MICROWAVE ASSISTED HYDROFLUORIC ACID DIGESTION OF SOLID MATRICES FOR TOTAL METALS DETERMINATIONS (Adapted from EPA Method 3052 for the Milestone Ethos UP microwave system)

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1. SCOPE AND APPLICATION

1.1. This method details a microwave oven assisted hydrofluoric acid (HF) digestion of solid matrices for total metals determinations. This method was adapted from procedures contained within EPA method 3052.

1.2. Samples logged in for test IDs S-ICP-TO and S-ICPMS-TO are digested as detailed in this SOP and analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and/or Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2. SUMMARY OF THE METHOD

2.1. A sample is homogenized in the sample container. A portion of the homogenized sample must then be dried for percent solid determination at 105 °C.

2.2. If the sample is 20 % solid or greater, a portion of the homogenized sample is ball milled and placed into the 60 °C oven for another percent solid determination.

2.3. If the sample is under 20 % solid, a portion of the homogenized sample is placed into the 60 °C oven for another percent solid determination.

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2.4. The 60 °C dried aliquot is then digested using microwave radiation with a combination of hydrogen peroxide and nitric, hydrochloric, and hydrofluoric acids.

3. APPARATUS AND EQUIPMENT

3.1. Eppendorf 500 µL and 1000 µL pipettes

3.2. 1-10 mL bottle-top dispenser

3.3. 2-5 mL HF resistant bottle-top dispenser

3.4. Balance with readability of at least 0.001 g.

3.5. Milestone Ethos UP microwave system

3.6. Milestone Ethos UP Operator Manual (MA182) and Milestone SK-15 Operator Manual (MA176)

3.7. Milestone high pressure reaction vessel and rotor assemblies, SK-15

3.8. Teflon or stainless steel or plastic spatulas (Quaver vibrating spatula)

3.9. Polypropylene graduated 50 mL digestion tubes and caps, Environmental Express or equivalent

3.10. Retsch PM 200 Planetary Ball Mill

3.11. NIST-traceable thermometer

3.12 Environmental Express Digestion Block

3.13 CTL Scientific fluoride test paper

4. REAGENTS AND CHEMICALS

See DEP SOP MT-069 for standard and reagent documentation, labeling requirements, and expiration dates. Save all certificates of analysis for reagents to network folder, //FLDEP1/DEAR/Labs/Lab5/Chemistry/InorganicPrep/Certificates of Analysis for Reagents and Standards.

4.1. Deionized (DI) water

4.2. 30 % Hydrogen peroxide (H_2O_2). Stored in a refrigerator. If the manufacturer provides an expiration date, it shall be used.

4.3. Concentrated trace metal grade nitric acid (HNO_3). Stored in cabinet below fume hood. The expiration date is provided by the manufacturer.

4.4. Concentrated trace metal grade hydrochloric acid (HCl). Stored in cabinet below fume hood. The expiration date is provided by the manufacturer.

4.5. Concentrated trace metal grade hydrofluoric acid (HF). Stored in cabinet below fume hood. The expiration date is provided by the manufacturer.

4.6. 5 % (w/v) Boric Acid Solution (H_3BO_3): Prepare by adding 50 g of boric acid to 750 mL of DI water in a 1 L Teflon bottle. Cap and place bottle in a 60 °C oven

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until solids dissolve into solution. Remove from oven and allow to cool under a fume hood. Transfer solution to a 1 L volumetric flask, bring to volume with DI water. The expiration date for this prepared solution is 1 year and it is stored at room temperature in the laboratory.

4.7. Hydrofluoric acid burn kit, including calcium gluconate gel. The expiration date is provided by the manufacturer.

4.8. Standards and spiking solutions: The analysis group prepares these solutions. Inform the supervisor of the metals analytical group when the prepared stocks are either close to expiration, as indicated by the label on the bottle, or about to run out of volume. The expiration date is provided by the manufacturer and the solutions are stored at room temperature.

4.8.1. Sediment Spike Solution – SEDSPK4. This spike is prepared in two parts, SED SPK4A and SED SPK4B using the primary or second source single element standards. SED SPK4A is prepared with 2 % HNO_3 and 1 % HCl while SED SPK4B is prepared with 2 % HNO_3 only, for better silver stability. Refer to Appendix B of DEP SOP MT-061 for spike concentrations.

4.8.2. Mineral Spike Solution – ICPMINA. Purchased spike, refer to Appendix B of DEP SOP MT-061 for spike concentrations.

4.9. MESS-4: Marine Sediment Reference Material. Purchased from the National Research Institute of Canada. This solid is stored in a desiccator at room temperature in B411. See 7.1.4. for more information. The expiration date is provided by the manufacturer.

4.10. 2 % HNO_3 / 1 % HCl Solution: Prepare by adding 20 mL of HNO_3 and 10 mL of HCl to 500 mL of DI water in a 1 L Teflon bottle. After acid addition, fill the bottle to a final volume of 1 L with DI water.

5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Solid samples do not require preservation for metals analysis. The laboratory has established a six-month holding time for solid samples. Since the majority of samples submitted for metals analysis are also logged in for other chemical tests requiring refrigeration for preservation, the solid samples for metals analysis are stored in the receiving room in either refrigerator # 1 or # 8. Allow the chilled samples to come to room temperature before beginning the preparation procedure.

6. SAMPLE PREPARATION/DIGESTION PROCEDURE

6.1. Obtain custody of up to 20 samples scheduled for total metals testing.

6.2. Allow the samples to equilibrate to room temperature.

6.3. In this procedure, two sample aliquots are necessary for determining percent solid, one aliquot for the 105 °C percent solid test and another aliquot for the 60 °C percent solid test. The difference must be taken into account when calculating

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the sample results for reporting in mg/kg dry weight. The dry weight is calculated from the 60 °C and 105 °C percent solid results in the MT-TD form:

$$Dry\ weight\ (g) = Sample\ aliquot\ dried\ at\ 60\ °C\ (g)\ x\ (\frac{105\ °C\ percent\ solid\ result}{60\ °\ percent\ solid\ result})$$

If the 60 °C percent solid result is less than the 105 °C percent solid result, the aliquot weighed out and dried at 60 °C will be used as the dry weight. This ensures the calculated dry weight is not greater than the aliquot weighed out that was dried at 60 °C. First, the sample is homogenized in the sample container and a representative aliquot of the sample from the non-ball milled portion is then weighed and used for the determination of the percent solid content at 105 °C (see DEP SOP MT-055). **If the percent solid is less than 20 % based on the 105 °C percent solid data, the sample does not require ball milling. The sample is ready for digestion after the 60 °C percent solid has been determined.**

6.3.1. If the percent solid is 20 % or greater based on the 105 °C percent solid data, homogenize a new sample portion with a planetary ball mill (see DEP SOP MT-064). This portion will be dried at 60 ºC. Milling the sample is critical to the success of the digestion. Failure to reduce the particle size during this step will make it difficult to completely digest the sample aliquot due to a reduced surface area. **If necessary, place an aliquot of the ball milled sample into a 15 mL centrifuge tube with the Nutrients (TKN/TP) sample ID prior to being dried at 60 °C (see DEP SOP MT-064, section 5.).**

6.3.2. Weigh a representative 75 to 110 g portion of the ball milled sample into a clean ceramic evaporating dish. Dry the aliquot in an oven at 60 °C until the sample does not exhibit any further weight loss (2 to 4 days for low percent solid samples). Calculate the percent solid content of the sample dried at 60 °C in the same manner as described in DEP SOP MT-055. Save the completed MT-60C-PS form in the folder: \\FLDEP1\DEAR\Labs\Lab5\Chemistry\InorganicPrep\METALS\% SOLID LOG BOOK\PS60% & GRINDING-2018. After the 60 °C percent solid determination, transfer a portion of the dried sample into a new 50 mL disposable digestion tube with a screw cap and label the tube with the Metals sample ID. **If necessary, transfer another portion of the dried sample into a 15 mL centrifuge tube with the Nutrients (S-TOC) sample ID.**

6.4. Obtain the necessary number of clean **Milestone Ethos UP** SK-15 microwave digestion vessels. Be sure that each digestion vessel liner and cap has been thoroughly cleaned as per instruction in the Milestone Ethos UP manual. This cleaning should be followed with a thorough rinsing of each item with DI water. Assemble the required number of **Milestone Ethos UP** SK-15 vessels, excluding the support modules. All vessels and components must be dry before proceeding. Moisture will lead to error in sample mass determination, and will create steam in the microwave, which may damage the digestion vessels.

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6.5. Print sample labels and set them aside for later use.

6.6. Verify the analytical balance calibration by measuring the mass of three standard masses (surrounding the target mass range) and recording the results in the balance logbook (see DEP SOP CM-011).

6.7. Open the Excel form 'MT-TD-1.1 Template' located at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\InorganicPrep\METALS\Total Digestion Microwave and enter the sample IDs for each sample scheduled for digestion in this batch.

6.8. Enter both percent solid results, at 60 °C and at 105 °C and verify that the minimum weight needed for 0.25 g of dry weight has been calculated automatically and correctly. The equation for determining the minimum weight necessary for 0.25 g dry weight when the sample is dried at 60 °C is:

$$0.25 \times \frac{60\ ^{\circ}C\ \%\ Solid}{105\ ^{\circ}C\ \%\ Solid}$$

6.9. Save a copy of this form as 'TD-*YYMMDD*'" in the 'Total Digestion Microwave' folder. Use a laptop/tablet computer to record data to the Excel preparation form (MT-TD).

6.10. Open the Word document form 'MT-TD-CHK-LIST-1.0' located at \\FLDEP1\DEAR\LABS\LAB5\Chemistry\InorganicPrep\METALS\Total Digestion Microwave. This form is a preparation check list.

6.11. Print a copy of this Prep Check List sheet for digestion steps during sample preparation. At the end of the procedure, include the physical prep checklist with the printed preparation sheets.

6.12. Tare the balance with the empty vessel on the pan and add approximately 0.25 g of the homogenized sample to its correspondingly labeled vessel. Record this mass in the field labeled as '60 °C Sample Weight'. Repeat this step for each sample in the batch.

6.13. Transfer all of the sample vessels to a fume hood.

6.14. Add reagents to each sample in the following order:

Note: It may be necessary to add these reagents to the samples in smaller increments until the proper volume is reached (11 mL) due to the reactive nature of some samples (i.e. high organic content). This will prevent the sample from "foaming" out of the digestion tube during heating.

(**Follow Prep Check List sheet when adding reagents**)

6.14.1. Add 2 mL of 30 % H_2O_2.

6.14.2. Add 2 mL of HNO_3.

6.14.3. Observe sample reaction and wait until effervescence has subsided, cap samples with vessel lids and allow the acid to react with the sample for 1 hour at room temperature.

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6.14.4. Add 1 mL of 30 % H_2O_2.

6.14.5. Add 6 mL of HNO_3.

6.14.6. After the remaining reagents are added, place the capped samples into the oven at 60 °C for one hour.

6.15. Remove samples from oven and allow them to cool down to room temperature before weighing each fully assembled vessel (i.e. lid, adapter plate, and safety spring). Do not weigh sleeves, reference vessel, or housing. Record this measurement on the preparation sheet in the field labeled 'Total Vessel Weight, stage 1'.

6.16. Beginning with the reference vessel, place each vessel into a sleeve, and place fully assembled vessel into its support module.

6.17. Tighten the support screw finger tight, and then tighten it with the torque tool.

6.18. Place the modules into the carousel as they are assembled.

6.19. The control vessel is equipped with a temperature sensor. The control vessel should contain reagents only. Insert the end of the temperature sensor tubing into the receptacle of the line valve and the tubing from the other end of the valve into the sensor module. Twist the probe (plug side only) a quarter turn to lock it into place on the microwave sensor module. Exercise care when handling the temperature sensor, as it is very fragile.

6.20. Review the instruction manual (SK-15 Operator Manual MA176) and verify that all of the microwave vessels have been assembled properly.

6.21. Place the first carousel into the microwave. The turntable and carousel have a complimentary shape that must fit together to operate properly.

6.22. Press the circular arrow key on the keypad to rotate the control vessel to the left rear corner of the microwave (as you are looking inside the chamber). Insert the sensor module into the receptacle on the right wall of the microwave chamber.

6.23. Close and latch the door. The microwave will not start until the door is closed correctly. See the manual (Milestone Ethos UP Operator Manual MA182) for further information.

6.24. Run the Milestone Microwave System using the 'Session 1' program. This is a ramp to temperature program. The parameters are 1800 Watts of power, a ramp time of 25 minutes to 95 ºC, and a hold time of 30 minutes at 95 ºC.

6.25. Under normal circumstances, allow the program to finish and save run data as 'YYMMDD' and carousel I.D. A or B. Remove the first carousel and place it inside a fume hood.

6.26. Repeat the microwave digestion procedures in steps 6.21. – 6.25. for the second carousel while the other carousel is cooling.

6.27. When the microwave program has finished for the second carousel, shut down the microwave and allow the samples to cool in the microwave overnight. The next

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morning or after the samples have completely cooled, beginning with the carousel in the hood, remove the support modules from the carousel one at a time. Vent each vessel by slowly loosening the vent fitting. Loosen the nut and remove the vessel from the support module. Remove the vessel from its jacket and place in a rack.

6.28. Weigh each fully assembled vessel. Do not weigh sleeves, reference vessel, or housing. Record this measurement on the MT-TD form in the field labeled 'Total Vessel Weight, After First Microwave Session'.

6.29. Add 1 mL of 30 % H_2O_2 and 1 mL of HNO_3 to each sample. Allow to react for ~60 minutes.

6.30. Cap each vessel.

6.31. Weigh each sample and record this as the 'Total Weight, before Second Microwave Session'.

6.32. Reassemble the first carousel and place it back in the microwave by repeating steps 6.21. – 6.23.

6.33. Run the Milestone Microwave System using the 'Session 2' program. This is a ramp to temperature program. The parameters are 1800 Watts of power, a ramp time of 25 minutes to 190 ºC, and a hold time of 30 minutes at 190 ºC.

6.34. Under normal circumstances, allow the program to finish and save run data as 'YYMMDD' and carousel I.D. A or B.

6.35. After the first carousel has completed the second heating stage and properly cooled, remove the carousel and place it in the hood.

6.36. The second carousel (now in the hood) will need to be taken through the same procedures as described in steps 6.32. – 6.35.

6.37. The following morning or after the samples have completely cooled, remove the fully assembled digestion vessels from the microwave carousel(s) and measure the mass of each vessel by repeating steps 6.27. – 6.28. Record this mass on the preparation sheet as the 'Total Weight, After Second Microwave Session'.

6.38. In addition to the normal practice of wearing proper eye protection, gloves, and a lab coat wear the following safety gear when working with concentrated HF:

6.38.1. Face shield

6.38.2. Rubber apron

6.38.3. Rubberized or Silver Shield sleeve covers

6.38.4. Heavy gauge Neoprene rubber gloves

6.39. Add 3 mL of HF to each sample. Allow to react for ~30 minutes, and then cap each vessel.

6.40. Weigh each sample and record this as the 'Total Weight, Before Third Microwave Session'.

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6.41. Reassemble the first carousel and place it back in the microwave by repeating steps 6.21. – 6.23.

6.42. Run the Milestone Microwave System using the 'Session 2' program. This is a ramp to temperature program. The parameters are 1800 Watts of power, a ramp time of 25 minutes to 190 °C, and a hold time of 30 minutes at 190 °C.

6.43. Under normal circumstances, allow the program to finish and save run data as 'YYMMDD' and carousel I.D. A or B.

6.44. After the first carousel has completed the third heating stage and properly cooled, remove the carousel and place it in the hood.

6.45. The second carousel (now in the hood) will need to be taken through the same procedures as described in steps 6.41 – 6.44.

6.46. The following morning or after the samples have completely cooled, remove the fully assembled digestion vessels from the microwave carousel(s) and measure the mass of each. Record this mass on the digestion sheet as the 'Total Weight, After Third Microwave Session'

6.47. After this mass has been recorded, transport the fully assembled digestion vessels to a fume hood.

6.48. Add 3 mL of HCl to each vessel, secure vessels back into their wedges, and place wedges into a 60 °C vented oven for 2 hours. Then, allow wedges to cool inside the fume hood.

6.49. Swirl each microwave vessel 3 to 4 times to collect any particles on the bottom of the tube in order to aid transfer of the sample. Gently tap any condensation on the inner Teflon cap into the vessel. Transfer each sample from its microwave vessel into an appropriately labeled 50 mL disposable hot block digestion tube. Rinse the vessel liner with the 2 % HNO_3 / 1 % HCl solution and pour the rinse into the hot block tube making sure that the entire contents of the vessel, including any remaining solids, are transferred into the digestion tube. Make sure that the sample ID labels are affixed to the digestion tubes.

6.50. Rinse the vessel at least two more times with the 2 % HNO_3 / 1 % HCl solution. Adequate transfer will usually require 15 mL of the 2 % HNO_3 / 1 % HCl solution.

6.51. Now repeat the transfer procedure for each sample in the second carousel.

Note: The following step is to remove residual HF left over from the microwave heating stage - HF is hazardous to the analysts and/or instrumentation if not neutralized. The neutralization is a slow process and requires heating. Maintain using all HF PPE until after the samples have cooled down (6.54)

6.52. Add 4 mL of the 5 % (w/v) boric acid solution to each sample. Bring each sample to 50 mL mark with the 2 % HNO_3 / 1 % HCl solution.

6.53. Place the digestion tubes on a digestion block and heat for 4 hours at 95 °C. Use a NIST-traceable thermometer to record the temperature of the samples in the hot

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block by placing the thermometer in a digestion tube containing DI water. Document the temperature on the MT-TD form (Digestion Block Temperature 1). The acceptable range is 92 – 97 °C.

6.54. After 4 hours of heating, note the volume for each sample. The volume should be less than or equal to 10 mL. If not, continue heating until the sample volume is less than or equal to 10 mL for every sample.

6.55. **DO NOT** allow any portion of the sample tube to become dry. If a sample does develop a dry portion on the bottom of the tube then it will need to be discarded and re-digested. This is critical as several analytes (As, Sb and Se in particular) can be volatilized if heated to dryness.

6.56. After 4 hours, remove the samples from the block and allow them to cool in the hood for ~20 min.

6.57. Slowly add 1 mL H_2O_2 and 1 mL HNO_3 to each sample and heat on the block for an additional 1 hour at 95 °C. Record the temperature of the hot block as in 6.53 and document on the MT-TD form (Digestion Block Temperature 2).

6.58. Remove the samples from the block and bring to 50 mL mark with the 2 % HNO_3 / 1 % HCl solution.

6.59. Tighten each cap and invert 8-10 times to mix the sample thoroughly.

6.60. Dilute the sample by 2 with the 2 % HNO_3 / 1 % HCl solution in a new 50 mL digestion vessel and place the diluted digestates back on the hot block for 4 hours at 95 °C. After heating, re-constitute to 50 mL with the 2 % HNO_3 / 1 % HCl solution. Record the temperature of the hot block as in 6.53 and document on the MT-TD (Digestion Block Temperature 3).

6.61. The samples are now ready for analysis. Consult with your supervisor on the completeness of the digestion and make sure that your supervisor has looked over the preparation worksheet.

6.62. Change the status of the samples to ‘V’ in the LIMS ‘Prep Worksheet Manager’. The Preparation ID that should be used is ‘SOP-MT-063’. The Prep/Digestion Start Day and Time should be the day the digestion is started. The Prep/Digestion End/Completion Day and Time should be after the diluted samples have been reconstituted (see step 6.60). Take the samples, a copy of the MT-TD form, and the MT-TD-CHKLIST form down to the metals analytical lab (B310).

7. QUALITY CONTROL

7.1. A preparation batch is comprised of 20 samples or less and should contain the following quality control samples:

7.1.1. Digestion blank - One per digestion batch of 20 samples or less. As the laboratory is not aware of any suitable materials that may be used in preparing valid method blanks, empty digestion tubes are used for the digestion of soils samples. The purpose of method blanks is to serve as negative controls in the assessment of potential positive bias during

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sample preparation and analysis. With regard to that goal, including a material that may itself contain measurable analytes can only obfuscate that assessment. The laboratory has investigated various materials and has not found any suitable for serving the stated purpose of a method blank.

7.1.2. Trace metal matrix spikes - One sample is spiked per batch of 20 samples or less. Spike the chosen sample in duplicate. Spike each replicate with 1 mL of 'SED SPK 4A' and 1 mL of 'SED SPK 4B'.

7.1.3. Mineral matrix spikes - Spike one sample with 2 mL of 'ICPMINA'. This spike is used for reporting spike recoveries for samples with a high mineral content in the QC sample.

7.1.4. Standard reference material (SRM) - One per batch of 20 samples or less. Since many SRMs for this type of testing are not certified for all analytes, one should be chosen that contains as many requested analytes at quantifiable levels as possible. If an SRM cannot be procured that contains all requested analytes at quantifiable concentrations, then an LFB should be prepared with the appropriate metals. The SRM is used as the laboratory control sample for the preparation batch. MESS-4 is used as the current SRM (see 4.9). The acceptable recovery range for MESS-4 is 80 – 120 %, except for silver, 74 – 126 %.

7.2. Microwave digestion control samples - Each carousel has a control vessel for temperature and pressure monitoring. Reagents alone are used in each control vessel to minimize fluctuation in microwave radiation exposure from carousel to carousel.

8. SAFETY/HAZARDOUS WASTE MANAGEMENT

8.1. Always wear safety glasses and lab coats when in the laboratory.

8.2. Read the handling guidelines in Appendix A before working with hydrofluoric acid.

8.2.1. Hydrofluoric acid can cause serious injury or death if it comes in contact with the skin. It can absorb through the dermal layers and penetrate the muscular tissue and bones scavenging calcium and disrupting normal bodily processes. Proper safety gear, described in section 6.38. and 8.2.3. must be worn at all times when working with hydrofluoric acid. Refer to the material safety data sheet (MSDS) for HYDROFLUORIC ACID and the hydrofluoric acid burn kit's instruction manual for further information. In the event of skin contact with hydrofluoric acid, treat the affected areas immediately with the calcium gluconate in the hydrofluoric acid spill kit and contact a supervisor immediately.

8.2.2. Hydrofluoric acid is very dangerous and can cause serious injury or death. In order to minimize the potential hazards, only work with small volumes (i.e. 10 or 20 mL maximum) at a time. Keep the workspace in the hood

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very clean and free from obstructions to minimize the possibility of an accidental hydrofluoric acid spill.

8.2.3. Face shields, rubber apron, rubberized or Silver Shield® sleeves, Neoprene gloves, lab coat, and safety glasses must be worn when working with hydrofluoric acid.

8.3. All samples are handled as if they are hazardous materials. Gloves should be worn when handling all samples, spiking solutions, acids, and other reagents used in this procedure. Excess solid sample that has been removed from the original sample container should be disposed of in the trash.

8.4. Any excess spiking solution should be disposed of into the containers labeled 'Metals Waste'. When 90 % full, these must be emptied into the large metals waste drums in the hazardous waste storage room on the loading dock within 3 days (do not fill waste containers over 90 % full).

8.5. Gloves, protective eyewear, and a lab coat should be worn when handling any reagents (acids, H_2O_2, etc.). Reagents should be added to samples in a fume hood with the sash lowered to the designated levels to reduce exposure to fumes and protect in case of splashing.

8.6. Used filters and dirty glassware: Gloves, protective eyewear, and a lab coat should be worn when handling any filters or labware that has come into contact with samples and/or standards.

8.7. Gloves, protective eyewear, and a lab coat should be worn when handling the post-analysis samples. The digestates still contain high concentrations of acid. All non-hazardous samples can be disposed of down the sink if the acid concentration is diluted to 2 %. Store any wastes that cannot be disposed of down the sink in a properly labeled hazardous waste container.

9. REFERENCES

9.1. EPA Method 3052, Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices

9.2. EPA Method 6010C, Inductively Coupled Plasma-Atomic Emission Spectrometry

9.3. EPA Method 6020A, Inductively Coupled Plasma-Mass Spectrometry

9.4. Milestone Ethos UP Operator Manual (MA182)

9.5. Milestone SK-15 Operator Manual (MA176)

9.6. DEP SOP CM-011, Gravimetric Analysis: Analytical Weight and Balance Calibration

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

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

9.9. DEP SOP MT-064, Homogenization and Pulverization of Solid Samples

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

9.11. Laboratory Health and Safety Plan, located on the DEAR internet homepage.

9.12. DEP SOP MT-074, Analysis of Metals Using the Thermo ICAP Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

Appendix A. Hydrofluoric Acid Handling Guidelines

INTRODUCTION

Hydrofluoric Acid (HF) is highly corrosive and toxic. Even relatively small exposures of HF can be fatal. Proper treatment immediately following exposure is critical and can greatly affect the chances of a victim's survival.

CHEMICAL PROPERTIES

HF is a colorless liquid with an acrid odor. It is stable at room temperature, but should not be stored in metal or glass containers. Use and store HF in polyethylene, polypropylene, or Teflon containers. HF is corrosive and light sensitive.

The HF concentration used at DEP laboratory ranges from 48 – 52 %.

TOXICOLOGICAL PROPERTIES

HF is an extremely hazardous liquid and vapor. It may be fatal if inhaled or ingested. HF is readily absorbed through the skin. Skin contact may be fatal. Exposure to hydrofluoric acid can produce harmful health effects that may not be immediately apparent.

The unique toxicological properties of HF are due to the action of the fluoride ion. Fluoride ion causes soft tissue necrosis (similar to alkali damage) and bone damage by binding calcium. Fluoride ions are both acutely and chronically toxic. Acute effects of HF exposure include extreme respiratory irritation, immediate and severe eye damage, and pulmonary edema.

Skin contact with HF is probably the most common route of exposure for laboratory personnel (often under fingernails, on hands, faces, and legs); however, HF can cause damage through eye contact, inhalation, or ingestion as well. Exposures to concentrated (> 50 %) HF solutions will cause immediate, severe, penetrating burns. Exposure to less concentrated solutions may have equally serious effects, but the appearance of symptoms may be delayed for up to 8 hours for concentrations of 20 - 50 % and up to 24 hours for concentrations less than 20 % HF.

Concentrations of HF > 50 % can be fatal even if only 2 % (~ an 8-inch square) of the body is exposed. Large or multiple burns totaling over 25 square inches of body surface area may also cause hypocalcemia (depletion of calcium in the body) and other toxic effects which may be fatal. Working with HF is extremely dangerous because of the mist produced, which presents a severe inhalation hazard. **If you are exposed to hydrofluoric acid, seek medical attention immediately, even if you do not feel pain right away.**

ACCIDENTAL HF EXPOSURE

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The OSHA permissible exposure limit for HF is 3 PPM, but exposure concentrations should be kept as low as possible. Local ventilation should always be used when working with HF. Work in a laboratory hood whenever possible and always work in a hood when handling concentrated HF, anhydrous HF, or when heating HF solutions.

Quick response to HF exposures will help to minimize the damage. All exposures should be treated immediately even though burns may not be felt for hours. Affected personnel must receive medical attention for all eye and inhalation exposures, and all but the most minor skin burns. Maintain a copy of these procedures and MSDS to take to the emergency room or doctor's office.

Skin Contact – Immediately wash all affected areas with water. Be sure to remove any clothing or jewelry that could trap HF (remove goggles last). Flush skin for fifteen minutes or until medical attention is available. Flushing can be reduced to five minutes if calcium gluconate gel (2.5 %) is immediately available. Apply calcium gluconate gel to the affected area (use rubber gloves) every fifteen minutes and massage continuously. Seek medical attention.

Eye Contact – Immediately flush eyes for at least fifteen minutes with water while holding eyelids open. Get medical attention. Flushing can be limited to five minutes if medical personnel are immediately available to administer sterile calcium gluconate (1 %) solution (via continuous drip into eyes).

Inhalation – Move to fresh air as soon as possible. Get medical attention. Medical personnel can administer pure oxygen and calcium gluconate (via nebulizer) to patient.

Laboratory personnel should only attempt to clean up small HF spills that do not involve personnel contamination and that are contained and under control. Be sure that good ventilation is available and that personal protective equipment is worn before attempting to clean up a HF spill.

Always wear gloves, a lab coat, a rubber apron, rubber arm sleeves, and chemical safety face shield when working with any HF solution. Not all gloves provide adequate protection against HF; high quality gloves made from butyl, neoprene, rubber or nitrile are recommended. Two pairs, "double gloving", are recommended.

Always check gloves for holes or leaks prior to use.

PERSONAL PROTECTION EQUIPMENT (PPE)

The following PPE is required for HF use.

- Lab coat
- Rubber apron
- Plastic arm coverings, "sleeves"
- Gloves (non-latex)
    - Butyl, neoprene, rubber or heavy nitrile. Gloves should have a thickness of at least 18 mil
- Face shield in conjunction with a fume hood sash

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- Closed toed shoes
- Long pants and a long sleeve shirt with a reasonably high neck (no low cut)

TRAINING

Anyone using HF must meet DEP training requirements and have supervisor's approval showing they know the hazards of working with HF.

- Read all MSDS, SOPs and adjacent document dealing with the use of HF.
- HF should only be used in the designated HF fume hood.
- First Aid - Know the location of the HF first aid kit that includes 2.5 % calcium gluconate gel. Check periodically for expiration dates.
- Spill - An HF spill kit with calcium compounds such as calcium carbonate, calcium sulfate, or calcium hydroxide. **Sodium bicarbonate should never be used** since it does not bind the fluoride ion and can generate toxic aerosols. Use fluoride test paper to evaluate if a spill contains HF.

REFERENCE DOCUMENTS

See network location \\FLDEP1\DEAR\Labs\Lab5\Chemistry\InorganicPrep\METALS\Total Digestion Microwave\Hydrofluoric Acid for the following documents:

Univ of Colorado – HF use.pdf

Honeywell HF Neutralization procedures.pdf

Cornell HF Use.pdf

Honeywell HF MSDS.pdf

Appendix B. Appendix of Significant Changes

11/26/2008	Section 6 added additional sample prep
	Section 7: Added solid matrix information for LCS.
11/24/2009	Removed the requirement to store solid samples for metals analysis at 4° C. Section 5
	Added information for using an SRM as the LCS for the preparation batch.
11/05/2010	Section 4.7. Calcium gluconate specifically noted as a crucial part of the HF spill kit
	Added Appendix A. Hydrofluoric Acid Handling Guidelines
	Added Table of contents as the SOP is now longer than 10 pages.
10/29/2012	Section 6.51 was added to prevent silver precipitation and improve silver recovery.

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09/10/2013	Section 7. Laboratory fortified blank was removed as QC from the digestion because it was not being reported with the data.
09/13/2013	Sections 2. and 6.3. Procedure changed for handling of samples below 20 % solid.
10/13/2014	Sections 2 and 6 edited due to changes in the handling of samples below 20 % solid.
10/13/2017	SOP updated for the Milestone Ethos UP microwave. Section 6 edited for new dry weight policy. Section 7 edited for change of SRM.

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