# STANDARD OPERATING PROCEDURE

for

## METALS DIGESTION

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| Approved by: | Supervisor | 1/26/12 Date |
| | QA Manager | 1/26/12 Date |
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# METALS DIGESTION

## 1. SCOPE AND APPLICATION

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

## 2. METHOD SUMMARY

One-gram equivalent dry weight sediment, sludge, or soil samples are digested with repeated additions of nitric acid ($HNO_3$) and hydrogen peroxide ($H_2O_2$). For GFAA and ICP-MS analysis the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL. For ICP-OES and flame AA analysis, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed prior to dilution to a final volume of 100 mL.

## 3. DEFINITIONS

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

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

3.3. **Sample**

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

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

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

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

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

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

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

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

## 4. INTERFERENCES

Refer to the determinative method for a discussion of interferences.

## 5. SAFETY

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

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

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

## 6. SAMPLE COLLECTION, PRESERVATION AND STORAGE

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

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

## 7. APPARATUS AND EQUIPMENT

7.1. 125 mL plastic cup beaker cup, calibrated at 50mL and 100mL

7.2. Borosilicate watch glasses

7.3. Block Digester, calibrated to maintain 95°C ± 2°C

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

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

7.6. Evergreen disposable tubes 50 ml: an Accuracy and Precision verification check must be made with each new vendor lot prior to use. Refer to the SOP for *Checking Volumetric Labware ADM-VOLWARE*, for further detailed instructions. Performance data must meet the accuracy and precision requirements specified in Table 1 (*ADM-VOLWARE*) for non volumetric Labware used for measuring initial and/or final digestate volumes.

7.7. USS # 10 sieve.

## 8. STANDARDS AND REAGENTS

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

8.2. Reagent water: ASTM Type I water (resistivity $\geq$18 MΩ-cm, conductivity $\leq$0.056 uS/cm).

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

8.4. Concentrated Hydrochloric Acid: EMD GR ACS

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

8.6. Metals spiking solutions: Three spiking solutions are needed to prepare the matrix spike sample; SS1, SS2, SS3, and SS6. Follow the formulations laid out on the "Metals Spike Form" (see Attachments for example). These solutions are prepared in acid rinsed Class A volumetric flasks using purchased custom mixed standards or 1000 ppm single analyte

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standards. Aliquots are made using acid rinsed Class A volumetric pipettes of the appropriate size.

8.6.1. SS1 ( Al, Ag, Ba, Be, Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni, Sb, V, and Zn): Fill a 1000 mL volumetric flask approximately half full with reagent water, add 50 mL of nitric acid and mix. Next add 100 mL of the custom mixed standard (CAS-CAL-14) purchased from "Inorganic Ventures". In addition add 50 mL of 1000 ppm Antimony. Dilute to volume with reagent water, mix thoroughly and transfer to a 1000 mL Teflon bottle for storage. The solution expiration date is determined by the earliest expiration date of any single component in the solution.

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

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

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

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

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

## 9. PREVENTIVE MAINTENANCE

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

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

9.3. Each hotplate or block digestor is uniquely identified and the temperature is verified with each batch of samples. To perform the verification, a certified thermometer is placed in a container half filled with mineral oil, which is then placed in the center of the hotplate or block digester. A clamp is used to ensure the thermometer does not touch the bottom of the beaker. The temperature is turned to the 95°C setting and the mineral oil is allowed to come to temperature. The analyst will verify that the hotplate gives a temperature of 95°C ± 2°C. If not, the thermostat is adjusted until the thermometer reads and maintains 95°C ± 2°C. The thermostat is then marked to clearly indicate the correct setting to be used during sample digestion. The thermostat position and thermometer reading are recorded for each unit in a logbook.

## 10. RESPONSIBILITIES

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

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

## 11. PROCEDURE

11.1. Record all digestion and sample information on the applicable benchsheet. To assist the analyst, a brief description of the procedure is given on the backside of the benchsheet (see Attachments).

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

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

11.4. Weigh approximately 1g of sample into a 125ml plastic beaker cup and record the weight to the nearest 0.01g. For sludge's and sediments that have high moisture content, use more sample. A plastic 10.0 mL disposable pipette is used to measure 10.0 mL of sample. The volume and weight of the pipetted sample is recorded. In cases where the sludge is very

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thick a 10.0 mL graduated cylinder may be used. The objective is to use about 1g of dry weight sample. For analysis of Lead by Flame AA, use about 2.5g of dry wt. sample and change the final dilution volume to 50ml. This will achieve a lower detection limit needed for most projects. At this point add the appropriate spiking solutions directly onto the designated spike sample prior to addition of reagents.

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

**Note:** The 95°C hotplate temperature must be monitored and documented on a per-batch basis.

11.6. Cool the sample and add 3 mL of 30% $H_2O_2$. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat in the hot block until effervescence subsides. Remove from hot block and cool the beaker.

11.7. Continue to add 30% $H_2O_2$ in 3ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% $H_2O_2$. When the peroxide additions are complete cover the sample with a watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°± 5°C without boiling for 2 hours. Do not let the samples go to dryness, by ensuring the solution covers the bottom of the vessel at all times.

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

**Note:** for ICP-MS digestates, the tubes must be pre-rinsed with 25% HCl.

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

11.9. Cover and reflux the Flame AA and ICP samples for 15 minutes at 95$^{o}$C. After cooling, the samples may be diluted to 100ml for ICP analysis, or 50ml for Flame AA analysis.

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

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

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

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

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

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

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

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

## 12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation

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

12.2. Monitor hotplates on a monthly basis. Report all deficiencies to the Lab Manager. Corrective action must be taken.

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

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

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

12.6. Soil spikes are prepared by adding 2.0 mL of spike solution #1, and 1 mL each of spike solutions 5 and 6 directly to the sample aliquot, prior to the addition of any water or acid. Fill out a spiking data sheet and keep it with the digestion data sheets.

For ICP and ICP-MS digestions 2.0 mL of SS1 and 1.0 mL of SS5 and SS6 are added to the sample aliquot designated as the matrix spike sample. For GFAA digestions 2.0 mL of SS4 is added to the sample aliquot designated as the matrix spike sample. The matrix spike sample is then digested as per the procedure.

## 13. REPORTING

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

13.2. Spiking sheets are completed including all spike data and volumes of spiking solutions used (See Attachments).

## 14. CORRECTIVE ACTION

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

14.2. Handling out-of-control or unacceptable data

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

14.2.2. Documentation of a nonconformity must be done using a Nonconformity and Corrective Action Report (NCAR) when: a) corrective action is not taken or not possible b) corrective action fails to correct an out-of-control problem on a

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laboratory QC or calibration analysis c) reanalysis corrects the nonconformity but is not a procedurally compliant analysis.

## 15. METHOD PERFORMANCE

Available method performance data is given in the reference method. In addition, this procedure was validated through single laboratory studies of accuracy and precision as in the determinative procedure. The method detection limit(s) and method reporting limit(s) are established for the determinative procedure.

## 16. POLLUTION PREVENTION

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

## 17. WASTE MANAGEMENT

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

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

## 18. TRAINING

18.1. Training outline

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

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

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

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

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

## 19. METHOD MODIFICATIONS

19.1. The method uses 2 mL of water and 3 mL of $H_20_2$ in step 11.6. The lab does not add the 2 mL of water. 3.0 mL aliquots of 30% $H_20_2$ in lieu of 1.0 mL aliquots are added subsequently.

## 20. REFERENCES

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

## 21. CHANGES SINCE THE LAST REVISION

21.1. Sec 3.1 – 3.4 is new
21.2. Sec 7.1 – updated
21.3. Sec 8.1 is new
21.4. Sec 9.3 – replaced the word calibrated with verified
21.5. Sec 11.4 – second and third sample is new
21.6. Sec 11.6 – changed 2 mL of water followed by H2O2 to 3 mL of 30% H2O2
21.7. Sec 11.7 – changed 1 mL to 3 mL. Last sentence re-worded for clarity
21.8. Sec 11.8 edits for clarity
21.9. Sec 12.1 is new
21.10. Sec 19 is new

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# Table A

## METALS SPIKING SOLUTIONS CONCENTRATIONS FORM

| Solution Name | Element | mLs of 1000ppm Solution | Final Volume | Solution Conc. mg/L | Concentration in the digest mg/L |
|---|---|---|---|---|---|
| **SS1** | HNO3 | 50.0 | 1000ml | - | |
| | Al | 100* | 1000ml | 200 | 2 |
| | Ag | 100* | 1000ml | 5 | 0.05 |
| | Ba | 100* | 1000ml | 200 | 2 |
| | Be | 100* | 1000ml | 5 | 0.05 |
| | Cd | 100* | 1000ml | 5 | 0.05 |
| | Co | 100* | 1000ml | 50 | 0.5 |
| | Cr | 100* | 1000ml | 20 | 0.2 |
| | Cu | 100* | 1000ml | 25 | 0.25 |
| | Fe | 100* | 1000ml | 100 | 1 |
| | Pb | 100* | 1000ml | 50 | 0.5 |
| | Mn | 100* | 1000ml | 50 | 0.5 |
| | Ni | 100* | 1000ml | 50 | 0.5 |
| | Sb | 50 | 1000ml | 50 | 0.5 |
| | V | 100* | 1000ml | 50 | 0.5 |
| | Zn | 100* | 1000ml | 50 | 0.5 |
| **SS2** | HNO3 | 25.0 | 500ml | - | |
| GFAA SPIKE | As | 2.0 | 500ml | 4 | 0.04 |
| | Cd | 2.0 | 500ml | 4 | 0.04 |
| | Pb | 2.0 | 500ml | 4 | 0.04 |
| | Se | 2.0 | 500ml | 4 | 0.04 |
| | Tl | 2.0 | 500ml | 4 | 0.04 |
| | Cu | 2.0 | 500ml | 4 | 0.04 |
| **SS3** | HNO3 | 25.0 | 500ml | - | |
| | As | 50.0 | 500ml | 100 | 1 |
| | Se | 50.0 | 500ml | 100 | 1 |
| | Tl | 50.0 | 500ml | 100 | 1 |
| **SS4** | HNO3 | 25 | 500ml | - | |
| | B | 50 | 500ml | 100 | 1 |
| | Mo | 50 | 500ml | 100 | 1 |

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