HOT BLOCK DIGESTION OF SOIL, SEDIMENT, WASTE, AND TISSUE SAMPLES FOR TOTAL RECOVERABLE METALS

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1. SCOPE AND APPLICATION

1.1. This method details the hot block digestion of soil, sediment, tissue, and waste samples for total recoverable metals analysis. This method is based on EPA method 3050B.

1.2. Samples digested by this method are suitable for analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES [DEP SOP MT-061]) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS [DEP SOP MT-074]).

1.3. This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become ‘environmentally available’. By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment.

2. SUMMARY OF THE METHOD

A representative (0.5 - 1 g wet weight or approximately 0.5 g dry weight) sample is digested by refluxing with nitric acid and hydrogen peroxide. The sample is then further

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refluxed with hydrochloric acid. A separate sample portion is dried for a percent dry solids determination if necessary.

3. APPARATUS AND EQUIPMENT

3.1. Eppendorf pipette (adjustable volume, 100-1000 µL).

3.2. Eppendorf pipette (adjustable volume, 1-10 mL).

3.3. 50 mL Environmental Express or SCP polypropylene digestion tubes.

3.4. Reflux caps.

3.5. Balance - Top-loading or analytical balance, accurate to 0.001 g.

3.6. Stainless steel spatulas.

3.7. Digestion block - Environmental Express SC-100 located inside a fume hood.

3.8. Aluminum and polystyrene weigh boats.

3.9. Environmental Express resin pellets solid matrix, catalog # SC400.

3.10. Digital thermometer with a NIST-traceable manufacturer's certificate of calibration.

3.11. Digital timer with a NIST-traceable manufacturer's certificate of calibration.

4. REAGENTS AND STANDARDS

See DEP SOP MT-069 for further instruction on reagent documentation. All bottles of reagents and standards (purchased and prepared) in the laboratory are required to have laboratory information management system (LIMS) labels which include the unique serial number. Save all certificate of analyses for standards and reagents to the network folder: \\floridadep\data\DEAR\Labs\Lab5\Chemistry\InorganicPrep\Certificates of Analysis for Reagents and Standards\Standards and Standard Reference Materials.

4.1. Deionized (DI) water - Provided on tap at the laboratory sink and stored in clean wash bottles.

4.2. Trace metal grade nitric acid (HNO_3) - The expiration date is provided by the manufacturer. Stored in the fume hood cabinet at room temperature.

4.3. Trace metal grade hydrochloric acid (HCl) - The expiration date is provided by the manufacturer. Stored in the fume hood cabinet at room temperature.

4.4. 30% hydrogen peroxide solution (H_2O_2) - 10 year expiration date if none noted on Certificate of Analysis. Stored in refrigerator #10 in B411. Store the entire bottle including the bottle-top dispenser in a Ziploc bag.

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4.5. 50% HNO_3 - Prepare by diluting 500 mL HNO_3 to 1 L with DI water. Always add acid to water and stir to dissipate heat. The expiration date will be no longer than the expiration date provided by the manufacturer of the trace metal grade nitric acid (HNO_3).

4.6. Spike and Practical Quantitation Limit (PQL) Solutions: These solutions are purchased or prepared by the metals analysis group. **Inform the supervisor of the Metals Group when the prepared stocks are either within two weeks of expiration, as indicated by the label on the bottle, or within two weeks of depletion.** Refer to Appendix A for the concentrations of the spike solutions. These spike solutions are used to prepare preparation batch Laboratory Fortified Blanks (LFBs) (See Section 8.4). The LFBs prepared at the concentrations specified in Appendix A also serve as the four quality control samples required for Initial and Continuing Demonstrations of Capability (DOC) for each prep technician or analyst. Acceptable analysis of a blind sample, such as a Proficiency Testing sample, may also serve as a Continuing DOC in lieu of four quality control samples, but not as an Initial DOC.

4.6.1. SED SPK 4A and SED SPK 4B - Purchased (i.e. Fisher or High Purity) single-element stock standards are used to prepare the spike solutions for the 'LFBSED' laboratory fortified blank. The expiration date of these solutions will be no later than the soonest expiration date provided by the manufacturer of the single-element stock standards from which they were made. Stored at room temperature.

4.6.2. ICPMINA spike - Custom stock solution from Spex CertiPrep or Inorganic Ventures purchased through Fisher is used to prepare the minerals laboratory fortified blank (LFBMIN). Expiration date provided by the manufacturer. Stored at room temperature in lab B411.

4.6.3. SDPQLICAP# - This is the practical quantitation level check standard for Test ID S-ICPMS. Digested with each batch of samples. A suffix is added to the standard name to indicate the current PQL solution used (e.g. 1, 2, etc.). The expiration date of this standard will be no later than the soonest expiration date provided by the manufacturer of the single-element stock standards from which it was made. Stored at room temperature in lab B411.

4.6.4. SDPQLDV# - This is the practical quantitation level check standard for Test ID S-ICP. Digested with each batch of samples. A suffix is added to the standard name to indicate the current PQL solution used (e.g. 1, 2, etc.). The expiration date of this standard will be no later than the soonest expiration date provided by the manufacturer of the single-element stock

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standards from which it was made. Stored at room temperature in lab B411.

4.6.4.1. SDPQLDV#_AG - This is the practical quantitation level check standard for silver for Test ID S-ICP. Digested with each batch of samples. A suffix is added to the standard name to indicate the current PQL solution used (e.g. 1, 2, etc.). The expiration date of this standard will be the same expiration date provided by the manufacturer as the single-element silver standard from which it was made. Stored at room temperature in lab B411.

5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1. Soil, sediment, waste, and tissue samples for metals analysis are stored in one of the refrigerators located in the receiving room.

5.2. The holding time from time of collection to digestion is 180 days.

5.3. All glassware should be cleaned according to DEP SOP MT-007.

6. SAMPLE PREPARATION PROCEDURE

6.1. Sample Custody and Preparation Worksheet - Check the samples out from the receiving room and set aside to allow equilibration to room temperature. Refer to DEP SOP LB-023 for information on sample custody and the check-out procedure. Once custody has been established, create a prep worksheet using the LIMS Prep Worksheet Manager, found at Laboratory> Technical> Prep Worksheet Manager. Click the ‘Create a prep worksheet’ icon. Under ‘Preparation ID’, select ‘3050-SED’, ‘3050-WAS’, or ‘3050-TISS’ depending on the matrix being digested (See Section 8). Click the ‘Samples Checked Out’ icon and follow the prompts to add the samples to the worksheet from the appropriate user with custody. Under ‘Assign To…’, select the appropriate lab prep technician. Click the ‘Create the new worksheet’ icon. (This step may be done before or during the sample preparation process).

6.2. Prepare the Labels - In LIMS, navigate to Laboratory> Receiving> Print Preparation Labels. Click on the ‘Metals Prep. Labels’ icon. You may populate the label information by typing manually; or by clicking on the ‘Load Sample IDs from prep worksheet’ icon or clicking on the ‘Load sample IDs checked out by operator’ icon. Select the appropriate worksheet or user from the pop-up window and click ‘OK’. The digestion tubes shall be labeled with the sample ID and/or the QC name (See Section 8). Print the required sample labels from the SATO label printer and place each one on the outside of the appropriate digestion tube.

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6.3. Sample Homogenization - If the sample cannot be thoroughly mixed within its container without spilling, empty the entire sample into a clean stainless-steel tray. Do not decant any liquid or remove any objects from the sample. Please contact the supervisor if any non-representative material is found in the sample. A mortar and pestle can be used if necessary. Any large metal pieces should be cut up or crushed, but not removed from the sample. Return the homogenized sample to the jar.

6.4 Weighing Samples:

6.4.1. Soil and Sediment samples - The sample results for soil and sediment samples are reported on a **dry weight** basis. Therefore, the percent dry solid results shall be determined to calculate the proper sample wet weight needed to obtain a final dry weight of approximately 0.5 g. Refer to DEP SOP MT-055 for the determination of percent dry solids. If the percent solid results have already been uploaded to the LIMS, then the Prep Worksheet Manager module of LIMS will automatically calculate the wet weight needed to obtain 0.5 g dry weight.

Note: Use a balance adjacent to a computer to record the sample aliquot weights directly into the LIMS prep worksheet. Do not record weights using a pen and paper.

6.4.1.1. Place a dry sample tube onto the balance and tare the balance. Next, weigh the amount of homogenized sample needed to reach approximately 0.5 g **dry weight**. Record the weight on the prep sheet to the nearest 0.001 g in the field marked 'sample weight'. Make sure that the entire sample is in the vessel and none has spilled onto the balance pan.

6.4.2 Waste and Tissue samples - The sample results for waste and tissue samples are reported on a **wet weight** basis. Place a dry sample tube onto the balance and tare the balance. Weigh approximately 0.5 g of homogenized sample. Make sure that the entire sample is in the vessel and none has spilled onto the balance pan. Record the weight on the prep sheet to the nearest 0.001 g.

6.5. Digesting Samples

6.5.1. Under the fume hood, SLOWLY add 5 mL of 50 % HNO_3 to each vessel. Beware of a possible violent reaction with certain matrices. If foaming occurs, gently swirl the sample tubes to break up the bubbles. Samples that exhibit a high reactivity with the acid should be allowed to sit for approximately 30 minutes before heating.

6.5.2. Preheat the hot block to approximately 95 ºC (temperature reading of a digestion tube, not the hot block display). The temperature of the heating

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block must be monitored and recorded before digestion on each day of use. Place 1 tube containing DI water randomly on the block and insert a thermometer. After the temperature has stabilized and reached the acceptable temperature range of 92 – 97 °C, read the temperature of the thermometer inserted into the digestion tube and record it on the LIMS prep worksheet in Prep Worksheet Manager in the 'Block Temperature' box. The thermometer used in this temperature verification must be calibrated against a NIST-traceable thermometer annually. To check the calibration of a thermometer, use the procedure from DEP SOP LB-035, Calibration of Lab Thermometers using a Constant Temperature Calibration Bath. The thermometer calibration shall be recorded in the 'Lab Thermometer Calibration Logbook (Fluke 7103 Temperature Calibration Microbath)' stored in B319. Label the thermometer with the date of calibration. Alternatively, digital thermometers with a manufacturer's NIST-traceable certificate of calibration may be used.

Note: Use a NIST-traceable digital timer to monitor the time of heating during digestion.

6.5.3. Cover each vessel with a reflux cap, place each into the hot block, and reflux for 15 minutes without boiling. Remove the samples from the hot block and allow them to cool.

6.5.4. Add 2.5 mL of concentrated HNO_3 to each tube, replace the reflux caps, and put the sample tubes back into the hot block and reflux for an additional 20 minutes. Remove the tubes from the hot block and allow them to cool. For samples with high organic content, additional refluxing may be necessary. This will be evident by the generation of brown fumes upon refluxing during this step. If brown fumes evolve from the sample, repeat this step (addition of 2.5 mL concentrated HNO_3) for those samples until no further brown fumes are detected. If additional refluxing is required, note this in the comments section of the prep sheet. Document any additional HNO_3 added to individual samples in the comment column of the prep worksheet.

Note: Do not allow the solution volume to reduce low enough such that the bottom of the digestion vessel becomes exposed. If a digestion vessel is heated to dryness, contact the supervisor. The sample will need to be re-digested.

6.5.5. Continue to heat the samples at 95 °C for one hour without boiling, then remove the vessels from the hot block and allow them to cool. The reflux cap is not needed during this step; however, do not allow the samples to dry completely. It is important to ensure complete coverage of the bottom of the vessel at all times.

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6.5.6. Add 1 mL of DI water and 1.5 mL of a 30 % H_2O_2 solution to each vessel and cover with a reflux cap. Place the vessels back into the hot block and heat (the sample solution will effervesce from the addition of the H_2O_2). Heat the samples until the effervescence subsides. Care must be taken to prevent sample loss from excessive effervescence. Remove the sample tubes from the hot block and allow them to cool. Add additional H_2O_2 in 0.5 mL aliquots followed by heating until the effervescence is minimal or the general appearance of the solution is unchanged. **Do not add more than a total of 5 mL H_2O_2 to each sample.** Contact the supervisor if 5 mL of peroxide has been added but the samples are still effervescing. Document any additional H_2O_2 added to individual samples in the comment column of the prep worksheet.

6.5.7. Cover each tube with a reflux cap, if not already covered, and carefully heat without boiling for 90 minutes or until the solution volume is reduced to about 2.5 mL. Periodically observe the ongoing digestion and make sure the volume in the digestion vessel is sufficient to cover the bottom of the vessel. Remove the tubes from the hot block and allow them to cool. Add 5 mL of concentrated HCl to each vessel. Place onto the hot block and reflux for 15 minutes. Remove the vessels from the hot block and allow them to cool. The samples are now ready to be brought to volume.

6.5.8. Reconstitute the samples to the 50 mL graduation with DI water. Cap the tubes and gently invert 8-10 times to mix the sample completely. The samples are now ready for analysis.

6.5.9. Write the prep worksheet (e.g. 3050-SED, WAS, or TISS, _####) ID on a label and place the label on the sample rack. Make sure all documentation is completed properly on the prep worksheet, including but not limited to: the prep technician, digestion start and end date, digestion start and end time, reagent serial numbers, spike solution serial numbers, sample IDs, block ID, block temperature, thermometer ID, and sample comments. Be sure to record all information in the sample comments column that might be useful to the analyst and/or reviewer. Notify the supervisor when all fields of the prep worksheet are complete. The supervisor will verify the completeness and correctness of the prep worksheet, and if acceptable, will add their name in the ‘Reviewed By’ field. Once the prep worksheet has been successfully reviewed and accepted, complete the prep worksheet in Prep Worksheet Manager by clicking on the ‘Complete’ button at the bottom left of the open prep worksheet window. This will change the samples’ status from ‘W’ to ‘V’, indicating that sample preparation is complete and that samples are awaiting analysis. This **must** be done

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BEFORE the tray is sent up to the metals analysis lab. Print a copy of the completed prep worksheet and send it along with the sample tray to the metals analysis lab.

6.5.10. If necessary, dilutions are prepared by the analyst prior to sample analysis. Generally, samples designated for ICPMS analysis require a dilution factor of 5.

7. SAMPLE ANALYSIS PROCEDURE

Samples prepared in this manner are suitable for analysis by ICP-AES (DEP SOP MT-061) or ICP-MS (DEP SOP MT-074); see appropriate SOP for instructions regarding analysis.

8. QUALITY CONTROL

8.1. A digestion batch is defined as a set of 20 samples or less, consisting of samples with similar matrices, and having similar physical characteristics and of the same general composition.

8.1.1. The three possible matrix groups are:

A. Soils, fresh water sediments, marine sediments, and similar materials. This group is reported on a dry weight basis. LFBs for a sediment/soil matrix digestion batch must consist of ~0.5 g of Environmental Express resin pellets to represent a solid matrix, along with their appropriate spike solutions. Weights must be recorded appropriately.

B. Aqueous wastes, non-aqueous wastes, solid wastes, and similar materials. This group is reported on a wet weight basis. For solid matrices, the LFB must consist of ~0.5 g of Environmental Express resin pellets and the appropriate spike solutions.

C. Tissues of all kinds. This group is reported on a wet weight basis. For solid matrices, the LFB must consist of ~0.5 g of Environmental Express resin pellets and the appropriate spike solutions.

8.1.2. Samples within the same matrix group that share similar physical characteristics and general composition are to be digested in the same batch. If there are more than 20 samples of the same matrix, arrange the samples in batches of twenty samples or less to be digested together. Each batch requires its own set of quality control samples.

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8.2. Selecting Samples for Quality Control - Randomly choose a sample to be used for the preparation of matrix spikes. This sample should best represent the samples in the batch.

8.3. Digestion Blank - One per digestion batch of 20 samples or less. Add ~0.5 g of Environmental Express resin pellets to the digestion blank when preparing soils, sediments, wastes, and tissues.

8.4. Laboratory Fortified Blanks (LFB) – The 'LFBSED' is prepared by spiking 1 mL of SED SPK 4A and 1 mL of SED SPK 4B to 50 mL of DI water. One 'LFBSED' is required for every batch. If minerals (Al, Ca, Fe, Mg, K, or Na) are requested, an 'LFBMIN' is also required. Spike 1 mL of ICPMINA into 50 mL of DI water. Environmental Express resin pellets are used as the quality system matrix for all LFBs. Add approximately 0.5 g of the resin pellets to the LFB.

8.5. Duplicate Matrix Spikes – Spike 1 mL of SED SPK 4A and 1 mL of SED SPK 4B into two separate 50 mL aliquots of the QC sample. If minerals are requested, spike 1 mL of ICPMINA into a third aliquot of the QC sample.

8.6. Digestion Practical Quantitation Limit (PQL) Standards – One per batch per Test ID. Digestion PQL spike solutions (SDPQLICAP#, SDPQLDV#, and SDPQLDV#_AG) are prepared by metals analysts in Lab B310. A suffix is added to these abbreviations to indicate the current PQL solution used (e.g. 1, 2, etc.). For the ICPMS Digestion PQL, spike 1 mL of the SDPQLICAP# solution into 50 mL DI water. For the ICP Digestion PQL, spike 1 mL each of the SDPQLDV# and SDPQLDV# AG solutions into 50 mL DI water. Add approximately 0.5 g of the resin pellets to the PQL.

9. SAFETY/HAZARDOUS WASTE MANAGEMENT

9.1. Gloves, safety glasses or goggles, and lab coats must always be worn when handling all samples, spike solutions, acids, hydrogen peroxide, and other reagents.

9.2. Excess sample and spike solutions shall be disposed of in the containers labeled Metals Hazardous Waste. When 90 % full, these containers must be emptied into the large metals waste drums in the laboratory waste rooms.

9.3. Reagents should be added to samples in a fume hood with the sash lowered as far as possible to reduce exposure to fumes and to protect in case of splashing.

9.4. Post analysis sample digestates - If positive results exceeding the pollutant limitations (sewer discharge limits, see DEP SOP MT-007) are found, the sample digestates shall be discarded in the container labeled Metals Hazardous Waste**.** See the DEP Health and Safety Manual or your supervisor if you have any

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questions. All other sample digestates can be disposed of in the sink if the acid concentration is less than 2 % or if they are diluted by a factor of 50 or greater.

10. REFERENCES

10.1. EPA Method 3050B, Revision 2, December 1996

10.2. DEP SOP MT-007, Procedure for Cleaning Metals Labware

10.3. DEP SOP MT-055, Determination of Percent Dry Solids

10.4. DEP SOP MT-061, Analysis of Selected Metals by Dual View Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

10.5. DEP SOP MT-069, Metals Standard and Reagent Preparation Procedure

10.6. DEP SOP MT-074, Standard Operating Procedure for the Thermo ICAP Inductively Coupled Plasma Mass Spectrometer

10.7. DEP Health and Safety Manual, located on the Florida DEP Division of Environmental Assessment and Restoration intranet site.

10.8. Laboratory Quality Manual, located on the Florida DEP Division of Environmental Assessment and Restoration internet site.

10.9. DEP SOP LB-035, Calibration of Lab Thermometers using a Constant Temperature Calibration Bath.

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Appendix A

Spike Concentrations

Metal	Water Spike HW6 (1/50 dilution) µg/L	Sediment Spike SEDSPK4 (1/50 dilution) µg/L	Water Spike ICPMINA (1/50 dilution) mg/L
Al	4000	8000	20
Sb	200	400	
As	200	400	
Ba	400	800	
Be	2	4	
B	500	400	
Cd	10	20	
Ca	4000	8000	80
Cr	100	400	
Co	100	200	
Cu	100	100	
Fe	4000	8000	20
Gd	50		
Pb	100	400	
Mg	4000	8000	40
Mn	200	400	
Mo	50	200	
Ni	100	200	
K	4000	8000	10
Se	200	400	
SiO_2			
Ag	20	40	
Na	4000	8000	80
Sr	2000	4000	
Tl	50	100	
Sn	100	400	
Ti	40	200	
V	100	200	
Zn	500	400	

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Appendix B

Appendix of Significant Changes

02/10/2009	Edited section 6.3.1 to clarify that the laboratory will not remove anything from the sample during preparation.
01/14/2010	Edited section 6.5 to say that we use reflux caps instead of watch glasses during sample reflux. Also, added a note about solid matrix waste samples needing to be digested with an LFB containing Ottawa Sand to represent matrix added to Section 8.4, point 2.
12/18/2012	Environmental Express resin pellets solid matrix, catalog # SC400 replaces Ottawa Sand throughout SOP.
12/10/2014	Section 4 edited for more detail. Section 6 edited to include procedure for the new Prep Worksheet Manager. Appendices added.
12/14/2017	Expiration date for the 50 % HNO_3 reagent changed to 1 year from preparation.
12/04/2019	Section 4.5 was edited to note that the expiration date for the 50 % HNO_3 reagent will be no longer than the expiration date provided by the manufacturer of the Trace metal grade nitric acid (HNO_3).
10/15/2026	Section 4.6 was expanded to state that routine LFB concentrations also serve as the four quality control samples required for Initial Demonstrations of Capability and is acceptable for Continuing DOCs. Updated Section 6.1 and 6.2 to expand upon sample custody procedure and label printing. Updated Section 8.6 to include PQL preparation. Minor grammatical and syntactical updates throughout the document. Updated Reference for DEP Health and Safety Manual.

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