PREPARATION OF SAMPLING KITS FOR THE COLLECTION OF TRACE LEVEL MERCURY WATER SAMPLES

1. SCOPE AND APPLICATION

This SOP describes procedures for cleaning and preparing sampling kits for shipment to customers requesting trace-level mercury analysis involving clean sampling methods. Cleaning and packing procedures are carried out in the Laboratory Clean Room, B110. The procedure applies to the cleaning of 500 mL clear glass bottles from I-Chem, 2 L PETG (polyethylene terephthalate) bottles, Teflon tubing, and C-flex tubing. The cleaning procedure applies to samples requiring analysis by EPA method 1631E with test identifiers (Test ID) W-HG-AF and W-HG-AF-F.

2. SUMMARY OF METHOD

Proper cleaning is essential to minimize the possibility of contamination of samples. All surfaces which come in contact with the sample must be rigorously cleaned. For the clear glass sample bottles, used for collection of samples for total mercury analysis, this is accomplished by using highly oxidizing cleaning reagents which oxidize and thereby dissolve any mercury adhering to the walls of containers. The components of the sampling kit (bottles, tubing, filters, etc.) are double bagged in clean polyethylene bags and shipped in pre-cleaned coolers to the sampling team.

3. APPARATUS AND EQUIPMENT

3.1 Peristaltic pump (Cole-Parmer Masterflex series).

3.2 Assorted glass beakers (2 L, 500 mL, etc.).

3.3 Teflon tubing, 3/16” × 1/4” OD.

3.4 Cole-Parmer C-flex tubing, size 24.

3.5 Plastic Ziploc re-sealable bags in the following sizes: 10”×6”, 13”×18”, 4”×6”, 9”×18”.

3.6 Lint-free clean room wipes.

3.7 Shipment coolers.

3.8 500 mL I-Chem clear glass sampling bottles.

3.9 DI water bottles - 2 L PETG bottles for South Florida Water Management District (SFWMD) and Florida Fish and Wildlife Conservation Commission (FWCC).

3.10 Glass class A 100 mL graduated cylinder.

3.11 Glass 500 mL graduated cylinder for preparing aqua regia cleaning solution.

3.12 20 L Polyethylene carboy with a dispenser tab.

3.13 2 L Fluorinated polyethylene bottles.

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3.14 15 L Carboy.

3.15 Tyvek lab coat.

3.16 Clean lab shoe covers.

3.17 Clean lab hair caps.

4. REAGENTS AND CHEMICALS

Note: See DEP SOP MT-069 for standard and reagent documentation, labeling requirements, and expiration dates.

4.1 DI water.

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

4.3 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.

4.4 5 % Aqua Regia Cleaning Solution - To a 20 L polyethylene carboy half filled with DI water, slowly add 750 mL of HCl, and 250 mL of HNO_3. Dilute to the 20 L mark and mix thoroughly.

4.5 Citranox soap solution.

4.6 Potassium Bromate ($KBrO_3$, 0.1 M) / Potassium Bromide (KBr, 0.2 M) Solution – Add 8.4 g of $KBRO_3$ and 11.9 g of KBr to an acid cleaned 1 L Teflon bottle. Dilute and dissolve both salts with DI water to 1 L. The solution is prepared as needed and it is stored at room temperature. Expiration date for this reagent is 1 year. Purge the solution for at least 2 hours with a stream of nitrogen before use.

Note: If contamination is suspected, bake $KBRO_3$ at 250 °C overnight in a glass scintillation vial in a mercury free oven to remove traces of Hg in the salt. Do the same with KBr in a clean glass vial.

5. RECEIVING PROCEDURE

5.1 Insulated plastic coolers are used to ship sampling kits to clients and to return the samples. All low-level mercury sample coolers received by the lab should be processed by following the protocol outlined below.

5.2 Coolers are received from the field by the receiving staff on the second-floor loading dock. The receiving staff will remove the field paperwork from the cooler necessary to log the samples into the laboratory's LIMS and document the temperature of the samples. An email will be sent to the mercury staff notifying that the cooler is available for pick up. Before bringing the cooler into the clean lab, wipe the cooler with a damp lint-free clean room wipe to remove any dirt or dust.

5.3 Unload the samples from the cooler and preserve according to Table 1 and Appendix A for rainwater samples and sort the samples as needed. **Document**

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the date and the lot number of the HCl used for preservation in the Preservation and UV Box Logbook.

TABLE 1

Test	Preservation Time	Preservation Solution	Holding Time
W-HG-AF(-F) (out of bottle digestion)	within 48 hours of collection	2.5 mL HCl per 500 mL of sample	90 days from sample collection
W-HG-AF(-F) (in bottle digestion)	within 28 days of collection	2.5 mL HCl per 500 mL of sample	90 days from sample collection

5.4 Log-in checklist - The log-in checklist is a form attached to the field sheets by the Receiving Room staff. The Receiving Room staff will document the temperature of the samples in the cooler and then the log-in checklist will accompany the cooler to the clean lab for unpacking. Sign and date the log-in checklist and verify that all information is correct. If any information appears incorrect, contact a supervisor. The clean lab staff must verify that the total mercury samples were preserved within 48 hours of collection and **document the date and time** the total mercury samples were preserved on the log-in checklist.

5.5 Used sampling equipment from the field, including trains and 2 L PETG bottles are generally shipped in separate coolers. **Document** the sampling trains that are returned in the Bottle Cleaning/Sampling Train/DI Water logbook. Sampling trains for each customer will have unique, numbered identity tags.

5.6 After removing all samples/equipment from the received coolers, the coolers can be taken to the receiving room on the second floor loading dock. Dump the ice in the sink and place the cooler with other empty coolers that arrived that day. The coolers will be cleaned and dried by the Receiving Room staff.

6. CLEANING SAMPLING EQUIPMENT

Note: Equipment for sampling events designed to determine compliance at the 0.012 µg/L surface water criteria concentration do not require cleaning (6.1). These types of sampling kits do not require sampling trains or bottles of DI water. 500 mL capped, clear glass bottles are removed from the manufacturer's packaging and packed into coolers with double Ziploc bags and bubble wrap. Follow section 6.2 for the bottle labeling protocol. See supervisor to determine the type of sampling event.

6.1 The non-compliance samples are collected and preserved in cleaned 500 mL clear glass bottles purchased from I-Chem. The clear bottles are subject to cleaning procedures in the laboratory in lots of up to 50 bottles (maximum oven capacity). The bottles are filled with 495 mL of 5 % aqua regia and 5 mL of the $KBr/KBrO_3$ solution and are allowed to soak for at least 2 hours. After this time the bottles

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are rinsed four to five times with DI water, taking care to clean both the threads on the neck of the bottle and the interior of the caps. Then, the bottles are dried in the oven for at least 4 hours. While the bottles are in the oven, soak the caps in a 5 % aqua regia solution using a 2 L fluorinated polyethylene bottle for one hour. Rinse the caps four times with DI water and then place on lint-free clean lab wipes to dry until the bottles are removed from the oven. To check the cleaning procedure of the clear glass bottles, approximately 4 % of the cleaned bottles are filled with DI water, logged into LIMS, and analyzed (1 bottle for up to 25 samples, 2 bottles for over 25 samples). The results of the cleaned bottles must be verified to be below the method detection limit. No bottles are shipped out before this verification has been completed. If mercury is detected in any of the cleaned bottles, the entire lot must be re-cleaned.

Note: When cleaning bottles for a sampling kit, some will be used as quality control to ensure the bottles are clean so more bottles than requested by the customer need to be cleaned.

6.2 Glass sample bottle labeling protocol:

The procedure is used to assign unique field identifiers to each bottle and the samples contained in them.

6.2.1 Bottles that are cleaned and dried together are assigned a batch ID. The batch ID naming convention uses the date (year/month/day) followed by a set of letters identifying the client, for example 20160819-FWCC. Print labels and place on each bottle in the batch. **Document** the cleaning procedure in the Bottle Cleaning/Sampling Train/DI water logbook. Enter the date the lot of bottles are cleaned, the number of bottles that were cleaned, the lot # ID, and the lab IDs of the bottles that were logged in to verify the bottles are clean.

6.2.2 From the batch of bottles that are cleaned, select a random 4 % of the clear bottles and take to the receiving staff to be logged in for analysis to verify that they are clean. The batch ID (ex. 20190819-FWCC) of the bottles should be used as the field ID of the cleaned bottles.

6.2.3 Once a batch of bottles is verified to be clean, labeling of the bottles can begin. The bottles must have additional labels placed on them to distinguish between the different bottles. The labeling convention for individual bottles uses the date the bottles are packed, for example 0621-T1:

Clear Glass Bottles (THg)
0621-T1
0621-T2
0621-T3
0621-T4

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The T1 suffix refers to a total mercury sample (T1). The numbers following the T are assigned in ascending order to each bottle.

6.2.4 Attach one of the duplicate individual bottle labels directly to the glass bottle, and the other to the **inner** Ziploc bag. Each bottle is double bagged in 6" x 9" polyethylene Ziploc bags. Always include at least one spare clear bottle for every 15 bottles being shipped. Also include 2 – 3 spare caps with each shipment.

6.3 PETG bottles for the SFWMD and FWCC:

6.3.1 The PETG 2 L bottles are single use containers. If these bottles are returned from a sampling event, they can be discarded. They must not be used again to transport DI water to the field.

6.3.2 To clean the unused 2 L PETG bottles, rinse the interior of the bottles and caps three times with DI water only. Then fill the bottles to just below the brim with DI water, dry the exterior of the bottles and double bag the bottles immediately in new 9" x 18" Ziploc bags.

6.4 All sampling trains are cleaned following the steps outlined below:

6.4.1 Begin by washing the exterior of the sampling train thoroughly with DI water to remove all traces of dirt.

6.4.2 Next, wash the trains by circulating 2 L of a 1 % solution of Citranox in tap water through the train for 15 minutes. Use this solution to clean a maximum of 6 trains.

6.4.3 Next, wash the trains by pumping ~ 10 L of DI water through the train with **no** recirculation.

6.4.4 Now rinse the sampling trains by circulating 2 L of 5 % aqua regia through the train for 15 minutes. Use this solution to clean a maximum of 6 trains.

6.4.5 Finally rinse the trains by pumping 10 L of DI water through the train with **no** recirculation.

6.4.6 Collect the last 500 mL of DI water pumped through the train in step 6.4.5 in a 500 mL clean clear glass bottle. Log this sample into LIMS along with the samples from step 6.1. Use the date, customer initials, and sampling train ID as the field ID (ex. 20160819-SFWMD-149). This sample will be analyzed and verified to be below the method detection limit prior to the sampling trains being shipped to the customer.

6.4.7 Immediately after the final DI water rinse, allow the sampling train tubing to drain completely. Carefully inspect the exterior of the tubing to see that no rust stains (from the peristaltic pump) are present. If any stains are

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observed, wipe off the stains with a damp clean room wipe. Use a small amount of acetone to remove the stains if necessary. Pack the train in a **new** 13" × 18" clean Ziploc bag for shipment. Cleaned trains should be used within one month of cleaning. If a (cleaned) train has not been used in more than a month, clean it again prior to shipment.

7. PACKING AND SHIPPING PROCEDURE

7.1 If no clean coolers are available when preparing a sampling kit to send to the field, use the following procedure to clean the cooler. Wash the exterior of the cooler with tap water (and soap) if necessary. The exterior of the cooler will probably have soil, packing tape etc. adhering to its sides. This step is critical in minimizing contamination of the clean room.

7.2 Wash the interior of the cooler with tap water. Allow the cooler to drain as much as possible and dry the interior with clean paper towels. Store the cleaned cooler in the clean lab or in a designated area in the adjacent gown room.

7.3 A temperature monitoring bottle must be placed in the cooler. The temperature monitoring bottle must be the same type of bottle as the ones used for sample collection. The temperature monitoring bottle must also be packed the same as a sample bottle – double Ziploc bag and a bubble bag. Place a label on the outside of the bubble bag of the temperature monitoring bottle to distinguish it from the samples.

7.4 Check the number of bottles cleaned for shipment against the number of bottles listed in the shipment schedule and the cover letter included with the shipment.

7.5 Using the Bottle Cleaning/Sampling Train/DI Water logbook, **record** the sampling trains as well as any 2 L bottles used for DI water that are being sent to each customer.

7.6 Make sure that there is a copy of the cover letter in every cooler being shipped. Close the coolers and seal them with tape for shipment. Check the address on the Fed Ex shipping form against the address on the cover letter.

7.7 Take the coolers to the loading dock and ship them by Fed Ex ground. In the event of an emergency shipment, ship the coolers by next day air only when necessary. Emergency coolers are normally requested as part of monthly shipping schedules biannually, and should normally be shipped via ground.

8. SAFETY AND HAZARDOUS WASTE MANAGEMENT

8.1 Review the Laboratory Health and Safety Manual located on the Division of Environmental Assessment and Restoration's intranet site.

8.2 The mercury content of the waste aqua regia generated from the cleaning of the sampling trains and polyethylene bottles is low, and far below the city's sewer discharge limit of 38 µg/L for mercury. This acidic waste may be disposed

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directly in the sink as long as the acid concentration is less than 2 % or diluted by 50 or greater.

8.3 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.

8.4 Store any wastes that cannot be disposed of down the sink in 6 L HDPE Nalgene containers properly labeled with hazardous waste labels in the fume hood. Make sure the 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, 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. REFERENCES

9.1 Laboratory Health and Safety Plan.

9.2 EPA Method 1631E, August 2002

9.3 DEP SOP HG-001, Trace-Level Total Mercury in Water by Purge and Trap (Dual Gold Traps) and Cold Vapor Atomic Fluorescence Detection (CVAF)

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

9.5 City of Tallahassee Industrial Pretreatment Sewer Use Manual located on the City of Tallahassee website.

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Appendix A: Rainwater HCl Preservation and BrCl Volumes

Rainwater HCl Preservation and BrCl Volumes

Volume of Sample (mL) * 0.005 = amount of HCl to add (mL)

Sample	HCl	KBr·KBrO3
1000 mL	5 mL	20 mL
900 mL	4.5 mL	18 mL
800 mL	4 mL	16 mL
700 mL	3.5 mL	14 mL
600 mL	3 mL	12 mL
500 mL	2.5 mL	10 mL
450 mL	2.25 mL	9 mL
400 mL	2 mL	8 mL
350 mL	1.75 mL	7 mL
300 mL	1.5 mL	6 mL
250 mL	1.25 mL	5 mL
200 mL	1 mL	4 mL
150 mL	0.75 mL	3 mL
100 mL	0.5 mL	2 mL
75 mL	0.375 mL	1.5 mL
50 mL	0.25 mL	1 mL
40 mL	0.2 mL	0.8 mL
30 mL	0.15 mL	0.6 mL
25 mL	0.125 mL	0.5 mL
20 mL	0.1 mL	0.4 mL
15 mL	75 uL	300 uL
10 mL	50 uL	200 uL
5 mL	25 uL	100 uL
4 mL	20 uL	80 uL
3 mL	15 uL	60 uL
2 mL	10 uL	40 uL

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Appendix of Significant Changes

06/10/2008	Minor revisions to the text were made for format and clarity.
06/09/2009	Updated sample preservation in section 5.1.1
	Clarified the glass sample bottle cleaning and labeling procedure in section 5.2
	Clarified 5.3.3 (the time the acid is left in the DI water bottle for cleaning)
04/22/2010	Updated the type of DI water bottles currently used. Updated the name of the logbooks currently used. Removed section 5.5.
05/06/2014	The procedure for cleaning amber glass bottles used for the collection of samples for methylmercury analysis was added (section 6.1)
04/29/2015	The temperature monitoring bottle requirement was added.
05/03/2016	References to methylmercury analysis were removed from the SOP.

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