MERCURY GROUP STANDARDS PREPARATION PROCEDURES

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the preparation of all intermediate standards, including certified standard reference materials (SRMs), used for the analysis of total mercury in waters, tissues, sediments, and wastes. This SOP is applicable to the preparation of standards for the following tests: W-HG-H, W-HG-H-F, T-HG-H, T-HG-AF, S-HG-H, WASTE-HG-H, TCLP-HG-H, W-HG-AF, W-HG-AF-F, W-HG-H-R, SPLP-HG-H, and SPLP-HG-AF.

2. APPARATUS AND EQUIPMENT

2.1. Polystyrene weigh boats

2.2. Scout Pro balance

2.3. Mettler Toledo New Classic MF top-loading Balance, model MS1602S/03

2.4. Class A Glass Volumetric Flasks: 1.0 L, 500 mL, 250 mL, 200 mL, 100 mL, 50 mL.

2.5. Pipettes:

2.5.1. 50 µL, 100 µL, 250 µL, 1000 µL Eppendorf pipettes

2.5.2. Eppendorf repeater pipette

2.5.3. 1-5 mL and 5-10 mL Finn pipettes

3. REAGENTS AND CHEMICALS

Note: Reagents used for preparation of standards 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. See DEP SOP **MT-069** for instruction on reagent preparation documentation and expiration dates. Templates for all reagent log sheets can be found in the folder 'Solution logs for high and low level Hg' on the Bureau's computer network at \\FLDEP1\DEAR\Labs\Lab5\Chemistry\InorganicPrep\Mercury\Prep\Solution Logs for High and Low Level Total Hg. The following reagent log sheets are created in Microsoft Excel and then printed and included with the laboratory report for each analysis/preparation:

- High Level Mercury Analysis Reagent Log - Used to record reagent information while preparing analysis standards and reagents.
- Low Level Mercury Analysis Reagent Log - Used to record reagent information while preparing analysis standards and reagents.
- High Level Mercury Standard Preparation Reagent Log - Used to record reagent information for intermediate standards.

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- Low Level Mercury Standard Preparation Reagent Log - Used to record reagent information for intermediate standards.

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

3.2. Trace Metal Grade (TMG) Hydrochloric Acid (HCl) - The purchased acid is stored in the fume hood cabinet and the expiration date is provided by the manufacturer.

3.3. Optima Grade Glacial Acetic Acid - Optima grade glacial acetic acid is used as a preservative for aqueous phase methylmercury standards. The purchased acid is stored in the fume hood cabinet. If the manufacturer of this purchased acid assigns an expiration date, it shall be used. An expiration date is not required if not assigned by the manufacturer.

3.4. Potassium Bromate ($KBrO_3$, 0.05M)/Potassium Bromide (KBr, 0.1M) Solution - Place 8.4 g of $KBrO_3$ in a glass scintillation vial and bake it at 175 ^{O}C overnight in a mercury free oven to remove all traces of Hg in the salt. Do the same with 11.9 g of KBr weighed in a clean glass vial. After removing both salts from the oven, allow them to cool, and dissolve both salts in 1 L of deionized (DI) water in an acid cleaned Teflon bottle. Expiration date for this prepared reagent is one year from preparation.

3.5. Optima 2-propanol (Isopropanol) and Methanol - Methanol or isopropanol is used as the solvent for preparing methylmercury standards. The purchased solvents are stored in a fume hood cabinet for solvents only. Do not store with acids. If the manufacturer of this purchased acid assigns an expiration date, it shall be used. An expiration date is not required if not assigned by the manufacturer.

3.6. Optima Grade Acetone - Used as a solvent for preparing methylmercury standards. The purchased solvent is stored in a fume hood cabinet for solvents only. Do not store with acids. If the manufacturer of this purchased acid assigns an expiration date, it shall be used. An expiration date is not required if not assigned by the manufacturer.

4. INORGANIC STANDARDS FOR HIGH-LEVEL TOTAL MERCURY ANALYSIS

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 the standard prep tracker and placed on the bottle of standard in the laboratory.

4.1. Primary Standard (1000 mg/L) - The primary standard consists of a 1000 mg/L NIST traceable standard in 10 % HNO_3 purchased from a vendor such as SPEX Certiprep, EM Science, or Accustandard. Calibration standards, matrix spikes, laboratory fortified blanks (LFBs), and practical quantitation standards (PQLs) are prepared from this source. The expiration date for this purchased standard is assigned by the manufacturer. Save a pdf of the certificate of analysis in the 'Certificates of Analysis for Reagents and Standards' folder located on the

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network at \\FLDEP1\DEAR\Labs\Lab5\Chemistry\InorganicPrep\Certificates of Analysis for Reagents and Standards\Standards and Standard Reference Materials.

4.2. **THG-1** (100 mg/L) - This is an intermediate standard for sediment, waste, and tissue samples prepared by diluting 10 mL of the 1000 mg/L primary standard to 100 mL in a class A glass volumetric flask. Half fill a clean 100 mL class A volumetric flask with DI water. Add 5 mL HNO_3, 3 mL HCl, and 3 mL of the bromide/bromate solution to the flask. Pipette 10 mL of the primary standard into the flask. Fill the flask up to the mark with DI water. Cap, and shake well. The expiration date for this prepared standard is one year from preparation.

4.3. **WTHG-1** (100 mg/L) - This is an intermediate standard for water samples prepared by diluting 10 mL of the 1000 mg/L primary standard to 100 mL in a class A glass volumetric flask. Half fill a clean 100 mL class A volumetric flask with DI water. Add 5 mL of HNO_3. Pipette 10 mL of the primary standard into the flask. Fill the flask to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is 28 days from preparation.

4.4. **THG-2** (500 µg/L) - This is an intermediate standard for sediment, waste, and tissue samples prepared by diluting 5 mL of the **THG-1** intermediate standard to 1 L in a class A glass volumetric flask. Half fill a clean 1 L class A volumetric flask with DI water. Add 50 mL HNO_3, 30 mL HCl, and 30 mL of the bromide/bromate solution. Pipette 5 mL of the **THG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is one year from preparation.

4.5. **WTHG-2** (500 µg/L) - This is an intermediate standard for water samples prepared by diluting 5 mL of the **WTHG-1** intermediate standard to 1 L in a class A glass volumetric flask. Half fill a clean 1 L class A volumetric flask with DI water. Add 50 mL HNO_3. Pipette 5 mL of the **WTHG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is 28 days from preparation.

4.6. **THG-3** (250 µg/L) - This is an intermediate standard for sediment, waste, and tissue samples prepared by diluting 500 µL of the **THG-1** intermediate standard to 200 mL in a class A glass volumetric flask. Half fill a clean 200 mL class A volumetric flask with DI water. Add 10 mL HNO_3, 6 mL HCl, and 6 mL of the bromide/bromate solution. Pipette 500 µL of the **THG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is one year from preparation.

4.7. **WTHG-3** (250 µg/L) - This is an intermediate standard for water samples prepared by diluting 500 µL of the **WTHG-1** intermediate standard to 200 mL in a class A glass volumetric flask. Half fill a clean 200 mL class A volumetric flask with DI water. Add 10 mL HNO_3. Pipette 500 µL of the **WTHG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is 28 days from preparation.

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4.8. **THG-4** (200 µg/L) - This is an intermediate standard for sediment, waste, and tissue samples prepared by diluting 1 mL of the **THG-1** intermediate standard to 500 mL in a class A glass volumetric flask. Half fill a clean 500 mL class A volumetric flask with DI water. Add 25 mL HNO_3, 15 mL HCl, and 15 mL of the bromide/bromate solution. Pipette 1 mL of the **THG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is one year from preparation.

4.9. **WTHG-4** (200 µg/L) - This is an intermediate standard for water samples prepared by diluting 1 mL of the **WTHG-1** intermediate standard to 500 mL in a class A glass volumetric flask. Half fill a clean 500 mL class A volumetric flask with DI water. Add 25 mL HNO_3. Pipette 1 mL of the **WTHG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is 28 days from preparation.

4.10. **NIST3133** SRM (~10,000 mg/L) - The SRM consists of a 9.954 ± 0.053 mg/g (9954 mg/L) NIST SRM in water, preserved in 10 % HNO_3 and purchased from NIST. The expiration date is assigned by the manufacturer.

4.11. **NIST3133-1** SRM (~10 mg/L) - This is an intermediate standard prepared by diluting 1 mL of the **NIST3133** primary SRM to 1 L in a class A glass volumetric flask. Half fill a clean 1 L class A volumetric flask with DI water. Add 50 ml HNO_3. Pipette 1 mL of the **NIST3133** primary SRM into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is 28 days from preparation.

4.12. **NIST3133-2** SRM (~50 µg/L) - This intermediate standard is prepared by diluting 5 mL of the **NIST3133-1** intermediate standard to 1 L in a class A glass volumetric flask. Half fill a clean 1 L class A volumetric flask with DI water. Add 2 ml HNO_3. Pipette 5 mL of the **NIST3133-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is 28 days from preparation.

5. ORGANIC STANDARDS FOR HIGH-LEVEL TOTAL MERCURY ANALYSIS

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

5.1. Primary Standard - The primary standard consists of neat methylmercury chloride powder obtained from Alfa Johnson Matthey or Strem Chemicals. All methylmercury standards have concentrations reported as 'methylmercury as Hg'. If the manufacturer of this purchased material assigns an expiration date, it shall be used. An expiration date is not required if not assigned by the manufacturer.

5.2. **MHG-1** (1000 mg/L) - This is an intermediate standard prepared by dissolving 0.1255 g of the neat methylmercury chloride in 100 mL of optima grade isopropanol. Place 5 mL of optima grade acetone in a clean 100 mL class A

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volumetric flask. Add the methylmercury chloride powder to the flask and swirl gently. The powder will rapidly dissolve in the acetone. Half fill the flask with optima grade isopropanol and swirl the solution to ensure good mixing. Wait for approximately 2 minutes. (Due to the thermodynamics of mixing, when acetone and isopropanol are mixed the final volume of the mixture is greater than the sum of the individual volumes of the two components - this effect takes a little over a minute to manifest itself), and then fill the flask to the mark with isopropanol. Cap the flask firmly, and shake well to ensure complete mixing. Store this solution in an amber bottle in a freezer at -15 to -19 °C. The expiration date for this prepared standard is two years from preparation.

5.3. **MHG-2** (10 mg/L) - This is an intermediate standard prepared by diluting 2 mL of the **MHG-1** intermediate standard to 200 mL in a class A glass volumetric flask. Half fill a clean 200 mL class A volumetric flask with DI water and add 20 mL HNO_3. Pipette 2 mL of the **MHG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. Store this standard in a refrigerator. The expiration date for this prepared standard is one year from preparation.

5.4. **MHG-3** (1.252 mg/L) - This is an intermediate standard prepared by diluting 626 µL of the **MHG-1** intermediate standard to 500 mL in a class A glass volumetric flask. Half fill a clean 500 mL class A volumetric flask with DI water and add 10 mL HNO_3. Pipette 626 µL of the **MHG-1** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. Store this standard in a refrigerator. The expiration date for this prepared standard is one year from preparation.

6. INORGANIC STANDARDS FOR TRACE-LEVEL TOTAL MERCURY ANALYSIS

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

6.1. **THG-5** (10 mg/L) - This is an intermediate standard prepared by diluting 1 mL of the primary standard (see section 4.1) to 100 mL in a class A glass volumetric flask. Half fill a clean 100 mL class A volumetric flask with DI water. Add 5 mL HNO_3, 4 mL HCl, and 3 mL of the bromide/bromate solution. Pipette 1 mL of the primary standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is one year from preparation.

6.2. **THG-6** (200 µg/L) - This is an intermediate standard prepared by diluting 2 mL of the **THG-5** intermediate standard to 100 mL in a class A glass volumetric flask. Half fill a clean 100 mL class A volumetric flask with DI water. Add 5 mL HNO_3, 4 mL HCl, and 3 mL of the bromide/bromate solution. Pipette 2 mL of the **THG-5** intermediate standard into the flask. Fill the flask up to the mark with

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DI water. Cap and shake well. The expiration date for this prepared solution is one year from preparation.

6.3. **THG-7** (1.0 µg/L) - This is an intermediate standard prepared by diluting 1.25 mL of the **THG-6** intermediate standard to 250 mL in a class A glass volumetric flask. Half fill a clean 250 mL class A volumetric flask with DI water. Add 12.5 mL HNO_3, 10 mL HCl, and 7.5 mL of the bromide/bromate solution to it. Pipette 1.25 mL of the **THG-6** intermediate standard to the flask. Fill the flask up to the mark with DI water. Cap and shake well. The expiration date for this prepared standard is 60 days from preparation.

6.4. **NIST1641D** SRM (1.557 mg/L) - The SRM consists of a 1.557 ± 0.020 mg/kg NIST SRM in water, preserved in 2 % HNO_3 and purchased from NIST. The expiration date is assigned by the manufacturer.

6.5. **NIST1641D-1** SRM (15.57 µg/L) - Pipette 10 mL of 1.557 ± 0.020 mg/kg NIST1641D SRM into a 1 L class A volumetric flask half filled with DI water. Add 50 mL HNO_3, 40 mL of HCl, and 30 mL of the bromide/bromate solution. Bring the volume up to the mark, and mix well. The expiration date for this prepared standard is one year from preparation.

7. ORGANIC STANDARDS FOR TRACE-LEVEL TOTAL MERCURY ANALYSIS

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

7.1. **MHG-4** (10 mg/L) - This is an intermediate standard in optima grade isopropanol prepared by diluting 1 mL of the **MHG-1** intermediate standard (5.2.) to 100 mL in a class A glass volumetric flask. Half fill a clean 100 mL class A volumetric flask with isopropanol and pipette 1 mL of the **MHG-1** intermediate standard into the flask. Fill the flask up to the mark with isopropanol. Cap and shake well. Store this standard in an amber bottle in a freezer at -10 to - 20 °C. The final concentration of the standard is 10 mg/L. The expiration date for this prepared standard is one year from preparation.

7.2. **MHG-5** (100 µg/L) - This is an intermediate standard in optima grade isopropanol prepared by diluting 1 mL of the **MHG-4** intermediate standard to 100 mL in a class A glass volumetric flask. Half fill a clean 100 mL class A volumetric flask with isopropanol and pipette 1 mL of the **MHG-4** intermediate standard into the flask. Fill the flask up to the mark with isopropanol. Cap and shake well. Store this standard in an amber bottle in a freezer at -10 to - 20 °C. The final concentration of the standard is 100 µg/L. The expiration date for this prepared standard is one year from preparation.

7.3. **MHG-6** (1.0 µg/L) - This is the aqueous intermediate standard prepared by diluting 0.5 mL of the **MHG-5** intermediate standard to 50 mL in a class A glass volumetric flask. Half fill a clean 50 mL class A volumetric flask with DI water, and pipette 1 mL of optima grade glacial acetic acid and 100 µL of HCl into it.

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Next pipette 0.5 mL of the **MHG-5** intermediate standard into the flask. Fill the flask up to the mark with DI water. Cap and shake well. Store this standard in an amber bottle in a refrigerator at 2 to 10 °C. The expiration date for this prepared standard is 60 days from preparation.

8. SAFETY/HAZARDOUS WASTE MANAGEMENT

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

8.2. All standards should be handled as if they contain hazardous levels of analyte. **Always** wear proper protective eye wear and lab coats while in the lab. Gloves should be worn while handling any standard. Excess inorganic Hg standard should be disposed of in the 6 L HDPE Nalgene containers labeled Metals Waste with Hg. When 90 % full, these must be emptied into the "Metals Waste' waste drum in room C217 by appropriate personnel. The key for C217 must be checked out from the KeyWatcher in room A311. Refer to DEP SOP **HG-013** for additional details.

8.3. Organic mercury solutions contain methylmercury chloride, and are especially toxic to humans. Special care should be taken to ensure that these solutions do not come into contact with skin. These standards contain organic solvents (isopropyl alcohol or methanol) which facilitate transport of methylmercury through the skin. Refer to DEP SOP **HG-013** for additional details on the disposal of organic wastes. Once the properly labeled organic solvent + methyl mercury waste container is 90 % full in the laboratory, the container should be placed on the shelves of the organic waste room (C218) located on the laboratory loading dock.

8.4. Aqueous methyl mercury waste with concentrations < 10 µg/L must be first oxidized to less toxic total mercury before disposal in the sink. Aqueous methyl mercury waste with concentrations above 10 µg/L should be stored separately and once the container is 90 % full, place the properly labeled container on a shelf in the inorganic waste room, C217 See DEP SOP **HG-013** for additional details.

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

9. REFERENCES

9.1. DEP SOP **HG-013**, Mercury Waste Disposal

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

9.3. Health and Safety Plan, located on the Division of Environmental Assessment and Restoration web page.

Appendix of Significant Changes

07/15/2008 Minor revisions to the text were made for format and clarity.

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07/15/2009 Updated Apparatus and Equipment section.

07/07/2010 Updated Section 8, Safety/Hazardous Waste Management

08/04/2014 The potassium bromate / potassium bromide solution was removed from the intermediate standards used for the water matrix.

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