

Acid Digestion of Solid Samples for Metals Analysis

References: **Method 3050B**, Acid Digestion of Sediments, Sludges and Soils, Test Methods for Evaluating Solid Waste, SW-846, Third Edition (Revision 2) as promulgated in the Final Update, December 1996..

Method 6020A, Inductively Coupled Plasma-Mass Spectrometry, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Draft Update IVA, May 1998.

EPA/625/R-96/110a, Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air, Compendium Method IO-3.1. SELECTION, PREPARATION AND EXTRACTION OF FILTER MATERIAL. U.S. EPA, Cincinnati, OH 45269, June, 1999.

1. Scope and Application

Matrices: The method is applicable to soil and sediment.

Definitions: Refer to Alpha Analytical Quality Manual.

Two procedures are discussed in this SOP. One technique yields samples applicable for analysis by ICP-AES and one technique yields samples applicable for analysis by GFAA or ICP-MS.

Lab Method 3050:1T

This acid digestion procedure is used to prepare solid samples for analysis of total metals by inductively coupled plasma argon emission spectroscopy (ICP-AES). Samples prepared by this method may be analyzed by ICP for all the metals listed below. Silver and antimony can be analyzed by ICP MS using this digestion.

<u>Element</u>	<u>CASRN</u>	<u>Element</u>	<u>CASRN</u>	<u>Element</u>	<u>CASRN</u>
Aluminum (Al)	7429-90-5	Cobalt (Co)	7440-48-4	Nickel (Ni)	7440-02-0
Antimony (Sb)	7440-36-0	Copper (Cu)	7440-50-8	Potassium (K)	7440-09-7
Arsenic (As)	7440-38-2	Iron (Fe)	7439-89-6	Silver (Ag)	7440-22-4
Barium (Ba)	7440-39-3	Lead (Pb)	7439-92-1	Selenium (Se)	7782-49-2
Beryllium (Be)	7440-41-7	Magnesium (Mg)	7439-95-4	Sodium (Na)	7440-23-5
Cadmium (Cd)	7440-43-9	Manganese (Mn)	7439-96-5	Thallium (Tl)	7440-28-0
Calcium (Ca)	7440-70-2	Molybdenum (Mo)	7439-98-7	Vanadium (V)	7440-62-2
Chromium (Cr)	7440-47-3			Zinc (Zn)	7440-66-6

Lab Method 3050:2T

This acid digestion procedure is used to prepare solid samples for analysis by GFAA or ICP-MS. Samples prepared by this method may be analyzed by GFAA or ICP-MS for all the metals listed below. *If Silver (Ag) and Antimony (Sb) are required for ICP-MS analysis, preparation method 3050:1T MUST be used for those elements.*

<u>Element</u>	<u>CASRN</u>	<u>Element</u>	<u>CASRN</u>	<u>Element</u>	<u>CASRN</u>
Aluminum (Al)	7429-90-5	Copper (Cu)	7440-50-8	Selenium (Se)	7782-49-2
Arsenic (As)	7440-38-2	Iron (Fe)	7439-89-6	Sodium (Na)	7440-23-5
Barium (Ba)	7440-39-3	Lead (Pb)	7439-92-1	Thallium (Tl)	7440-28-0
Beryllium (Be)	7440-41-7	Magnesium (Mg)	7439-95-4	Tin (Sn)	7440-31-5
Cadmium (Cd)	7440-43-9	Manganese (Mn)	7439-96-5	Titanium (Ti)	7440-32-6
Calcium (Ca)	7440-70-2	Molybdenum (Mo)	7439-98-7	Vanadium (V)	7440-62-2
Chromium (Cr)	7440-47-3	Nickel (Ni)	7440-02-0	Zinc (Zn)	7440-66-6
Cobalt (Co)	7440-48-4	Potassium (K)	7440-09-7		

2. Summary of Method

Lab Method 3050:1T

5mL of 1:1 nitric acid is added to 1-2g of solid sample measured into a digestion tube. The sample is heated in a block at 90-95°C for 15 minutes. 2.5mL of concentrated nitric acid is added, and sample is refluxed for 30 minutes. The sample is then cooled and 2.5mL of concentrated nitric acid is added again. The sample is refluxed for an additional 30 minutes. 0.5mL of 30% hydrogen peroxide is added to the cooled sample, and the sample is re-heated in the block until the sample no longer is effervescing. 1.0mL of hydrogen peroxide is added to the sample three more times and the sample is heated in the block between each aliquot addition of 30% hydrogen peroxide. 5mL of concentrated Hydrochloric acid is added, and the sample is heated on the block for 15 minutes. After cooling, the sample is diluted up to 50mL with deionized water.

If the sample should go to dryness, the sample must be re-prepared.

All solid samples require filtration due to insoluble silicates and the formation of precipitates during digestion.

Lab Method 3050:2T

5mL of 1:1 nitric acid is added to 1-2g of solid sample measured into a digestion tube. For analysis of an air sampling filter, cut a one inch by eight inch section of filter using high carbon steel scissors and place into a digestion vial. The sample is heated in a block at 90-95°C for 15 minutes. 2.5mL of concentrated nitric acid is added, and the sample is refluxed for 30 minutes. The sample is then cooled and 2.5mL of concentrated nitric acid is added again. The sample is refluxed for an additional 30 minutes. 0.5mL of 30% hydrogen peroxide is added to the cooled sample and the sample is re-heated in a block until the sample no longer is effervescing. 1.0mL of hydrogen peroxide is added to the sample three more times and sample is heated in the block between each aliquot addition of 30% hydrogen peroxide. After cooling, the sample is diluted up to 50mL with deionized water.

If the sample should go to dryness, the sample must be re-prepared.

All solid samples require filtration due to insoluble silicates and the formation of precipitates during digestion.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

2.1 Method Modifications from Reference

A final extract volume of 50mL is used instead of 100mL specified in the reference method. All reagent volumes have been reduced proportionately.

3. Reporting Limits

For information regarding the aqueous RLs, see the appropriate analytical SOPs. These values are equivalent to the lowest standard in the initial calibration curve, and may be approximately 3-5X the calculated MDL.

4. Interferences

All re-usable glassware or plastic must be acid cleaned prior to use to remove residual trace elements.

Based on historical information, or by sample observation, it may be noted that all solid samples will require filtration after digestion, and prior to analysis, due to insoluble silicates and the formation of precipitates. After sample digestion, the associated method blank and laboratory control sample must be filtered with the associated batch samples.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking,

smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. Pipetting by mouth is not permitted. All Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept alphabetically in the centrally located file storage, in the common area outside of the Information Technology (IT) offices.

Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at **all** times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting device and/or a secondary outer container. Chemical storage is properly segregated and adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

Spilled samples, solvents, reagents, and water must be cleaned up from bench tops, instruments and autosampler surfaces immediately. A spill is considered a quantity of hazardous material if it is two times greater than the normal working volume. Concentrated solvents, acids or bases present a moderate to extreme hazard to the skin and mucous membranes. If contact with the skin occurs, immediately flush with large volumes of water. In the case of acidic/basic spills, the *Spill Kit* located in each laboratory shall be utilized before attempting to cleanup the spill. Although procedures are designed to minimize the possibility of an accident, all injuries or accidents, regardless of the nature or severity, are to be reported to the Section Head Supervisor immediately. If an employee discovers a potentially unsafe condition, this must be reported to the Section Head Supervisor immediately. No employee should feel compelled to work in a situation where they do not feel entirely informed, trained, or safe.

Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

Compressed gas cylinders shall only be moved with the dolly supplied for this specific purpose. The cap must be on the cylinder while it is being moved. The tank must be secured when in its final position. All spent tanks are to be returned in the same manner, and secured until removed by the vendor. Liquid argon or nitrogen represents a potential cryogenic hazard and safe-handling procedures must be used at all times.

All additional company safety practices shall be followed at all times as written in the *Chemical Hygiene Plan*.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

A minimum of 10g of sample must be collected in a pre-cleaned 2oz or 4oz glass jar with a Teflon lined screw cap.

6.2 Sample Preservation

No preservatives are used. See Section 6.4.

6.3 Sample Shipping

No special sample shipping requirements. Typical shipping procedures may be found in the Alpha Sample Receipt & Log-In SOP (01-01).

6.4 Sample Handling

Samples are stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Sediment and soil samples may be stored at $-20^{\circ}\text{C} \pm 10^{\circ}\text{C}$. The hold time for solid samples for metals digestion is 6 months. Air sampling filters may be stored at room temperature. Tissue samples are stored frozen with a hold time of 1 year.

Refer to the Sample Receipt & Log-In SOP (01-01) for Sample Receipt, Login and internal Sample Custody information.

7. Equipment and Supplies

7.1 Digestion Tubes: Pre-cleaned, graduated, disposable, 50 mL volume. The 50mL volume of each Lot of tubes is verified and documented in a logbook (Form No.: 105-02).

7.2 Watch covers

7.3 Filter Funnels: Glass or plastic

7.4 Electric Hot Plate: Adjustable and capable of maintaining a temperature of $90\text{-}95^{\circ}\text{C}$ equipped with graphite carbon blocks that each have 36 positions to hold the sample tubes.

NOTE: Hotplate/Block temperatures are monitored and recorded regularly using NIST calibrated and traceable thermometers. If any thermometer is suspected to not be reading the temperatures correctly, see the QAO for a certified replacement thermometer.

7.5 Other: Adjustable Eppendorf pipettes and replacement tips, pre-cleaned Filter Mate from Environmental Express (2.0um filter paper and plunger), 100mL and 200mL Class-A volumetric flasks, high carbon steel scissors.

8. Reagents and Standards

ACS Trace Metal grade chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

Solutions below expire 6 months from preparation, or expire on the manufacturer's expiration date, whichever comes first. Standards are stored out of direct light at ambient temperature. Reagents are stored at ambient temperature, under a hood if necessary. Acids are kept in a storage crate under a hood. Once opened, initialed and dated, they are kept in a hood. Acid expiration dates are generally provided by the manufacturer and printed on the label.

8.1 Deionized (DI) water: The DI water is ASTM Type II laboratory reagent grade water or better (*i.e.*, Type I). The Barnstead NANO-pure system provides Type I water used in the preparation of samples and standards.

8.2 Hydrochloric acid, concentrated (HCl): ACS reagent grade, Fisher #A508-212, or equivalent. Hydrochloric acid (1:1 HCl) - Add 500mL concentrated HCl to 400mL DI water and dilute to 1L. Store in or under fume hoods. Prior to use, the acid is analyzed to determine levels of impurity. If the method blank is less than the RL, the acid can be used. Results of this analysis are kept in a logbook.

8.3 Nitric acid, concentrated (HNO₃): ACS reagent grade, Fisher #A509-212, or equivalent. Nitric Acid (1:1 HNO₃) - Add 500mL concentrated HNO₃ to 400mL DI water and dilute to 1L. Prepare 1% Nitric Acid by diluting 1mL of concentrated HNO₃ up to 100mL in DI water. Store in or under fume hoods. Prior to use, the acid is analyzed to determine levels of impurity. If the method blank is less than the RL, the acid can be used. Results of this analysis are kept in a logbook

8.4 Spiking solutions:

All standard solutions are stored in cabinets out of direct light.

8.4.1 Laboratory Control Sample (LCS) and High Matrix Spiking (MS) solution for 3050:1T & 3050:2T: Spike 2mL of S1 into the LCS and MS samples. The final concentration in the LCS and MS samples are Be and Cd at 2.0mg/L; Sb, Ba, B, Cr, Cu, Co, Mn, Zn, Ni, Pb, V, Ti, As, Se and Mo at 4.0mg/L; Al, Ca, Fe, Mg, K, and Na at 20.0mg/L.

8.4.1.1 S1 Solution: Prepare by adding 5mL of concentrated HNO₃ to a 100mL volumetric flask using a 5mL glass pipette. Then add 10mL of ICUS-624 (Ultra Scientific) solution containing Be and Cd at 500mg/L, for a concentration of 50mg/L, and Sb, Ba, B, Cr, Cu, Co, Mn, and Mo at 1000mg/L, for a concentration of 100mg/L. Next add 10mL of ICUS-625 (Ultra Scientific) solution containing Zn, Ni, Pb and V at 1000mg/L for a concentration of 100mg/L, and Al, Ca, Fe, Mg, K, and Na at 5000mg/L, for a concentration of 500mg/L. Next add 10mL each of Ti, As and Se (Ultra, Absolute or equivalent) at 1,000mg/L for a concentration of 100mg/L. This solution is brought to volume with DI water.

8.4.2 Laboratory Control Sample (LCS) and Low Matrix Spiking (MS) solution for 3050:1T & 3050:2T: Spike 0.80mL of S3 (3050:1T only) into the LCS sample and MS sample.

8.4.2.1 S3 Solution: Prepare by adding 5mL of concentrated HNO₃ to a 100mL volumetric flask using a 5mL glass pipette. Then add 2.5mL of IQC-026 (Ultra Scientific) Elements solution containing Al, Sb, As, Se, Ba, Be, B, Cd, Cr, Ca, Cu, Co, Fe, Pb, Mg, Mn, Mo, Ni, Ag, Na, Ti, Ti and Zn at a concentration of 100ppm, K at 1000ppm, and Si at 50ppm. This solution is brought to volume with DI water.

8.5 LCS Solid Matrix Sample: Catalog # 540 from ERA.

8.6 30% Hydrogen Peroxide (H₂O₂): ACS reagent grade, BDH #BDH3742-1, or equivalent. Stored under the hood, kept in the plastic bag it comes in and placed in a "spill" dish pan. Expires according to the manufacturer's date, or 18 months from date received, whichever comes first.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

A method blank must be prepared once per every 20 samples or per digestion batch, whichever is more frequent.

Metals elements of interest must not be detectable in the method blank at a concentration greater than the reporting limit.

If required, and a blank solid material of a similar matrix type of high enough purity can be obtained to meet required reporting limits, a solid material may be used in the Method Blank preparation to matrix match QC samples and field samples.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. Digestion of the method blank and all associated samples must be performed until the blank is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Metals Section Head, Laboratory Director or QAO, if the samples associated with the out of control method blank are non-detect for the elements of interest, or if sample concentrations are greater than 10x the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

9.2 Laboratory Control Sample (LCS)

Laboratory control sample (LCS) must be prepared once per every 20 samples or per digestion batch, whichever is more frequent, and spiked with a solution prepared from a second source or lot number, other than the source used to verify the accuracy of the standard curve for the determinative analytical method. The LCS contains all target elements of interest, and is digested along with the samples as verification of the accuracy of the entire digestion procedure.

If required, a solid LCS may be prepared to matrix match QC samples and field samples.

The acceptable recovery QC limits are documented in the applicable analytical SOPs. The solid recovery limits are continuously monitored and documented in-house through control charts. The Control Limit Generation SOP (08-07) provides details explaining how control charts are generated and used for quality control.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the LCS recovery is still out of control, re-prepare and re-analyze the LCS and all associated samples. Samples cannot be reported until an acceptable LCS is obtained. Exceptions may be made with approval of the Metals Section Head, Laboratory Director or QAO, if the samples associated with the out of control LCS are also associated with a matrix spike that is in control. This is an acceptable measure of accuracy of the digestion and analytical procedures. An explanation of the out of control LCS recovery must be included in the project narrative to the client and the sample data reported noting the acceptable MS results as batch QC.

9.3 Initial Calibration Verification (ICV)

Not applicable to this method.

9.4 Continuing Calibration Verification (CCV)

Not applicable to this method.

9.5 Matrix Spike

A matrix spike (MS) sample must be performed once per 20 samples (5% frequency), or per digestion batch, whichever is more frequent. The MS contains all target elements of interest.

The acceptable % recovery QC limits are documented in the applicable analytical SOPs. The

aqueous % recovery QC limits are continuously monitored and documented in-house through control charts. The Control Limit Generation SOP (08-07) provides details explaining how control charts are generated and used for quality control.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the % recovery still exceeds the control limits and the LCS is compliant; include a project narrative with the results to client noting that there may be potential matrix effects on the accuracy of the reported results as evidenced by MS recovery outside of QC limits.

9.6 Laboratory Duplicate

Duplicate analyses (matrix or sample duplicate) must be performed once per 20 samples 5% frequency), or per digestion batch, whichever is more frequent.

Acceptable relative percent differences (RPD) of duplicates are documented in the applicable analytical SOPs. Acceptance criterion is not applicable to sample concentrations less than 5 times the reporting limit. Calculate the RPD as follows:

$$RPD = \frac{R1 - R2}{\frac{[R1 + R2]}{2}} \times 100$$

where:

R1 = sample Replicate #1

R2 = sample Replicate #2

The RPD limits are continuously monitored and documented in-house through control charts. The Control Limit Generation SOP (08-07) provides details explaining how control charts are generated and used for quality control.

Corrective Action: Analysis according to the appropriate analytical SOP may be repeated once to see if an analytical error has occurred. If the % RPD still exceeds the control limits; include a project narrative with the results to client noting that there may be potential matrix effects on the precision of the reported metals results as evidenced by the matrix duplicate %RPD exceedance.

9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

Refer to Analytical SOP 2137 for method sequence.

10. Procedure

10.1 Equipment Set-up

Samples are prioritized by the Metals Section Head or Preparation Group Leader for digestion based on hold time and client due date. Gather all samples for digestion from the Sample Custodian according to the procedures outlined in the Sample Receipt & Log-In SOP (01-01). Batch the samples that are being digested in the LIMS. Include the method blank, LCS, MS and Duplicate samples. **Note**: The proportional volume of reagents used for the digestions have been reduced from the volumes cited in the reference methods.

10.2 Initial Calibration

Not applicable to this method.

10.3 Equipment Operation and Sample Processing

10.3.1 Sample Digestion according to Lab Method 3050:1T:

- 10.3.1.1 Turn on the electric hotplates and monitor the temperature to 90-100°C. The hot blocks take approximately 120 minutes to reach the proper temperature. Using a plastic spoon, homogenize sample and weigh 1-2g of sample (to achieve a 1g dry weight) into a digestion tube. Label each tube with the sample batch ID.
- 10.3.1.2 Add 5mL of 1:1 Nitric Acid to each sample and spike the LCS and MS sample using the solutions prepared in Section 8.4.1. All sample spiking must be "spike witnessed".
- 10.3.1.3 Place the tubes into the block. Cover the samples with a watch cover. Heat the samples for a timed 15 minutes using caution not to let the samples go to dryness.
- 10.3.1.4 Remove the samples from the block. Add 2.5mL of concentrated nitric acid to each sample. Cover the samples with a watch cover, and place them back into the block. Reflux the samples for 30 minutes, then remove the samples and repeat by adding 2.5mL of concentrated nitric acid to each sample and heating for an additional 30 minutes. Continue and repeat adding nitric acid until NO brown fumes are given off by the sample indicating the complete reaction with the nitric acid.
- 10.3.1.5 Remove the sample, when cool SLOWLY add 0.5mL of 30% hydrogen peroxide and replace the watch cover, placing samples back into the block. Heat the samples until the effervescence subsides, then remove and cool the samples. Once cool, add 1.0mL of 30% hydrogen peroxide, replace the watch cover, and heat in the block until the effervescence subsides. When the samples are removed from the block and cooled, 1.0mL of 30% hydrogen peroxide is added 2 more times, and the samples should effervesce and cool between each 1.0mL aliquot addition. This step may take up to 2 hours to complete.
- 10.3.1.6 Remove the samples and add 5mL of concentrated hydrochloric acid. Heat the samples in the block for 15 minutes, then remove, and allow them to cool. Remove the watch covers and bring the samples up to the 50mL mark on the digestion tube with DI water. Cap the tubes and shake. There will be precipitate formed during digestion, such as silicates or other insoluble material that may clog the nebulizer, these samples will require filtration. See Section 10.3.3 for filtration procedures.

10.3.2 Sample Digestion according to Lab Method 3050:2T:

- 10.3.2.1 Turn on the electric hotplates and monitor the temperature to 90-100°C. The hot blocks take approximately 120 minutes to reach the proper temperature. Weigh 1-2g or sample (to achieve a 1g dry weight) into a digestion tube. For analysis of an air sampling filter, cut a one inch by eight inch section of filter using high carbon steel scissors and place into a digestion vial. Label each tube with the sample batch ID.

- 10.3.2.2** Spike the LCS and MS sample using the solutions prepared in Section 8.4.2. All sample spiking must be "spike witnessed".
- 10.3.2.3** Add 5mL of 1:1 nitric acid to each sample and place the tubes into the block. Cover the samples with a watch cover. Heat the samples for a timed 15 minutes using caution not to let the samples go to dryness.
- 10.3.2.4** Remove the samples from the block. When cool, add 2.5mL of concentrated nitric acid to each sample. Cover the samples with a watch cover, and place them back into the block. Reflux the samples for 30 minutes, remove the sample and repeat by adding 2.5mL of concentrated nitric acid to each sample and heating for an additional 30 minutes. Continue and repeat adding nitric acid until NO brown fumes are given off by the sample indicating the complete reaction with the nitric acid.
- 10.3.2.5** Remove the sample, when cool SLOWLY add 0.5mL of 30% hydrogen peroxide and replace the watch cover, placing sample back into the block. Heat sample until effervescence subsides, then remove, and cool the sample. Once cool, add 1.0mL of 30% hydrogen peroxide, replace the watch cover, and heat in the block until the effervescence subsides. When the sample is removed from the block and cooled, 1.0mL of 30% hydrogen peroxide should be added 2 more times and the sample should effervesce and cool between each 1.0mL aliquot addition. This step may take up to 2 hours to complete.
- 10.3.2.6** Remove samples and allow them to cool, then remove watch covers and bring the samples up to the 50mL mark on the digestion tube with DI water. Cap the tubes and shake. There will be precipitate formed during digestion, such as silicates or other insoluble material that may clog the nebulizer, these samples will require filtration. See Section 10.3.3 for filtration procedures.

10.3.3 Sample filtration after digestion:

- 10.3.3.1** After digestion, all samples, including the method blank and LCS are filtered with a pre-cleaned Filter Mate and plunger.
- 10.3.3.2** If, during the filtration step above, the digestion tube inadvertently cracks, have a clean new tube near by. Quickly transfer the remaining sample digestate (minimum of 5mL) to the new tube. If less than 5mL of digestate remains, the sample must be re-digested. *Under no circumstances should any foreign object be placed into the sample tube to retrieve or re-set the filter plunger, as this may cause sample contamination.*

10.4 Continuing Calibration

Not applicable to this method.

10.5 Preventive Maintenance

The Hot Block thermometers are calibrated on an annual basis by an instrument service company. Certificates are kept on file.

11. Data Evaluation, Calculations and Reporting

Procedures for data and record management for organic extraction must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the *Document Control* SOP (08-01). All records must be stored in such a manner as to be safe and accessible for at least 10 years.

The digestion batch bench sheets and other relevant laboratory notebooks must follow the

Printouts of this document may be out of date and should be considered uncontrolled. To accomplish work, the published version of the document should be viewed online.

specifications in the *Laboratory Notebook Usage* Work Instruction (108-01), and all record keeping and document control practices.

See the appropriate analytical SOPs, for details on sample analysis, data evaluation, calculations and data reporting.

All results for the metals elements of interests are reportable without qualification if digestion and analytical holding times are met, preservation (including cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference is not suspected during digestion or analysis of the samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-extraction and/or re-analysis.

QC Parameter	Acceptance Criteria
Method Blank	< reporting limit
Laboratory Control Sample	See the applicable analytical SOP for acceptance criteria
Matrix Duplicate	See the applicable analytical SOP for acceptance criteria
Matrix Spike	See the applicable analytical SOP for acceptance criteria
Matrix Spike Duplicate (if needed)	See the applicable analytical SOP for acceptance criteria

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Section 9 and the appropriate analytical SOPs outline sample batch QC acceptance criteria. If non-compliant inorganic element results are to be reported, the Metals Section Head and/or the Laboratory Director, and the QA Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may chose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The instrument analyst or Section Head performing the secondary analytical review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

The *Hazardous Waste and Sample Disposal* SOP (G-006), must be referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

Once sample batches have completed digestion, the sample containers are stored in the metals lab and held for 30 days. If there is no sample remaining in the sample collection bottle, it may be rinsed and thrown away. It must be noted in the *Internal COC* that there is no sample remaining in the bottle, and the bottle was discarded.

Once the samples have been held for 30 days, any aqueous sample remaining must be disposed in a 55-gallon drum labeled "Corrosive Liquid".

Once satisfactory inorganic element results have been generated, the digestates are held for 30 days, or longer if specified by a client contract, then discarded into a 55-gallon drum labeled "Corrosive Liquid".

All reagent waste generated during digestion must be stored in satellite containers in the metals preparation laboratory.

Once the reagent waste satellite containers are full, they must be emptied into 55-gallon drums marked "Corrosive Liquid".

15. Referenced Documents

Chemical Hygiene Plan
Control Limit Generation SOP (08-07)
Document Control SOP (08-01)
Laboratory Notebook Usage WI (108-01)
Hazardous Waste and Sample Disposal SOP (G-006)
SOP/01-01 Sample Receipt & Log-In
SOP/08-05 MDL Generation
SOP/08-12 IDC Generation

16. Attachments

None.