second commercial source or a different lot than the primary standard from the same commercial supplier.

The CCV will be analyzed at a frequency of every 10 samples not including instrumental QC (i.e. CCV; blanks, etc.). The CCV will also be analyzed after each calibration and after the last sample.

The results of the CCV must agree $100\% \pm 30\%$ on at least one of the analytical lines and not exceed $100\% \pm 40\%$ on the other two analytical lines where there are no known interferences present in the CCV standard solution. The average of the interference lines must not exceed $100\% \pm 37\%$. The $100\% \pm 40\%$ is not applicable for the few analytes where a really viable and stable second or third line (noted in Table 1) does not exist readily exist.

11.10 A Matrix Spike (MS) and Matrix Spike Duplicate (MSD) is project specific and is prepared and analyzed at a rate of every batch of 20 or fewer samples of the same matrix.

11.10.1 The Percent (%) Recovery is calculated as follows:
(Acceptance Criteria $\pm 25\%$)

$$\%R = \frac{(MS-S)}{TV} \times 100$$

Where:

MS = value of the Matrix Spike

S = value of the sample (unspiked)

TV = Theoretical Value of the Spike (Concentration of spiked solution))

11.10.2 The relative percent difference (RPD) between duplicate determinations must be calculated as follows: (Acceptance Criteria $\pm 20\%$)

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

Where:

RPD = relative percent difference.

D₁ = first sample value.

D₂ = second sample value (duplicate)

A control limit of 35% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection reporting limit. If this limit is exceeded, the reason for this situation must be investigated and corrected if appropriate, and if any samples are affected, they should be reanalyzed.

- 11.11 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line or plasma viewing angle for which quality control data is established.
- 11.12 MDL's are performed annually; results will be on file in MCLinc's QA/QC files.

12.0 CALIBRATION

12.1 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.

12.1.1 Turn on the Argon flow (80 PSI minimum)

12.1.2 Turn on the water chiller.

12.1.3 Connect all pump tubing.

12.1.4 Ignite Plasma and allow for warm-up and performance of automated initialization sequence.

12.2 Perform *torch* alignment.

12.3 Set up the instrument with the proper operating parameters according to the methods development defined parameters.

12.4 During calibration perform a blank and wavelength correction for all of the elements wavelengths in the method preferably using the three lower standards.

12.5 Calibrate the instrument for the analytes of interest using the calibration blank and calibration standards, at the beginning of every run. Flush the system with the rinse blank between each standard solution. Use the average of at least three plasma readings per analyte for both calibration and sample analyses.

13.0 PROCEDURE

13.1 Solubilization and digestion procedures are presented in the sample preparation methods (e.g., EPA Methods 3005 - 3050). See SOP# MCL-7746, MCL-7752, and MCL-7753. For dissolved metals analysis, take an appropriate aliquot of the filtered sample and acidify with concentrated HNO₃ acid so that the final concentration of HNO₃ is 10%.

13.2 Initiate appropriate operating configuration of the instruments method file defining reporting units (ug/L liquid and mg/kg solids) calibration parameters, re-sloping parameters and frequency, CCV frequency, acceptance criteria and corrective actions, LCS Duplicate and matrix spike criteria. In the method file also define by element the 3 wavelengths to be used, axial or radial measurement and the specific plasma operational parameters.

13.3 *Set up the Sequence window, which defines the methods to be used, the sample information file to be used, the samples to be analyzed by each method and the Results file name. The Results file is the file in which the data is stored.*

13.4 Save the sample and method files, and run the sequence.

13.5 The sample run sequence will have a Cal Blk immediately following every CCV i.e.:

Cal Blk
Calibration Standards-Low to High
CCV
Cal Blk
LRL
LCS
samples including MB, MS, MSD
CCV
Cal Blk
samples
CCV
Cal Blk
Etc.

13.6 Flush the system with the rinse blank solution until the signal levels return to the method's levels of quantitation (defined in the established method based on time and flow rate) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (defined by the method, depending on flow rate and tubing length etc.) prior to collecting data.

13.7 Dilute and reanalyze samples that have concentrate ions exceeding the linear range for an analyte.

14.0 CALCULATIONS

14.1 Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter ($\mu\text{g/L}$) for aqueous samples and micrograms per gram ($\mu\text{g/g}$) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

14.2 For dissolved metals analyses:

$$\mu\text{g/L} = C \times \text{DF}$$

Where:

C = Digest concentration ($\mu\text{g/L}$)

DF = Dilution Factor

14.3 For digested aqueous samples:

$$\mu\text{g/L} = \frac{C \times \text{DF} \times V}{W}$$

Where:

C = Digest concentration ($\mu\text{g/L}$)

DF = Dilution Factor

V = Final volume in L after sample preparation
W = Initial volume in L of sample before sample preparation

14.4 Soil/Solid concentrations may be reported on the basis of the dry weight of the sample (A separate determination of percent solids must be performed):

$$\text{ug/g (dry weight)} = \frac{C \times DF \times V \times S}{W}$$

Where:

C = Digest concentration (ug/L)
DF = Dilution Factor
V = Final volume in L after sample preparation
W = Weight in g of wet sample
S = 100 / % Solids

14.5 Air filter samples may be reported as total microgram or milligrams per filter or if air volume is given as mg/cubic meter

$$\begin{aligned} \text{Total micrograms} &= C \times DF \times V \\ \text{Total milligrams} &= \text{micrograms} / 1000 \\ \text{Total mg/cubic meter} &= \frac{C \times DF \times V}{\text{Air volume in M}^3} \end{aligned}$$

Where:

C = Digest concentration (ug/L)
DF = Dilution Factor
V = Final volume in L after sample preparation

14.6 All results should be reported with up to three significant figures.

15.0 METHOD PERFORMANCE

15.1 Refer to Table 1 for Method Detection Limit information.

16.0 POLLUTION PREVENTION

16.1 To minimize hazardous materials generated with this method, minimal quantities of samples are digested (50 mls final volume), and minimal quantities of standards are prepared.

17.0 WASTE MANAGEMENT

17.1 It is the laboratory's responsibility to comply with all applicable federal, state, and local regulations governing waste management.

18.0 REFERENCES

18.1 SW 846 3rd Edition, Method 6010B, Inductively Coupled Plasma – AES

18.2 NIOSH Method 7300, Fourth Edition, Issue 2, August 15, 1994

18.3 *EPA SW846, Method 6010C, Inductively Coupled Plasma - AES*

Table 1: Wavelength and Reporting Limits

Analyte Element	View	Wave Length #1	Wave Length #2	Wave Length #3	Lower Cal/Reporting Limit (ug/L) ¹	Upper Cal/Reporting Limit (ug/L) ¹
Al	Attn. Axial	396.153	394.401	237.313	100	3000
Ca	Radial	422.673	317.933	315.887	100	3000
Mg	Radial	279.553	280.271	285.213	100	3000
K	Attn. Axial	766.490		769.896	100	3000
K	Axial		404.721		100	3000
Cr	Axial	267.716	205.560	206.158	10	1500
Ni	Axial	227.022	221.648	231.604	10	1500
Ag	Axial	238.068	338.289	233.137 ²	10	1500
Zn	Axial	206.200	213.857	202.548	10	1500
As	Axial	193.696	188.979	197.197	8	4000
Tl	Axial	190.801	276.787	351.924	8	4000
Cd	Axial	214.440	228.802	226.502	4	2000
Se	Axial	196.026	206.279 ²	203.985 ²	25	6000
Pb	Axial	220.353	217.00	283.306	50	6000
Fe	Radial	238.204	239.562	259.939	100	10000
Co	Axial	228.616	238.892	236.380	20	6000
Ba	Axial	455.403	493.408	233.527	4	1000
Mn	Attn. Axial	257.610	259.372	260.568	4	1000
Be	Attn. Axial	313.107	234.861		4	1000
Be	Axial			313.042	4	1000
Cu	Axial	324.752	327.393	224.700	20	5000
V	Axial	292.402	311.071	270.093	20	5000
U	Axial	385.358	367.007	409.014	20	20000
Sb	Axial	206.836	217.582 ²	231.146 ²	50	6000
Ti	Axial	334.940	336.121	337.279	34	8000
Li	Radial	670.784			10	2400
Li	Axial		413.256	610.362 ²	10	2400
Mo	Axial	202.031	203.845	204.597	10	2400
Sr	Radial	407.771	421.552	460.733	7	1600
P	Axial	214.914	177.434	178.221 ²	124	11000
B	Axial	249.677	249.772	208.957	20	8000
Sn	Axial	189.927	235.485 ²	283.998 ²	40	4000
Th	Axial	283.73	401.913	339.204	20	4000
Zr	Axial	343.823	339.197	257.139	10	4000
Si	Axial	251.611	212.412	288.158	50	8000
Cs	Axial	455.531	459.320	None	5000	200000

¹ Based on Standards preparation as of 01/01/05

² Line is not strong due to either poor response or strong interference; but best available

Note: these parameters are subject to change based upon further evaluation by the operator

Table 2: Wavelengths and Method Detection Limits

Analyte/ Element	Primary Wave length A (nm)	Primary Wave length B (nm)	Secondary Wave length (nm)	Lower Cal/ Report Limit (ug/L) Single Line	Upper Cal Report Limit (ug/L) Three Line	IDL (ug/L)	MDL Soil (ug/g)	MDL Water (ug/L)
Al								
Ag ²	328.98	338.289	243.778	10	100	TBD*	TBD*	TBD*
As	228.812	188.979	193.696	10	160	TBD	TBD	TBD
Ba	455.403	493.408	233.527	0.5	2	TBD	TBD	TBD
Be	313.107	234.861	313.042	2	10	TBD	TBD	TBD
Cd	214.440	228.802	226.502	2	5	TBD	TBD	TBD
Cr	267.716	205.560	284.325	1	5	TBD	TBD	TBD
Cu	324.752	327.393	224.700	15	20	TBD	TBD	TBD
Hg	184.886	194.168	253.652	20	75	TBD	TBD	TBD
Mn	257.610	260.568	259.372			TBD	TBD	TBD
Mo	202.031	203.845	204.597	1	5	TBD	TBD	TBD
Ni	231.604	221.648	227.022	4	10	TBD	TBD	TBD
Pb	220.313	217.00	283.306	40	100	TBD	TBD	TBD
Sb	252.851	206.836	217.582	2	20	TBD	TBD	TBD
Se ²	196.026	206.279	203.985	20	50	TBD	TBD	TBD
Sr	407.771	421.512	460.733	0.1	25	TBD	TBD	TBD
U	385.958	367.007	409.014	20	40	TBD	TBD	TBD
V	292.402	309.310	311.071	1	10	TBD	TBD	TBD
Zn	206.200	213.865	202.548	5	20	TBD	TBD	TBD

Note: The project will define the target concentration and reporting limit; the reporting limit for this SOP will be defined by the least sensitive of the three wavelengths used; unless otherwise noted.

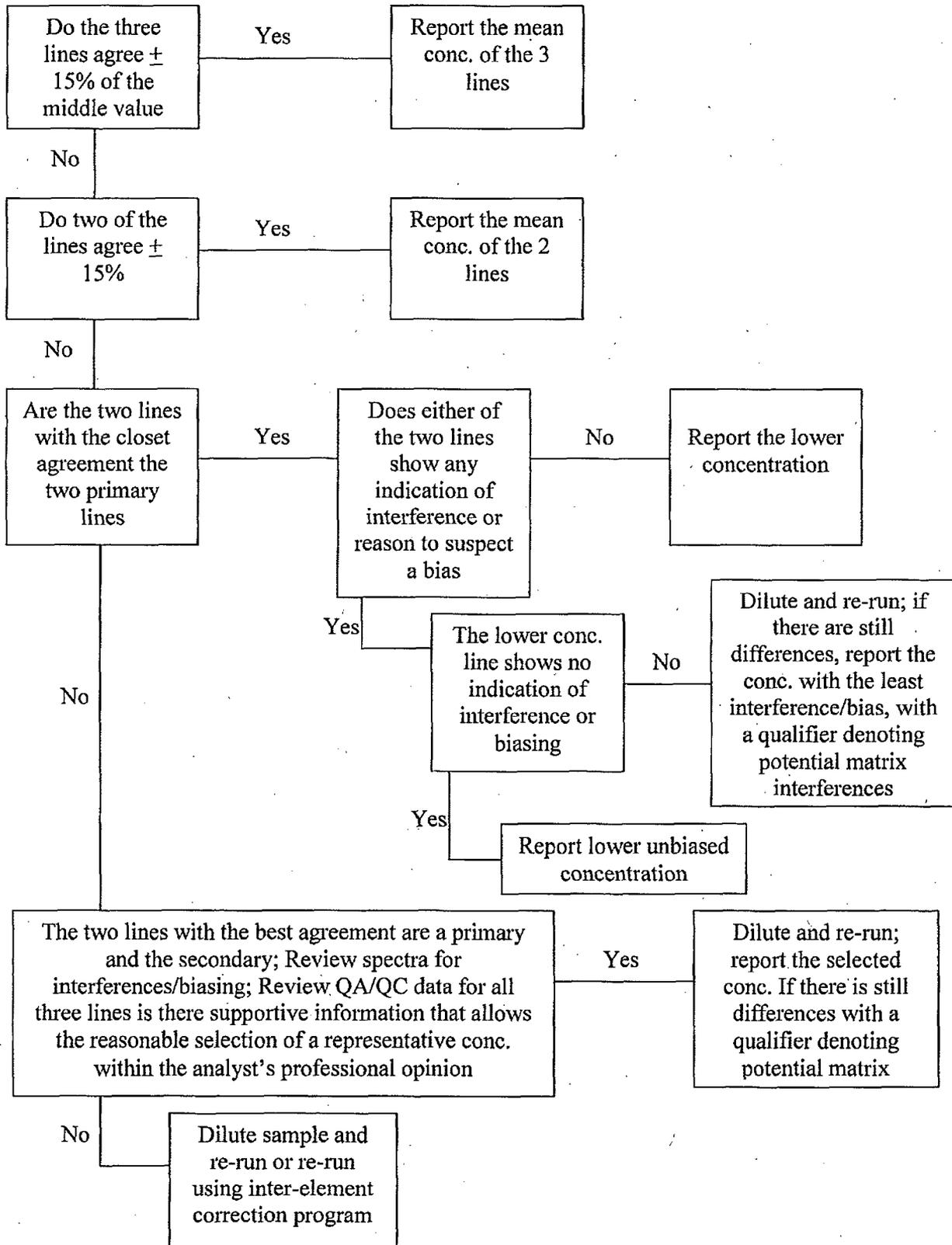
* To be determined and place in instrument log and QA files.

Table 3: QA/QC

Description	Frequency	Acceptance criteria*	Corrective Action
Calibration Curve Defining linear calibration range. 3 points minimum lower and upper defining reporting limits. 3 rd point preferably near the lower	Before the analysis of the sample where after instrumental repair or maintenance and when a CCV shows and existing calibration failed	Correlation Coef > 0.989	Check Standards, calibration range, operational parameters ; rerun calibration
Continuing Calibration Verification Std. (CCV) Standard containing all the target analytes prepared from a second source solution	After development of calibration curve; after ever 10 samples including non-blank QC's and at the end of analysis sequence	100%R+30% for at least 1 of 3 lines; 100%+40% on other two lines except where interference is occurring or other 2 lines are not viable lines for that element	Check both CCV and calibration standards preparation; re-calibrate
Calibration Blk.	Immediately following every CCV	No concentrations for any analyte in any wavelength exceeding half of the lower reporting limit	Check tubing and acid remake the solution
Laboratory Control Samples (LCSM) (LCSL) spiked clean material containing all or defined analytes processed through the entire preparation and analysis process according to EPA SW846 6010C	One each per batch of sample exceeding no more than 20 samples per batch	%R 100%+30% or as defined by developing recovery studies also is dependent on sample preparation methodology. Criteria according to EPA SW846 6010C	Re-run and if fails again, review all affiliated QA/QC and if deemed necessary by QAM re-prepare and analyze all affiliated samples
Method Blank Sample composed of all the reagents and process through the entire method	One per batch of sample exceeding no more than 20 samples per batch	No detected compounds exceeding 1/2 the lower reporting limit	Qualify reported data
Lower Reporting Limit (LRL) Reanalyze the lowest concentration calibration standard as a sample	Once per day per metal	100 ± 30%	Internal MCLinc requirement – Review with QAM

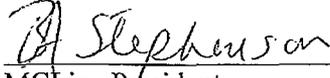
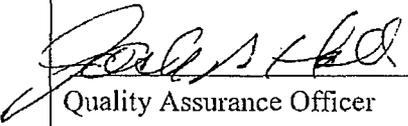
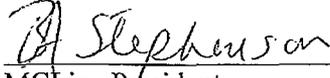
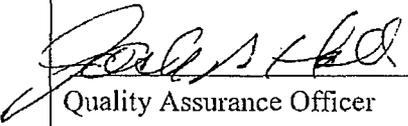
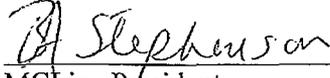
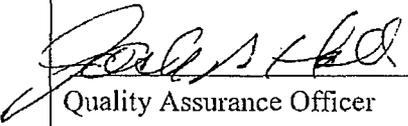
*For Air and Wipes, See AIHA Criteria

Attachment 1



**UNCONTROLLED
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MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE					
Acid Digestion of Aqueous Samples (EPA Method 3010A): Materials and Chemistry Laboratory, Inc.	<p>Approved:</p> <table style="width: 100%; border: none;"><tr><td style="width: 60%; text-align: center;"> MCLinc President</td><td style="width: 40%; text-align: center;"><u>02/21/08</u> Date</td></tr><tr><td style="text-align: center;"> Quality Assurance Officer</td><td style="text-align: center;"><u>2/2/08</u> Date</td></tr></table>	 MCLinc President	<u>02/21/08</u> Date	 Quality Assurance Officer	<u>2/2/08</u> Date
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 Quality Assurance Officer	<u>2/2/08</u> Date				

1.0 PURPOSE

This document describes the process for acid digestion of aqueous samples for subsequent analysis of metals based on the USEPA SW-846 Method 3010A.

2.0 SCOPE AND APPLICATION

2.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

2.2 Samples prepared by Method 3010 may be analyzed by ICP for the following:

- | | |
|-----------|------------|
| Aluminum | Magnesium |
| Antimony | Manganese |
| Arsenic | Molybdenum |
| Barium | Nickel |
| Beryllium | Potassium |
| Boron | Selenium |
| Cadmium | Silver |
| Calcium | Sodium |
| Chromium | Strontium |
| Cobalt | Thallium |
| Copper | Uranium |
| Iron | Vanadium |
| Lead | Zinc |
| Lanthanum | |

Other metals may be digested by the method if satisfactory laboratory control sample results are achieved.

3.0 RESPONSIBILITIES

MCLinc Analyst is responsible for following this procedure and reporting any anomalies that may occur and reviewing the results and properly documenting all elements as required in the procedure.

MCLinc Project Manager provides project oversight and is responsible to assure all users of this procedure on the project are trained and understand the procedure. The MCLinc Technical Director and QA Officer will provide support as needed.

4.0 SUMMARY OF METHOD

4.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

5.0 INTERFERENCES

5.1 Interferences are discussed in the referring analytical method (6010B).

6.0 APPARATUS AND MATERIALS

Beakers - 250-mL or equivalent

Watch glasses - Ribbed and plain or equivalent

Qualitative filter paper *or syringe/membrane syringe filter* or centrifugation equipment

Assorted glassware – graduated cylinders, volumetric flasks, pipettes, funnels

Hot plate or hot block – adjustable temperature with temperature monitoring capability

7.0 REAGENTS

7.1 Reagent grade chemicals are used in all tests, unless otherwise indicated. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.2 All Reagent water is to be interference free. All references to water in the method refer to reagent water unless otherwise specified

7.3 Nitric acid (concentrated), HNO_3 . Acids are analyzed to determine levels of impurities. If method blank is less than the MDL, the acid can be used. Trace metals grade acids meets this requirement, but must be checked by running blanks.

7.4 Hydrochloric acid (1:1), HCl . Prepared from water and hydrochloric acid. Hydrochloric acid is analyzed to determine level of impurities. If method blank is less than the MDL, the acid can be used. Trace metals grade acids meets this requirement, but must be checked by running blanks.

8.0 PROCEDURE

8.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 250-mL beaker and add 3 mL of concentrated HNO_3 . Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (15-20 ml), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker, rinse the ribbed watch glass into the beaker with reagent water and add another 3-mL of concentrated nitric acid. Cover the beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go below 10 ml, low recoveries will result. Should this occur, discard the sample and re-prepare.

8.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Cool the beaker. (If silver is an analyte of interest eliminate the next step using hydrochloric acid, since silver chloride has a very low solubility). Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation. **Caution:** Do not allow to boil since antimony is easily lost from a hydrochloric acid media. Do not allow sample to go below 10 ml, preferably 15-20 ml.

8.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis

9.0 ALTERNATE PROCEDURE USING HOT BLOCK DIGESTION

9.1 Transfer a 40mL aliquot of well-mixed sample to a 50mL digestion tube. Add 3mL conc. HNO_3 and 3mL conc. HCl . Cover tube with a ribbed watch glass. Reflux in hot block at 95°C for 1-2 hours to reduce volume to 30-36mL.

9.2 Remove digestion tubes from hot block and allow to cool to room temperature. If any insoluble material is present, filtration of the digestate will be necessary with filter paper or syringe/syringe filter. Rinse the filter paper/holder with dilute nitric acid to clean and discard the rinse solution. Quantitatively transfer the digestate with rinsing to a 50mL centrifuge tube containing 5mL conc HNO_3 or to a 100mL volumetric flask containing 10mL conc HNO_3 . *For samples prepared for ICP-MS analysis, omit the conc HNO_3 in this step.* Dilute to volume with deionized water.

10.0 QUALITY CONTROL

10.1 All quality control criteria described in analytical technique method/SOP must be met.

10.2 For each analytical batch of samples processed, a blank is carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

10.3 Matrix spike (MS) and matrix spike duplicate (MSD) are project specific and are used to determine accuracy. If required, one set of MS/MSD is included with each batch of 20 or fewer samples processed.

10.4 A Laboratory Control Sample (LCS) is run with each batch.

11.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Because all materials utilized in this procedure are potentially radioactive sources, all samples, waste, and standards will be appropriately labeled and handled according to MCL-7718 and MCL-7715.

The waste will be minimized by using small volumes and minimizing quantities utilized for sample preparation and standards preparation. Materials for disposal will be segregated and properly labeled. Where possible, the waste will be reduced by known treatment methodologies.

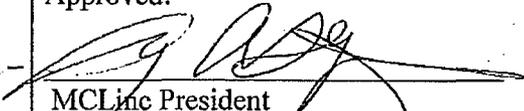
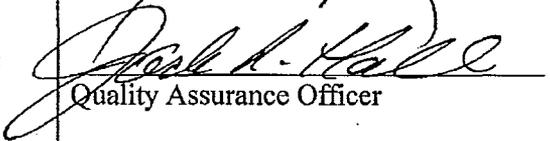
Rad waste will be measured and documented and where necessary turned over to an approved commercial handling and disposal service.

12.0 REFERENCES

USEPA SW-846 Third Edition Revision 2 December 1996 Method 3010A

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MATERIALS AND CHEMISTRY LABORATORY, INC. STANDARD OPERATING PROCEDURE	
Inductively Coupled Plasma – Mass Spectrometry Element/Metals Sample Preparation and Analysis: Materials and Chemistry Laboratory, Inc.	Approved:  MCLinc President Date 4/16/07
	 Quality Assurance Officer Date 4/16/07

1.0 PURPOSE

This document describes the procedures to determine elements/metals in properly prepared samples by inductively-coupled plasma – mass spectrometry (ICP-MS) based upon USEPA SW-846 Method 6020A. This document is also meant to determine elements/metals in properly prepared samples by ICP-MS based upon USEPA ORD Method 200.8. Any additional or slightly different requirements in Method 200.8 are given in Appendix 1.

2.0 SCOPE AND APPLICATION

2.1 Inductively coupled plasma – mass spectrometry (ICP-MS) determines trace elements/metals in solution. This method can be used for all elements/metals in Table 1. All matrices excluding filtered acidified groundwater samples and including other aqueous samples, industrial and organic wastes, soils, sludges, sediments and other solid wastes require digestion prior to analysis. Both non-digested and digested samples must be matrix-matched with the same type and concentrations of acids as found within the calibration standards.

Table 1 lists the elements that can be analyzed by this method. Elements other than those can be analyzed by this method if performance at the concentration levels of interest is demonstrated.

2.2 Users of this method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to the use of the method for analysis.

2.3 Use of this method is restricted to chemist/qualified operators who are knowledgeable in the correction of chemical and physical interferences described in this method. They must also have been appropriately trained on the instrumentation and its software.

2.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standard elements are ^6Li , ^{45}Sc , ^{74}Ge , ^{89}Y , ^{103}Rh , ^{115}In , ^{159}Tb , ^{165}Ho , ^{209}Bi . The lithium internal standard should have an enriched abundance of ^6Li so that interference from lithium native to the sample is minimized. The listed elements can be used as internal standards and other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standard elements. MCL is routinely using ^6Li , ^{45}Sc , ^{74}Ge , ^{115}In , ^{159}Tb and ^{209}Bi .

3.0 RESPONSIBILITIES

The **MCLinc Project Manager** is responsible for assuring that project QA/QC is clearly defined to the ICP operator and sample preparation analyst and any health and safety issues are understood.

The **MCLinc Analyst** is responsible for routine operation, inventory of all required materials, upkeep of equipment, reviewing and reporting of results and the housekeeping of the work area associated with the equipment.

The **MCLinc Operations Manager** represents the first level of management, provides project oversight and is responsible for supplying the resources for proper upkeep of the required instrumentation.

4.0 SUMMARY OF METHOD

4.1 Prior to analysis, samples, except for filtered and acid preserved groundwater samples, must be digested using appropriate sample preparation methods. This includes all total and "acid-leachable" samples.

4.2 This method describes the multi-element determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures 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.

5.0 DEFINITIONS

Applicable definitions are located throughout this SOP.

6.0 INTERFERENCES

- 6.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.
- 6.2 Isobaric, molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. The instrument software used corrects for isobaric and doubly-charged ion interferences. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Examples include $^{75}\text{ArCl}^+$ ion on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics. Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}\text{Ar}^{37}\text{Cl}^+$ at m/z 75 is a negligible 0.06% of the $^{40}\text{Ar}^{35}\text{Cl}^+$ signal):

$$\begin{aligned} &\text{Corrected arsenic signal (using natural isotopes abundances for coefficient approximations)} \\ &= (m/z 75 \text{ signal}) - (3.13) (m/z 77 \text{ signal}) + (2.73) (m/z 82 \text{ signal}) \end{aligned}$$

where the final term adjusts for any selenium contribution at 77 m/z ,

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

Similarly,

$$\begin{aligned} &\text{Corrected cadmium signal (using natural isotopes abundances for coefficient approximations)} \\ &= (m/z 114 \text{ signal}) - (0.027) (m/z 118 \text{ signal}) - (1.63) (m/z 108 \text{ signal}), \end{aligned}$$

where last 2 terms adjust for any $^{114}\text{Sn}^+$ or $^{114}\text{MoO}^+$ contributions at m/z 114.

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

NOTE: As for the arsenic equation above, the coefficients could be improved. The most appropriate coefficients for a particular instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 %) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. For example, this type of correction has been reported for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed gas plasmas have been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met. Common isobaric, double charge and oxide formation corrections are included in the instrument software and are performed automatically.

- 6.3 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both elemental and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid-digested samples. Acid-digested samples refer to samples digested by methods similar to SW 846 methods 3052, 3051, 3050, or 3015. Samples with percent levels of iron and aluminum should be avoided. The method also provides a procedure for preconcentration to enhance detection limits simultaneously with elimination of isobaric interferences. The method relies on chelating resins such as iminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified and these interferences cannot occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs. The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.
- 6.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes. When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30% of the signals

in the calibration standards) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Section 13.7).

6.5 Memory interferences or carry-over can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler or skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

7.0 SAFETY

7.1 General laboratory protection (safety glasses, lab coat and disposable latex/nitrile gloves) should be worn at all times when handling standards or samples.

7.2 Acid solutions may pose potential health risks. Extreme care should be utilized when handling these solutions.

8.0 EQUIPMENT AND SUPPLIES

8.1 Inductively coupled plasma-mass spectrometer such as Perkin Elmer Elan 9000 with: (See Appendix 1 for Method 200.8 requirements)

8.1.1 Capability of providing resolution, better than or equal to 1.0 amu at 10% peak height. .

8.1.2 Mass range from at least 6 to 240 amu.

8.1.3 Data system that has corrections for common isobaric, double charge and oxide interferences and the application of the internal standard technique.

8.2 Mass flow controller for argon nebulizer gas supply.

8.3 Peristaltic pump for delivery of sample to nebulizer.

8.4 Argon gas supply, high purity.

9.0 REAGENTS AND STANDARDS

9.1 Acids used in the preparation of standards and for sample processing must be of high purity. Nitric acid at less than 2% (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used. Concentrations of antimony and silver between 50-500 $\mu\text{g/L}$ require 1% (v/v) HCl for stability. For concentrations above 500 $\mu\text{g/L}$ Ag, additional HCl will be needed. Consequently, accuracy of analytes requiring significant chloride molecular ion corrections (such as As and V) will degrade.

- 9.2 Reagent Water: All references to reagent water in the method refer to reagent water which meets the electrical resistivity requirements (18 Mohms/cm) of ASTM Type I water or proven to be free of target analytes, unless otherwise specified. This is also referred to as the rinse blank in this procedure. A 1-3% (v/v) HNO₃ and reagent water is referred to as both the rinse and calibration blank. The rinse and calibration blank can be made in bulk amounts.
- 9.3 Standard stock solutions are either purchased commercially as certified standards or prepared from ultra-high purity grade chemicals or metals (99.99% or greater purity).
- 9.4 Mixed calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 1% (v/v) HNO₃ in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ⁶Li, ⁴⁵Sc, ⁷⁴Ge, ⁸⁹Y, ¹⁰³Rh, ¹¹⁵In, ¹⁵⁹Tb, ¹⁶⁵Ho, ²⁰⁹Bi. MCL is routinely using ⁶Li, ⁴⁵Sc, ⁷⁴Ge, ¹¹⁵In, ¹⁵⁹Tb and ²⁰⁹Bi.
- 9.5 Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Fresh mixed standards should be prepared, as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 9.7).
- 9.6 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for possible contamination resulting from the sample preparation procedure. The instrument blank is used to flush the system between all samples and standards.
- 9.6.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1% HNO₃ (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes.
- 9.6.2 The method (or preparation) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.
- 9.6.3 The instrument blank consists of 1% to 3% HNO₃ (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. If mercury is to be analyzed, the instrument blank should also contain 2 mg/L AuCl₃ solution.

- 9.7 The interference check solutions A and AB (ICS-A, ICS-AB) are prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$ and $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

NOTE: The final ICS solution concentrations in Table 2 are intended to evaluate corrections for known interferences on only the analytes in Table 1. If this method is used to determine an element not listed in Table 1, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of the correction on interferences on the unlisted element.

The ICS solutions can be obtained commercially or prepared from ultra-pure reagents.

- 9.8 The quality control standard is the second source standard used for initial calibration verification (ICV) and continuing calibration verification (CCV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration or from the same vendor but a different lot.
- 9.9 Mass spectrometer tuning solution is a solution containing elements representing all of the mass regions of interest to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 13.4). This solution is also used to verify that the instrument has reached thermal stability. For the Elan 9000 ICP-MS, the tuning solution contains 10 µg/L Be, Mg, Co, Rh, In, Ba, Ce, Pb and can also contain Cu, Cd and U.
- 9.10 Dual detector cross-calibration solution is required for the Elan 9000 ICP-MS for the calibration of the detector in the crossover range between the pulse and analog ranges. This solution will contain 250 µg/L each of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Tl, Th, U, V, Zn, Na, Ca, Mg, K, Fe, Sc, Y, In, Rh, Tb, Ho, and Bi and 1250 µg/L Ge.

10.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 10.1 Sample collection procedures should address all considerations described in the Quality Assurance Project Plan, (MCL-7701).
- 10.2 Only polypropylene or fluorocarbon containers are suitable for collection of samples for Method 6020A.

10.3 Aqueous samples should be preserved with 1:1 HNO₃ to a pH <2.

11.0 QUALITY CONTROL

- 11.1 The type and frequency of the quality control program will be defined by the project. Depending upon the project defined program, the following quality control data, as defined in Table 3 may be included. The resulting data should be maintained and be available for easy reference or inspection.
- 11.2 Instrument detection limits (IDLs) in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined every 3 months and kept on file.
- 11.3 The intensity of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 30% of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. Under these conditions, the detection limit has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is used: First, make sure that the instrument has not just drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise above the 30% limit. Reported results must be corrected for all dilutions.
- 11.4 To obtain data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxides can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantitation and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferent itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections is required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a

sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element of molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 6.2) for each instrument system are acceptable corrections for use in this method.

- 11.5 Dilution test (DT) (serial dilution): This test may be applied for unusual matrices. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the method blank, refer to Section 9.5.2), an analysis of fivefold (1+4) dilution must agree within $\pm 10\%$ of the original determination. If not, an interference effect must be suspected. One dilution test is included for each 20 samples (or less) of each matrix in a batch.
- 11.6 Post-digestion spike addition (PDSA): An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125% of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect.
- 11.7 There will be two different laboratory control samples (LCS) analyzed with each batch of 20 or fewer samples using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples:
- 11.7.1 LCSN (normal) is a solution spiked to yield concentrations in the low to midrange of the calibration curve for each target analyte. The acceptance criterion is $100\pm 30\%$.
- 11.7.2 LCSL (low) is a solution spiked to yield concentrations 2-4x the concentration of the lowest calibration standard for each target analyte. The acceptance criterion will be determined based on historical results of ICP-MS.
- 11.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:
- 11.8.1 Check instrument calibration using a calibration blank and the ICV.
- 11.8.2 Verify calibration at a frequency of every 10 analytical samples with the CCV and the calibration blank. These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

- 11.8.3 The results of the ICV and CCV must agree within $\pm 10\%$ of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-range calibration must be reanalyzed.
- 11.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-range condition must be found and corrected and affected samples reanalyzed.
- 11.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions. The analyst should be aware that precipitation from the ICS solutions may occur, particularly with silver.
- 11.10 The analysis of duplicate samples is project specific at the rate of one duplicate for every 20 or less samples. The acceptance criterion is $\pm 20\%$.

11.10.1 The relative percent difference (RPD) between duplicate determinations is calculated as follows:

$$\text{RPD} = 100 \times \frac{|D_1 - D_2|}{(D_1 + D_2)/2}$$

Where:

RPD = relative percent difference

D_1 = initial sample concentration

D_2 = duplicate sample concentration

A control limit of 35% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection reporting limit. If this limit is exceeded, the reason for this situation must be investigated and corrected if appropriate, and if any samples are affected, they should be reanalyzed.

- 11.11 Lower Reporting Limit Verification – After the ICV is analyzed and verified, the lower reporting limit (LRL) is verified by analyzing the lowest concentration calibration standard as a sample. The percent recovery should be $\pm 30\%$.
- 11.12 A matrix spike (MS) and matrix spike duplicate (MSD) is project specific and is prepared at the frequency of one for every batch of 20 or fewer samples. Acceptance criterion is $\pm 25\%$.

11.12.1 The % Recovery is calculated as follows:

$$\%R = 100 \times \frac{(MS - S)}{TV}$$

Where:
%R = % recovery
MS = concentration in matrix spike
S = concentration in sample
TV = theoretical concentration of the spike

12.0 CALIBRATION AND STANDARDIZATION

12.1 Conduct mass calibration and resolution checks in the mass regions of interest with the tuning solution. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.

12.2 Calibrate the instrument for the analytes of interest (recommended isotopes for analytes are given in Table 3), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank between each standard solution. Use the average of at least 3 integrations for both calibration and sample analyses.

NOTE: Analysts have noted improved performance in calibration stability if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 to 10 minutes before the calibration blank is run.

12.3 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 3.

12.4 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the CCV solution. When measurements exceed $\pm 10\%$ of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-range calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift, but resloping must not be used as an alternative to reanalyzing samples following an unacceptable QC sample, such as a CCV. A recalibration must then be followed immediately by a new analysis of a CCV and a calibration blank before any further samples may be analyzed.

13.0 PROCEDURE

13.1 Sample Preparation

Samples should be prepared according to Acid Digestion for Metals (MCL-7746).

- 13.2 Initiate appropriate operating configuration of the instrument computer according to the instrument manufacturer's instructions.
- 13.3 Set up the instrument with the proper operation parameters according to the instrument method file defining reporting units ($\mu\text{g/L}$ for liquid and mg/Kg for solids), calibration parameters, ICV and CCV frequency, acceptance criteria and corrective actions, ICS and LCS criteria. In the method file, also define by element the isotope(s) to be used and the specific plasma operational parameters.
- 13.4 Set up the Workspace file defining the analysis method, sample file, calibration file, data acquisition file, and the instrumental conditions file, which includes tuning, lens calibration and nebulizer calibration.
- 13.5 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 9.8) at least 4 times with relative standard deviations of $\leq 5\%$ for the analytes contained in the tuning solution.
- 13.6 Calibrate the instrument following the procedure outlined in Section 12.0.
- 13.7 The sample run sequence will have an instrument blank immediately following each CCV as shown in this sequence example:

Calibration Blank (Section 9.5.1)
Calibration Standards, Lowest Concentration to Highest (Section 9.4)
ICV (Section 9.7)
LRL (Section 11.11)
Instrument Blank (Section 9.5.3)
ICS-A (Section 9.6)
ICS-AB (Section 9.6)
LCSL (Section 11.7.2)
LCSN (Section 11.7.1)
Method Blank (Section 9.5.2)
Up to 10 Samples, including Duplicates and MS/MSD (MS/MSD only if required by project)
CCV (Section 9.7)
Instrument Blank
Up to 10 Samples, including Duplicates
PDSA (Section 11.6)
DT (Section 11.5)
CCV
Instrument Blank

The method preparation quality control samples: LCSL, LCSN, Method Blank, PDSA and DT are counted in the run sequence as samples, i.e., as one of the 10 samples between each ICV – CCV or CCV- CCV sequence.

- 13.8 Flush the system with the instrument blank solution (Section 9.5.3) until the signal levels return to the levels of quantitation defined in the method (usually about 30 seconds) before the analysis of each sample (see Section 12.3). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the CCV solution (Section 9.7) and calibration blank (Section 9.5.1) at a frequency of at least once for every 10 analytical samples. Flow injection systems can be used as long as they meet the performance criteria of this method.
- 13.9 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less abundant isotope. The linearity of the alternate mass must be confirmed by appropriate calibration (see Section 12.2 and 12.4). Alternatively, apply solid phase chelation chromatography to eliminate the matrix interference as described in Section 6.3.

14.0 DATA ANALYSIS AND CALCULATIONS

- 14.1 The quantitative values shall be reported in appropriate units, such as micrograms per liter ($\mu\text{g/L}$) for aqueous samples and milligrams per kilogram (mg/Kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All calculations must include appropriate interference corrections (see Section 6.2 for examples), internal-standard normalization, and the summation of signals at 206, 207 and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

- 14.2 For dissolved metals analyses:

$$\mu\text{g/L} = C \times \text{DF}$$

Where:

C = Sample concentration ($\mu\text{g/L}$)

DF = Dilution factor

- 14.3 For digested aqueous samples:

$$\mu\text{g/L} = \frac{C \times \text{DF} \times V}{W}$$

Where:

C = Digestate concentration ($\mu\text{g/L}$)

DF = Dilution factor

V = Final volume in L after sample preparation
W = Initial volume in L of sample used for sample preparation

14.4 Soil/Solid concentrations may be reported on the basis of the dry weight of the sample (a separate determination of % total solids must be performed):

$$\mu\text{g/g (dry weight)} = \frac{C \times DF \times V \times S}{W}$$

Where:

C = Digest concentration ($\mu\text{g/L}$)
DF = Dilution factor
V = Final volume in L after sample preparation
W = Weight in g of wet sample
S = 100 / % solids

14.5 Air filter sample concentrations may be reported as total μg or total mg per filter or if the air volume sampled is given, as mg/cubic meter (mg/m^3):

$$\begin{aligned} \text{Total } \mu\text{g} &= C \times DF \times V \\ \text{Total mg} &= \mu\text{g} / 1000 \\ \text{mg/m}^3 &= \frac{C \times DF \times V}{\text{Air volume in m}^3} \end{aligned}$$

Where:

C = Digest concentration ($\mu\text{g/L}$)
DF = Dilution factor
V = Final volume in L after sample preparation

15.0 METHOD PERFORMANCE

15.1 Refer to Table 1 for method detection limit information.

16.0 POLLUTION PREVENTION

16.1 To minimize hazardous materials generated with this method, minimal quantities of samples are digested (50-100 mL final digestate volume) and minimal quantities of standards are prepared.

17.0 WASTE MANAGEMENT

It is the laboratory's responsibility to comply with all applicable federal, state and local regulations governing waste management.

TABLE 1.
ELEMENTS THAT CAN BE ANALYZED BY ICP-MS ACCORDING TO EPA METHOD 6020A
AND DETECTION LIMITS

Element	Symbol	Lower Reporting Limit (µg/L)	Instrument Detection Limit (µg/L)	Method Detection Limit Soil (µg/g)	Method Detection Limit Water (µg/L)
Aluminum	Al	1.0	TBD*	TBD*	TBD*
Antimony	Sb	0.05	TBD	TBD	TBD
Arsenic	As	0.02	TBD	TBD	TBD
Barium	Ba	0.1	TBD	TBD	TBD
Beryllium	Be	0.02	TBD	TBD	TBD
Cadmium	Cd	0.02	TBD	TBD	TBD
Calcium	Ca	1.0	TBD	TBD	TBD
Chromium	Cr	0.05	TBD	TBD	TBD
Cobalt	Co	0.05	TBD	TBD	TBD
Copper	Cu	0.05	TBD	TBD	TBD
Iron	Fe	1.0	TBD	TBD	TBD
Lead	Pb	0.05	TBD	TBD	TBD
Magnesium	Mg	1.0	TBD	TBD	TBD
Manganese	Mn	0.1	TBD	TBD	TBD
Mercury	Hg	TBD	TBD	TBD	TBD
Nickel	Ni	0.05	TBD	TBD	TBD
Potassium	K	1.0	TBD	TBD	TBD
Selenium	Se	0.02	TBD	TBD	TBD
Silver	Ag	0.05	TBD	TBD	TBD
Sodium	Na	1.0	TBD	TBD	TBD
Thallium	Tl	0.02	TBD	TBD	TBD
Uranium	U	0.01	TBD	TBD	TBD
Vanadium	V	0.02	TBD	TBD	TBD
Zinc	Zn	0.1	TBD	TBD	TBD

* To be determined and placed in the instrument QA files

TABLE 2
RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND
CONCENTRATIONS

Solution Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Hg	0.0	0.020
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.050
V	0.0	0.200
Zn	0.0	0.100

TABLE 3
RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	Mass
Aluminum	<u>27</u>
Antimony	121, <u>123</u>
Arsenic	<u>75</u>
Barium	138, 137, 136, <u>135</u> , 134
Beryllium	<u>9</u>
Bismuth (IS)	209
Cadmium	<u>114</u> , 112, <u>111</u> , 110, 113, 116, 106
Calcium (I)	42, 43, <u>44</u> , 46, 48
Chlorine (I)	35, 37, (<u>77</u> , <u>82</u>) ^a
Chromium	<u>52</u> , <u>53</u> , <u>50</u> , 54
Cobalt	<u>59</u>
Copper	<u>63</u> , <u>65</u>
Holmium (IS)	165
Indium (IS)	<u>115</u> , 113
Iron (I)	<u>56</u> , <u>54</u> , <u>57</u> , 58
Lanthanum (I)	139
Lead	<u>208</u> , <u>207</u> , <u>206</u> , 204
Lithium (IS)	6 ^b , 7
Magnesium (I)	24, <u>25</u> , <u>26</u>
Manganese	<u>55</u>
Mercury	202, <u>200</u> , 199, 201
Molybdenum (I)	98, 96, 92, <u>97</u> , 94, (108) ^a
Nickel	58, <u>60</u> , 62, <u>61</u> , 64
Potassium (I)	<u>39</u>
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, <u>78</u> , <u>82</u> , <u>76</u> , <u>77</u> , 74
Silver	<u>107</u> , <u>109</u>
Sodium (I)	<u>23</u>
Terbium (IS)	159
Thallium	<u>205</u> , 203
Uranium	<u>238</u>
Vanadium	<u>51</u> , <u>50</u>
Tin (I)	120, <u>118</u>
Yttrium (IS)	89
Zinc	64, <u>66</u> , <u>68</u> , <u>67</u> , 70

NOTE: EPA Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

a These masses are also useful for interference correction (Section 6.2)

b Internal standard must be enriched in the ⁶Li isotope (Section 2.4)

TABLE 4
QUALITY ASSURANCE/QUALITY CONTROL

Description	Frequency	Acceptance Criteria	Corrective Action
Instrument Detection Limits (IDLs)	Every 3 months	See "Instrument Blank"	
Tuning Solution	At least 4X/day	RSD of $\leq 5\%$; Mass calibration < 0.1 amu from true value; < 0.9 amu full width at 10% peak height	Allow to warm up 30 minutes more
Calibration Blank	Before analysis of calibration curve standards	$< 3X$ current IDL	Allow instrument blank to flush system for 10-15 minutes and reanalyze
Calibration Curve Defining linear calibration range. 3 points minimum lower and upper defining reporting limits. 3 rd point preferably near the lower	Before the analysis of the sample; after instrument repair or maintenance; when a CCV shows an existing calibration curve failed	Correlation Coefficient > 0.989	Check standards, calibration range, operational parameters, Rerun calibration
Initial and Continuing Calibration Verification Std (ICV/CCV) Standard containing all the target analytes prepared from a second source solution	After development of calibration curve; after every 10 samples including non-blank QC samples and at the end of the analysis sequence	$100\%R \pm 10\%$	Check both CCV and calibration standards preparation; recalibrate
Instrument Blank	Immediately following every CCV	Less than $3X$ the current IDL for each element	Check tubing and calibration blank solution; remake solution
Internal Standards	Added to all blanks, calibration standards, samples, QC	In samples, the intensity of all internal standards should be $> 30\%$ of that in the initial calibration solution	Check instrument drift, if drift present, recalibrate; If no drift, dilute sample $5X$ and reanalyze
Laboratory Control Sample (LCS) Spiked clean material containing all or defined elements processed through the entire preparation and analysis process	One per batch of samples with a maximum of 20 samples per batch	$100\%R \pm 30\%$ or as defined by developing recovery studies	Re-prepare if fails review of all related QA/QC, and if necessary prepare and reanalyze all associated samples
Method Blank Sample composed of all reagents and processed through entire method	One per batch of samples with a maximum of 20 samples per batch	No analyte concentrations exceeding $\frac{1}{2}$ the lower reporting limit	Qualify reported data
Lower Reporting Limit (LRL) Analysis of lowest concentration calibration standard as a sample	Once per day for each metal analyzed	$100\%R \pm 30\%$	Internal MCL Inc requirement – Review with QA Manager

**APPENDIX 1
ADDITIONAL REQUIREMENTS OF EPA METHOD 200.8**

**TABLE 1-1
ELEMENTS THAT CAN BE ANALYZED BY ICP-MS ACCORDING TO EPA METHOD
200.8 AND DETECTION LIMITS**

Element	Symbol	Lower Reporting Limit (µg/L)	Instrument Detection Limit (µg/L)	Method Detection Limit Soil (µg/g)	Method Detection Limit Water (µg/L)
Aluminum	Al	1.0	TBD*	TBD*	TBD*
Antimony	Sb	0.05	TBD	TBD	TBD
Arsenic	As	0.02	TBD	TBD	TBD
Barium	Ba	0.1	TBD	TBD	TBD
Beryllium	Be	0.02	TBD	TBD	TBD
Cadmium	Cd	0.02	TBD	TBD	TBD
Chromium	Cr	0.05	TBD	TBD	TBD
Cobalt	Co	0.05	TBD	TBD	TBD
Copper	Cu	0.05	TBD	TBD	TBD
Lead	Pb	0.05	TBD	TBD	TBD
Manganese	Mn	0.1	TBD	TBD	TBD
Mercury	Hg	TBD	TBD	TBD	TBD
Nickel	Ni	0.05	TBD	TBD	TBD
Selenium	Se	0.02	TBD	TBD	TBD
Silver	Ag	0.05	TBD	TBD	TBD
Thallium	Tl	0.02	TBD	TBD	TBD
Thorium	Th	TBD	TBD	TBD	TBD
Uranium	U	0.01	TBD	TBD	TBD
Vanadium	V	0.02	TBD	TBD	TBD
Zinc	Zn	0.1	TBD	TBD	TBD

18.0 EQUIPMENT AND SUPPLIES

18.1.1 Instrument resolution is 1 amu peak width at 5% peak height.

18.1.2 Mass range from 5-250 amu.

18.1.4 Radio-frequency generator compliant with FCC regulations.

18.1.5 If an electron multiplier detector is used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Changes in instrument response or damage to the multiplier may result with exposure to high ion flux. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis.

NOTE: Equipment listed in Method 200.8 Sections 6.2 – 6.10 for the preparation of samples is listed in SOP# MCL-7746, MCL-7752 and MCL-7753.

19.0 QUALITY CONTROL

19.12 Initial Demonstration of Performance

19.12.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

19.12.2 Linear calibration ranges – Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limits must be diluted and reanalyzed. The LDRs should be verified whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

19.12.3 Quality control sample (QCS) – When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analysis of a QCS. To verify the calibration standards, the determined mean concentration from 3 analyses of the QCS must be within $\pm 10\%$ of the stated QCS value. If the QCS is used for determining acceptable on-going instrument performance, analysis of the QCS prepared to 100 $\mu\text{g/L}$ must be within $\pm 10\%$ of the stated value or within the acceptance limits listed in Table 5-1, whichever is greater.

19.13 Assessing Laboratory Performance (mandatory)

19.13.4 Instrument performance – For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration run the calibration blank and calibration standards as surrogate samples immediately following each calibration routine, after every ten analyses and at the end of the sample run. The results of the analyses of the standards will indicate whether the calibration remains valid. The analysis of all analytes within the standard solutions must be within $\pm 10\%$ of calibration. If the calibration cannot be verified within the specified limits, the instrument must be recalibrated. (The instrument responses from the calibration check may be used for recalibration purposes; however, it must be verified before continuing sample analysis.) If the continuing calibration check is not confirmed within $\pm 15\%$, the previous 10 samples must be reanalyzed after recalibration. If the sample matrix is responsible for the calibration drift, it is recommended that the previous 10 samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

19.14 Assessing Analyte Recovery and Data Quality

19.14.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix procedure is required.

19.14.2 The laboratory must add a known amount of analyte to a minimum of 10% of the routine samples. In each case, the LFM aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the LFB. For solid samples, the concentration added should be 100 mg/Kg equivalent (200 $\mu\text{g/L}$ in the analysis solution) except silver which should be limited to 50 mg/Kg. Over time, samples from all routine sample sources should be fortified.

19.14.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery of 70-130%. Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration.

19.14.4 If recovery of any analyte falls outside the designated range and laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the

unfortified sample is suspect due to either the heterogeneous nature of the sample or an uncorrected matrix effect.

20.0 PROCEDURE

20.1 Sample Preparation

NOTE: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L to preserve the mercury and to prevent it from plating out in the sample introduction system.

20.1.1 Aqueous Sample Preparation – Dissolved Analytes (from EPA Method 200.8)

20.1.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥ 20 mL) of the filtered, acid preserved sample into a 50 mL polypropylene (pp) centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO₃ to a 20 mL aliquot of sample). If direct addition is being used, add internal standards, cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations.

NOTE: If a precipitate is formed during acidification, transport or storage, the sample aliquot must be treated using the procedure in Section 13.1.2 prior to analysis.

20.1.2 Aqueous Sample Preparation – Total Recoverable Analytes (from EPA Method 200.8)

20.1.2.1 For the “direct analysis” of total recoverable analytes in drinking water samples containing turbidity < 1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 13.1.1.1 while making allowance for sample dilution in the data calculation. For the determination of total recoverable analytes in all other aqueous samples or for preconcentration drinking water samples prior to analysis follow the procedure given in Sections 13.1.2.2 through 13.1.2.8.

20.1.2.2 For the determination of total recoverable analytes in aqueous samples, transfer a 40 mL aliquot from a well mixed, acid preserved sample to a 50 mL pp digestion tube.

20.1.2.3 Add 2mL (1+1) HNO₃ and 1mL (1+1) HCL to the sample aliquot. Place the tube in a hot block at 95°C and cover with a pp raised watch glass. Reflux sample for 30-60 minutes. Do not boil. Some reduction in sample volume may occur.

20.1.2.4 Allow the sample in digestion tube to cool. Quantitatively transfer the sample solution to a labeled 50mL pp centrifuge tube. Dilute to 50mL with reagent water and mix.

20.1.2.5 Prior to analysis adjust the chloride concentration by pipetting 20mL of the prepared sample solution into a 50mL pp centrifuge tube. If the direct addition method is being used, add appropriate amounts of internal standards. Dilute to 50mL with reagent water and mix. The sample is now ready for analysis. All analyses should be performed as soon as possible after the completed preparation.

20.1.3 Solid Sample Preparation – Total Recoverable Analytes (from EPA Method 200.8)

20.1.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly to obtain a homogenous aliquot. Weigh 1.0 ± 0.10 g of dry sample into a 50mL pp digestion tube.

20.1.3.2 Add 4mL (1+1) HNO₃ and 10mL (1+4) HCL carefully to avoid loss of sample. Place the digestion tube in the hot block (in an appropriate fume hood) at 95°C. Cover with a raised pp watch glass.

20.1.3.3 Reflux the sample for 30 minutes at 95°C. Slight boiling may occur but vigorous boiling should be avoided to prevent loss of the HCl-H₂O azeotrope. Some solution evaporation will occur.

20.1.3.4 Allow the sample to cool and quantitatively transfer the extract to a 100mL volumetric flask. Filter if necessary to remove undissolved solids. Take care to avoid potential contamination from filtration.

20.1.3.5 Prior to analysis, adjust the chloride concentration by pipetting 10mL of the prepared solution into a 50mL pp centrifuge tube. If the direct addition method is being used, add appropriate amounts of internal standards. Dilute to 50mL with reagent water and mix. The sample is now ready for analysis. All analyses should be performed as soon as possible after the completed preparation.

TABLE 4-1
QUALITY ASSURANCE/QUALITY CONTROL

Description	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limits	annually		
Tuning Solution	At least 5X/day	RSD of $\leq 5\%$; Mass calibration < 0.1 amu from true value; < 0.75 amu full width at 5% peak height	Allow to warm up 30 minutes more
Calibration Blank	Before the analysis of Calibration standards		
Calibration Curve Defining linear calibration range. 3 points minimum lower and upper defining reporting limits. 3 rd point preferably near the lower	Before the analysis of the sample; after instrument repair or maintenance; when a CCV shows an existing calibration curve failed	Correlation Coefficient > 0.989	Check standards, calibration range, operational parameters; Rerun calibration
Continuing Calibration Verification Analysis of calibration blank and standards as surrogate samples	After development of calibration curve; after every 10 samples including non-blank QC samples and at the end of the analysis sequence	$100\%R \pm 10\%$	Check calibration standards preparation; recalibrate
Instrument Blank	Immediately following every CCV	Less than 3X the current IDL for each element	Check tubing and calibration blank solution; remake solution
Internal Standards	Added to all blanks, calibration standards, samples, QC	60-125% recovery of the response in the calibration blank	Flush with rinse blank and check response in calibration blank; Check instrument drift, if drift present, recalibrate
Laboratory Control Sample (LCS) Spiked clean material containing all or defined elements processed through the entire preparation and analysis process	One per batch of samples with a maximum of 20 samples per batch	$100\%R \pm 15\%$ or as defined by developing recovery studies	Re-prepare if fails review of related QA/QC, and if necessary re-prepare and reanalyze all associated samples
Method Blank Sample composed of all reagents and processed through entire method	One per batch of samples with a maximum of 20 samples per batch	10% or more of the analyte level in the samples or 2.2X the MDL, whichever is greater	Re-prepare and reanalyze fresh aliquots of samples for affected analyte(s)
Quality Control Sample (QCS) Second source standard	Initial Instrument verification; Quarterly thereafter	$100\%R \pm 10\%$ on the average of 3 runs	Recalibrate and reanalyze

TABLE 5-1
ACCEPTANCE LIMITS FOR QC CHECK SAMPLE
METHOD PERFORMANCE ($\mu\text{g/L}$)

Element	Symbol	QC Check Sample Concentration ($\mu\text{g/L}$)	Average Recovery %	Standard Deviation (S_r)	Acceptance Limits ($\mu\text{g/L}$)
Aluminum	Al	100	100.4	5.49	84-117
Antimony	Sb	100	99.9	2.40	93-107
Arsenic	As	100	101.6	3.66	91-113
Barium	Ba	100	99.7	2.64	92-108
Beryllium	Be	100	105.9	4.13	88-112
Cadmium	Cd	100	100.8	2.32	94-108
Chromium	Cr	100	102.3	3.91	91-114
Cobalt	Co	100	97.7	2.66	90-106
Copper	Cu	100	100.3	2.11	94-107
Lead	Pb	100	104.0	3.42	94-114
Manganese	Mn	100	98.3	2.71	90-106
Molybdenum	Mo	100	101.0	2.21	94-108
Nickel	Ni	100	100.1	2.10	94-106
Selenium	Se	100	103.5	5.67	86-121
Silver	Ag	100	101.1	3.29	91-111
Thallium	Tl	100	98.5	2.79	90-107
Thorium	Th	100	101.4	2.60	94-109
Uranium	U	100	102.6	2.82	94-111
Vanadium	V	100	100.3	3.26	90-110
Zinc	Zn	100	105.1	4.57	91-119

21.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Because all materials utilized in this procedure are potentially radioactive sources, all samples, waste, and standards will be appropriately labeled and handled according to MCL-7718 and MCL-7715.

The waste will be minimized by using small volumes and minimizing quantities utilized for sample preparation and standards preparation. Materials for disposal will be segregated and properly labeled. Where possible, the waste will be reduced by known treatment methodologies.

Rad waste will be measured and documented and where necessary turned over to an approved commercial handling and disposal service.