DIGESTION OF WATER SAMPLES FOR TOTAL MERCURY ANALYSIS

1. SCOPE AND APPLICATION

This SOP describes the digestion of aqueous samples for the determination of total mercury. The procedure is based on EPA Method 245.1 and SW-847 Method 7470A and is applicable to the digestion of surface, saline, effluent, waste waters, and TCLP/SPLP extracts. This digestion is applicable to samples logged in for the following tests: W-HG-H, W-HG-H-F, W-HG-H-R, SPLP-HG-H, and TCLP-HG-H (See Appendix A).

2. SUMMARY OF THE METHOD

2.1. Organic and inorganic forms of mercury may be present in aqueous samples. In order to perform the total mercury analysis, all mercury compounds must be oxidized to inorganic mercuric ions (Hg^{+2}).

2.2. To accomplish this, the samples are oxidized in an acidic media with nitric and sulfuric acids. Then the samples are further oxidized using potassium permanganate and potassium persulfate. Total mercury is then analyzed as Hg^{+2}.

3. APPARATUS AND EQUIPMENT

3.1. Isotemp water bath

3.2. 75 mL Pyrex culture tubes and caps

3.3. Class A, 50 mL graduated cylinder

3.4. Innova 2100 platform shaker

3.5. Weigh boats

3.6. Pipettes:

3.6.1. 100 µL Eppendorf

3.6.2. 1000 µL Eppendorf

3.6.3. Bottle-top dispenser

4. REAGENTS AND CHEMICALS

Note: Reagents used for preparation must be logged in to the LIMS Standard Prep Tracker to generate a serial number. The label printed from the LIMS Standard Prep Tracker must be placed on the bottle of reagent in the laboratory. The reagents used for preparation are documented on the LIMS Prep Worksheet Manager worksheet. See DEP SOP MT-069 for the labeling, documentation, and expiration dates required for reagents used in the laboratory.

4.1. De-ionized (DI) water - Available from the plastic spigots in the laboratory.

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4.2. Trace Metal Grade Nitric Acid (HNO_3) - The purchased acid is stored in the fume hood cabinet and the expiration date is provided by the manufacturer.

4.3. Trace Metal Grade Sulfuric Acid (H_2SO_4) - The purchased acid is stored in the fume hood cabinet and the expiration date is provided by the manufacturer.

4.4. 50 % Trace Metal Grade Nitric Acid (HNO_3) - Prepare this solution in a 500 mL squeeze bottle by pouring 250 mL of DI water into the squeeze bottle, followed by pouring 250 mL of concentrated nitric acid into the squeeze bottle. Mix and allow to cool before use. This solution is used to clean the 50 mL graduated cylinder which is used to measure aliquots of sample.

4.5. 5 % Potassium Permanganate Solution ($KMnO_4$) - Add 25 g of $KMnO_4$ crystals to a 500 mL Teflon bottle half full of DI water. Dilute to volume with DI water and mix well. The easiest way to mix is to use the shaker located in B411. Place the bottle into a holder and set the rpm to approximately 250 and turn on. This takes about an hour to do, so it is best to make the $KMnO_4$ solution in the morning before starting a digestion. The expiration date for this prepared reagent is one day after preparation.

4.6. 5 % Potassium Persulfate Solution ($K_2S_2O_8$) - Add 12.5 g of $K_2S_2O_8$ crystals to 250 mL Teflon bottle half full of DI water and dilute to volume with DI water. Mix well. The easiest way to mix is to use the shaker located in B411. Place the bottle into a holder and set the rpm to approximately 250 and turn on. This takes about an hour to do, so it is best to make the $K_2S_2O_8$ solution in the morning before starting a digestion. The expiration date for this prepared reagent is one day after preparation.

4.7. 9 % aqua regia cleaning solution - See DEP SOP HG-021 for preparation details

4.8. Standards and Spiking Solutions:

Note: Preparation of all Hg standards must be documented in the Laboratory Information Management System (LIMS) standard prep tracker module. A label must be printed from standard prep tracker and placed on the bottle of standard in the laboratory.

4.8.1. Inorganic Standard Solution, **WTHG-4** (200 µg/L) - This is an intermediate standard used for the preparation of the practical quantitation limit (PQL) standard. See DEP SOP HG-012 for preparation details.

4.8.2. Inorganic Standard Solution, **WTHG-3** (250 µg/L) - This is an intermediate standard used for the preparation of the laboratory fortified blank (LFB) and matrix spikes. See DEP SOP HG-012 for preparation details.

4.8.3 Mercury Standard Solution, **NIST3133-2** (~50 µg/L) - This is an intermediate mercury standard reference material prepared from a stock purchased from the National Institute of Standards and Technology. See DEP SOP HG-012 for preparation details.

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5. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1. Samples are preserved with HNO_3 to a pH below 2.0.

5.2. The holding time from sample collection to sample analysis is 28 days.

5.3. All samples should be considered as hazardous. Wear gloves whenever handling the samples.

5.4. All glassware should be cleaned according to the DEP SOP HG-021 for cleaning sample preparation labware.

6. SAMPLE PREPARATION PROCEDURE

6.1. Fill water bath with DI water up to the fill mark on the bath. Replace water in the water bath weekly. Turn on water bath in sample digestion room and set temperature so that the samples will heat to a temperature of 95 ± 2 °C. Each day, prior to use, check the temperature of the water bath with a NIST traceable thermometer and document on each LIMS Prep Worksheet Manager worksheet.

6.2. Water samples are digested in 75 mL Pyrex culture tubes. Make an exact count of the culture tubes required for the digestion set, including all QC samples. The easiest way to do this is by creating the LIMS Prep Worksheet Manager worksheet.

6.3. Prepare sample digestion tubes by placing labels on them and discarding the 9 % aqua regia cleaning solution that has been stored in the glassware. The aqua regia should be discarded in the sink and flushed thoroughly with water. The glassware should then be rinsed 6-8 times with DI water. When rinsing, fill the tube with DI water and pour this DI water over the inside of the cap. After rinsing the tube 6-8 times, replace the cap on the tube, leaving the tube empty.

6.4. Prepare a digestion blank by measuring out 50 mL of DI water into a pre-labeled culture tube. Prepare 1 digestion blank for every batch of 20 samples or less digested. The digestion blank must be carried through the entire sample preparation procedure.

6.5. Prepare a 0.50 µg/L PQL standard by adding 125 µL of 200 µg/L **WTHG-4** into a pre labeled culture tube filled with 50 mL of DI water. Prepare 1 PQL per digestion.

6.6. Prepare the W-NIST3133 NIST reference standard at 3.0 µg/L by adding 3 mL of 50 µg/L **NIST3133-2** working standard to a pre labeled culture tube. Dilute with 47 mL of DI water to a final volume of 50 mL. Prepare one W-NIST3133 per digestion.

6.7. Invert each sample bottle several times to homogenize any sample particulates. Carefully measure out 50 mL of thoroughly mixed water sample or SPLP extract into the respectively labeled culture tubes using a clean, acid rinsed class A 50 mL graduated cylinder (for TCLP extracts, see Appendix A). Between transferring

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each sample to their respective tubes, rinse the graduated cylinder once with 50 % HNO_3 and 4-5 times with DI water. When pouring the sample that will be spiked and the duplicate matrix spikes, mix the sample well before pouring each aliquot.

6.8. Choose (if possible) a sample that is NOT a trip blank, field blank, or equipment blank with which to prepare the sample, matrix spike, and a matrix spike duplicate. Measure 50 mL of the chosen sample with a class A graduated cylinder and pour into a labeled 75 mL culture tube. Prepare the two spikes at 1.0 µg/L by adding 200 µL of **WTHG-3** (250 µg/L) inorganic mercury spiking solution to 50 mL of the chosen sample. Prepare duplicate matrix spikes for every 20 samples digested. **If more than 10 samples are present in the batch, another matrix spike on a separate sample (different from the duplicate matrix spike) must also be prepared.**

6.9. Prepare an LFB by spiking with the same spike solution used for the matrix spikes (200 µL of **WTHG-3**) into 50 mL of DI water in a 75 ml culture tube. Prepare 1 LFB for every batch of 20 samples or less digested

6.10. Add 1.25 mL of HNO_3 to all culture tubes. Add 2.5 mL of H_2SO_4 to all culture tubes. Add 7.5 mL of 5 % $KMnO_4$ solution to all tubes.

Note: If permanganate purple color does not persist for at least 15 minutes, add sufficient excess 5 % $KMnO_4$ to the tube in 1 mL increments until color persists for at least 15 minutes. RECORD HOW MUCH EXTRA PERMANGANATE SOLUTION HAS BEEN ADDED on the LIMS Prep Worksheet Manager worksheet.

6.11. Add 4.0 mL of 5 % $K_2S_2O_8$ solution to every sample tube.

6.12. Tighten tube caps and gently invert tubes several times to mix. Loosen all caps and place sample tubes in a water bath set at 95 °C for 2 hours.

6.13. Cool samples and tighten caps.

6.14. When the digestion is completed, complete and print the LIMS Prep Worksheet Manager worksheet. The preparation worksheet should be kept with the sample batch during analysis and included in the laboratory report.

7. SAMPLE ANALYSIS PROCEDURE

Refer to DEP SOP HG-009 for analysis details.

8. QUALITY CONTROL

8.1. Digestion Blank - 1 per batch of 20 samples or less.

8.2. NIST reference standard W-NIST3133 (3.0 µg/L) - One per digestion.

8.3. PQL Standard - One per digestion.

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8.4. Sample Matrix Spikes - One set of duplicate matrix spikes per 20 samples. If there are more than 10 samples in the batch, another matrix spike on a sample different from the duplicate matrix spike must be prepared.

8.5. LFB - One per batch of twenty samples or less.

9. SAFETY/HAZARDOUS WASTE MANAGEMENT

9.1. Review the Laboratory Health and Safety Plan located on the Division of Environmental Assessment and Restoration internet page.

9.2. Use caution with strong irritants such as acids and bases. Avoid breathing the fumes of these irritants by using them in a fume hood and keeping the face away from open containers of these chemicals. Avoid contact of these irritants with skin and clothing by appropriate use of personal protective equipment (PPE) such as gloves, lab coat, face-mask, hood shield, etc. Safety glasses and lab coats must be worn at all times in the laboratory.

9.3. The water bath should be placed in the hood.

9.4. All samples should be vented in a hood.

9.5. Watch for possible violent reactions when adding reagents to the digestion vessel. The addition of reagents should be done in a hood.

9.6. All high level mercury standards (> 200 µg/L) should be handled with care and treated as hazardous. Unused or expired standards should be disposed as hazardous waste.

9.7. Store any wastes that cannot be disposed of down the sink in 6 L HDPE containers properly labeled with hazardous waste labels in the fume hood. The sewer discharge limit for mercury is 38 µg/L. Make sure the hazardous waste bottle stays capped after use and place the bottle in the cabinet below the hood when it is no more than 90 % full. When two bottles reach 90 % full, appropriate personnel will dump them into the 'Metals Waste' hazardous waste drum located in C217, the Acid Waste Room. The key for C217 must be checked out from the KeyWatcher in room A311.

9.8. All non-hazardous wastewater can be dumped into the sink if the acid concentration is less than 2 % or diluted by 50 or greater.

10. REFERENCES

10.1. EPA Method 245.1

10.2. DEP SOP HG-021, Procedure for High Level Mercury Glassware Cleaning.

10.3. DEP SOP HG-012, Mercury Group Standards Preparation Procedures.

10.4. DEP SOP HG-009, Analysis of Total Mercury in Water by Cold Vapor Atomic Absorption Spectroscopy.

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

10.6. Health and Safety Plan, located on the Division of Environmental Assessment and Restoration internet page.

10.7. Laboratory Quality Manual, located on the Division of Environmental Assessment and Restoration internet page.

APPENDIX A - TCLP SAMPLES

TCLP extracts are digested similarly to waters with a few exceptions. TCLP extracts are diluted 1:10, using 5 mL of TCLP extract and 45 mL of DI water. TCLP extracts should be batched separately with their own set of QC samples including an extraction fluid blank. The spikes are prepared using the same amount of Hg spike solution as a normal water spike, however, one PQL standard, DI water blank, and W-NIST3133 can be shared by all batches. Be sure to note the dilutions on the LIMS Prep Worksheet Manager worksheet.

Appendix of Significant Changes

06/18/2008 Minor revisions to the text were made for format and clarity. An adjustment was made to the sample according to the newly approved revision of the method.

06/16/2009 Minor edits to format of SOP. Edited section 6.9 and 8.5 to reflect that one LFB is required by EPA method 245.1.

08/04/2014 EPA Method 245.1 was re-validated. 1.25 mL of conc. HNO_3 is added to 50 mL of sample instead of 1.0 mL. 2.5 mL of conc. H_2SO_4 is added to 50 mL of sample instead of 1.0 mL of 1.5 N H_2SO_4. 7.5 mL of 5 % $KMnO_4$ is added to 50 mL of sample instead of 5.0 mL of 6 % $KMnO_4$. 4 mL of 5 % $K_2S_2O_8$ is added to 50 mL of sample instead of 4.0 mL of 6 % $K_2S_2O_8$.

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