LOW-LEVEL MERCURY 5.6.4.B

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Collecting and processing water samples for analysis of mercury at a low (subnanogram per liter) level requires use of ultratrace-level techniques for equipment cleaning, sample collection, and sample processing. **Established techniques and associated quality-assurance (QA) procedures for the collection and processing of water samples for trace-element analysis at the part-per-billion level (NFM 3–5) are not adequate for low-level mercury samples.** Modifications to the part-per-billion procedures are necessary to minimize contamination of samples at a typical ambient mercury concentration, which commonly is at the subnanogram-per-liter level.

Few laboratories provide low-level mercury analyses for filtered, unfiltered, and particulate total mercury and methylmercury samples. USGS samples are analyzed at the USGS Wisconsin District Mercury Laboratory (WDML)[1], which developed the sample-collection, processing, and handling procedures described in this section. The procedures described herein ensure that the requirements and recommendations of the WDML are fulfilled. Note that the general guidelines and precautions specified in this section are applicable to all mercury sampling at nanogram-per-liter or lower levels, regardless of the laboratory to be used.

Low-level mercury samples are susceptible to contamination from many sources, including improperly cleaned equipment; improper sample-collection techniques that allow dust, dirt, or metallic surfaces to contact samples; contaminated preservatives; atmospheric inputs from dust, dirt and rain; and the breath of field personnel having dental amalgam fillings, if the breath contacts the sample. To prevent equipment contamination, the protocol for cleaning low-level mercury equipment is exacting (see “Equipment, Supplies, and Equipment-Cleaning Procedures” below) and utilizes equipment not normally found in office laboratories. Therefore, the WDML provides the precleaned sampling and processing equipment and associated supplies needed for low-level mercury sampling. **USGS field personnel are advised to contact the WDML when planning their low-level mercury sampling and when ordering supplies.**

[1]The WDML’s Web address is http://infotrek.er.usgs.gov/mercury/ (accessed June 3, 2004). USGS personnel can e-mail the WDML at mercury@usgs.gov

It is strongly recommended that USGS project personnel maintain close communication with the WDML throughout the planning, sampling, and analysis phases of a low-level mercury-sampling project.

To prevent contamination of the sample being collected for low-level mercury analysis:

- Use appropriate equipment and reagents.
  - With few exceptions (discussed below), all sampling and sample-processing equipment must be composed of relatively inert materials, such as fluoropolymer or fluorocarbon polymer[2] (hereafter abbreviated as FP, unless the trade name is used). FP materials are used to minimize mercury adsorption to equipment or container walls and to eliminate mercury exchange into or out of the equipment or containers (Horvat and others, 1993).
  - Trace-pure 6 *N* hydrochloric acid is required for preserving unfiltered and filtered total mercury and methylmercury samples.
  - Project personnel are advised to obtain the precleaned and quality-assured containers, preservatives, and other supplies from the WDML.
- Use appropriate equipment-cleaning procedures. Contaminated equipment, including sampling containers, is the principle source of bias associated with low-level mercury analyses.

[2]**Fluorocarbon polymers and fluoropolymers (FP):** Fluorocarbon polymers (polyfluorocarbons) or fluoropolymers are composed of monomers (the smallest repeating compound segment of a polymer) consisting of carbon, fluorine, hydrogen, and, for one polymer, oxygen. The fluoropolymers have trade names that include, for example, Teflon® and Tefzel® (ethylene tetrafluoroethylene, products of the DuPont Company) and Kynar® (a polyvinylidene fluoride, a product of the Atofina Chemicals Company). Common types of fluoropolymers include FEP (fluorinated ethylene polypropylene), PFA (perfluoroalkoxy), PTFE (polytetrafluoroethylene), and PVDF (polyvinylidene fluoride). Each fluorocarbon polymer has different chemical and physical properties; however, at ambient temperatures all are relatively nonreactive chemically and do not leach monomers.

- Use Clean Hands/Dirty Hands (CH/DH) techniques when collecting and processing mercury samples (NFM 4.0.1). In addition:
  - Wear lint-free, non-particle-shedding clothing; avoid clothing that is an obvious source of particles (for example, natural wool, synthetic fleece, or dusty or dirty clothing). If particle-shedding clothing cannot be avoided, wear a disposable Tyvek suit or clean, nylon wind suit over the clothing.
  - Wear shoulder-length polyethylene gloves under wrist-length disposable powder-free gloves (nitrile, latex, or vinyl).
  - Double-bag all precleaned sample containers in zip-sealed plastic bags. Rebag all samples until processing and preservation.
  - Store and transport all clean sampling and processing equipment and supplies in a clean plastic container lined with a clean, clear plastic bag.
  - Avoid breathing directly over the samples.
  - Triple rinse the sampling equipment and sample bottles with the water to be sampled before beginning sample collection.

- **Implement quality control.** The collection and analysis of quality-control samples are required as an integral part of water-quality investigations. The quality-control plan should include collection of equipment-blank, field-blank, and replicate samples. Guidance on quality-control sample collection and processing can be found in NFM 4.3. The specific types, number, and distribution of quality-control samples should be determined according to the study design and data-quality requirements of the project.

  — Use reagent-grade water of the quality supplied by the WDML (WDML blank water) as the source solution for equipment blanks and field blanks. (The WDML assures the quality of the blank water as well as the other field equipment and supplies they provide).

  — Process and analyze equipment blanks before collecting any environmental samples. Identify the source of any contamination detected in the blanks, and correct the problem before using the equipment for sampling or processing.

  — Process an initial field blank to evaluate the potential for contamination associated with the field methods, materials used, and sampling environment. Subsequent field blanks should be collected to address field-site concerns, the sampling timeframe, and data-quality requirements. Field blanks are processed in the same manner and under the same environmental conditions as environmental samples (NFM 4.3.1.B).

  — Test at least 10 percent of the precleaned equipment used for sample collection and processing to assure cleanliness as follows: pass WDML blank water through the cleaned equipment and analyze this sample for total mercury. Note that the WDML only supplies equipment that has been appropriately precleaned and quality assured.

Equipment, Supplies, and Equipment-Cleaning Procedures

Refer to table 5–9 for a list of the equipment and supplies needed for low-level mercury sample collection and processing. Note that either FP (Teflon®) or polyethylene terephthalate copolyester, glycol-modified (PETG) bottles may be used, as described below.

- **Total mercury analysis**: Use 500-mL bottles for unfiltered (UTHg) and filtered (FTHg) samples.
- **Methylmercury analysis**: Use 250-mL bottles for unfiltered (UMHg) and filtered (FMHg) samples.

Contamination of sample containers and other sampling equipment is the most common source of bias associated with low-level mercury analysis. Equipment contamination can be prevented or at least minimized by (1) using equipment constructed of appropriate materials and (2) rigorously employing appropriate equipment-cleaning protocols, as described below. Most commercial plastics contaminate water samples with mercury at concentrations greater than the nanogram-per-liter level. Therefore, it is important to use only the plastics specified below.

- **Fluorocarbon polymer or fluoropolymer (FP) materials.** With a few notable exceptions, most equipment, including tubing and all sample-contacting equipment components, are to be composed of FP materials. FP equipment is reusable, but must be cleaned and stored properly.
- **Polyethylene terephthalate copolyester, glycol-modified (PETG)**. When collecting surface-water dip samples, **use only new PETG bottles–never previously used bottles.** (The samples subsequently are field filtered into FP sample bottles.)
  - — PETG bottles do not fit into any of the isokinetic samplers.
  - — PETG bottles do not require cleaning before use.
  - — PETG bottles are to be disposed of after each use. **Do not clean or reuse these bottles.**
- **C-flex tubing**. A small section of C-flex tubing may be used in the pump head of a peristaltic pump. FP connectors are used to connect the C-flex section with the FP tubing.

The rigorous nature of the cleaning protocol for equipment that directly contacts the water sample cannot be performed readily at most office laboratory facilities. Therefore, the WDML supplies and quality controls selected equipment that has been cleaned using the required, rigorous procedures listed later in this section. It is recommended that USGS project personnel contact WDML, either to obtain precleaned FP bottles and other FP equipment or to ship their equipment to the WDML for cleaning.

TECHNICAL NOTE: WDML precleaned Teflon® or other FP sample containers (bottles for unfiltered and filtered samples and petri dishes for particulate mercury filters) have two bar-code labels that contain: (1) the unique identification number of the container, and (2) a code representing the date that the container was removed from the acid bath. One bar code is placed in the sealed inner plastic bag with the sample container and the second bar code is placed in the outer plastic bag (see "Sample Preservation, Storage, and Shipment" below). The outer plastic bag is labeled by the WDML with the unique identification number using a permanent marker. Samples are tracked using the bar code to identify shipping and receiving dates and laboratory sample preparation and analysis steps.

- Sampling and processing equipment that directly contacts the water sample must be cleaned before use, using the procedures described below, unless the equipment has been obtained from or cleaned by the WDML.
- Sampling and processing equipment that does not directly contact the water sample should be cleaned using the standard cleaning protocols for inorganic constituents described in NFM 3.2.1.

Contact the WDML at least 2 to 4 weeks in advance of sampling for low-level mercury to arrange for the use of appropriately cleaned equipment.

Table 5–9. Checklist of equipment and supplies used for processing samples for low-level mercury analysis

[FISP, Federal Interagency Sedimentation Project; NFM, *National Field Manual for the Collection of Water-Quality Data*; FP, fluoropolymer or fluorocarbon polymer; PETG, polyethylene terephthalate copolyester, glycol modified; UTHg, unfiltered total mercury; FTHg, filtered total mercury; UMHg, unfiltered methylmercury; FMHg, filtered methylmercury; *N*, normal; PTHg, particulate total mercury; PMHg, particulate methylmercury; mL, milliliter; mm, millimeter; HIF, Hydrologic Instrumentation Facility of the USGS]

Item	Description	Applicable constituent(s)	Quantity required
Churn, US SS-1[1]	Fluoropolymer "churn" sample splitter, FISP part no. 011000. For compositing and splitting samples.	All, if splitting samples	1 per composited sample
Sample processing chamber[2]	For filtration and preservation of samples. NFM 2.2.2.	All	1
1,000 mL PETG bottle[2]	1,000-mL, square, wide-mouth sample bottle for collecting dip samples.	All, if collecting dip samples	1 per sample
UTHg bottle[3]	500-mL FP sample bottle for unfiltered total mercury samples.	UTHg	1 per sample
FTHg bottle[3]	500-mL FP sample bottle for filtered total mercury samples.	FTHg	1 per sample
UMHg bottle[3]	250-mL FP sample bottle for unfiltered methylmercury samples.	UMHg	1 per sample
FMHg bottle[3]	250-mL FP sample bottle for filtered methylmercury samples.	FMHg	1 per sample
6 *N* trace-pure hydrochloric acid[3]	Preservative for unfiltered and filtered mercury samples.	UTHg, FTHg, UMHg, and FMHg	10 mL for total mercury and 5 mL for methylmercury
Dry ice	For field preservation and shipment of particulate mercury samples.	PTHg and PMHg	As needed
Blank water[3]	Quality-assured, ultrapure deionized water for equipment and field blanks.	UTHg, FTHg, UMHg, and FMHg	1 bottle per blank sample
Vacuum desiccator fitted with modified filtration assembly, Tygon tubing, and 12-volt vacuum pump[3]	Equipment for vacuum filtration of samples for particulate and filtered mercury samples. See figs. 1 and 2, Savillex® filtration assembly, used with quartz fiber filters described below	FTHg[4], FMHg[4], PTHg, and PMHg	1 complete unit (must be precleaned for each sample)
Portable electronic bench scale, 1,200 grams minimum capacity[2]	For calculation of volume filtered for particulate mercury samples.	PTHg and PMHg	1

Table 5–9. Checklist of equipment and supplies used for processing samples for low-level mercury analysis–Continued

[FISP, Federal Interagency Sedimentation Project; NFM, *National Field Manual for the Collection of Water-Quality Data*; FP, fluoropolymer or fluorocarbon polymer; PETG, polyethylene terephthalate copolyester, glycol modified; UTHg, unfiltered total mercury; FTHg, filtered total mercury; UMHg, unfiltered methylmercury; FMHg, filtered methylmercury; *N*, normal; PTHg, particulate total mercury; PMHg, particulate methylmercury; mL, milliliter; mm, millimeter; HIF, Hydrologic Instrumentation Facility of the USGS]

Item	Description	Applicable constituent(s)	Quantity required
12-volt battery[2]	To power the vacuum pump for vacuum filtration of samples for particulate and filtered mercury samples.	FTHg[4], FMHg[4], PTHg, and PMHg	1
Quartz fiber filters (QFF)[3]	47-mm 0.7-micron nominal pore size, precombusted quartz fiber filters for particulate mercury samples; one precleaned filter per sample.	FTHg[4], FMHg[4], PTHg, and PMHg	1 per sample
FP petri dish[3]	50-mm stackable FP petri dish for storing particulate mercury filters.	PTHg and PMHg	1 per sample
FP forceps[3]	For handling quartz fiber filters for particulate mercury processing.	PTHg and PMHg	1 per sample
Peristaltic pump[2]	For processing filtered mercury samples when using capsule filters. Also used for sampling.	FTHg[5] and FMHg[5]	1
Capsule filters[3]	0.45-micron disposable capsule filter, polypropylene microfiber media, precleaned.	FTHg[5] and FMHg[5]	1 per filtered sample
C-Flex tubing[3]	Pump-head tubing for use with the peristaltic pump.	FTHg[5] and FMHg[5]	1 length per sample
Gloves[2]	Shoulder-length polyethylene gloves for sample collection and processing.	All	1 pair per person per site
Gloves[2]	Powderless nitrile, latex, or vinyl gloves to be worn over shoulder-length gloves.	All	As many as necessary
Tyvek coveralls[2]	Optional disposable clothing for personnel.	All	1 pair per person per site

[1]Contact Federal Interagency Sedimentation Project at http://fisp.wes.army.mil/ for vendors. For USGS use, obtain through One-Stop Shopping (supplied through HIF).
[2]Available on open market.
[3]Available from the USGS Wisconsin District Mercury Laboratory.
[4]Not required if using a capsule filter to process FTHg and FMHg samples.
[5]Not required if using vacuum filtration to process FTHg and FMHg samples.

To clean fluorocarbon polymer (FP) containers and equipment:

Note that new as well as previously used FP containers and equipment must be cleaned in advance of the current sampling effort (see step 2).

1. Wearing disposable powderless gloves, rinse bottles and other equipment with tap water.
2. Prepare a 4 *N* hydrochloric acid bath and heat to 65-75^{o} C.
   - **New FP containers and equipment:** Immerse rinsed equipment in the heated bath for at least 48 hours.
   - **Previously used FP containers and equipment:** Immerse rinsed equipment in the heated bath for at least 24 hours.
3. Remove the equipment from the bath and immediately immerse it in fresh reagent-grade water.
4. Repeat step 3 at least three times with fresh reagent-grade water.
5. Partially fill the FP bottles with a 1.0-percent (v/v) hydrochloric acid solution.
6. Cap the bottles and place them in a mercury-free Class 100 clean bench or laminar-flow hood until the outside surfaces are dry.
7. Double bag the dry equipment in new plastic zip-seal bags.

To clean FP and C-flex sample tubing:

1. Wearing disposable powderless gloves, fill tubing with a 50-percent (v/v) trace element-grade nitric acid solution.
2. Immerse tubing in a 10-percent (v/v) hydrochloric acid bath for a minimum of 7 days.
3. Dry tubing by purging with mercury-free air or nitrogen at the clean bench.
4. Double bag the tubing in new plastic zip-seal bags.

To prepare the capsule filter:

Many capsule filters are not chemically resistant to acids, and therefore, cannot undergo the preparation needed for low-level mercury sample processing (the standard capsule filter used to process samples for inorganic analysis should not be subjected to the acid-cleaning steps described below). It is recommended that precleaned filtration equipment, including acid-washed capsule filters, be obtained from the WDML, if possible. If WDML filtration equipment is not available for the study, obtain and prepare WDML-recommended filters as described below. Be sure to dispose appropriately the acid solutions used.

1. Wearing disposable powderless gloves, fill the capsule filter with a 50-percent (v/v) trace element-grade nitric acid solution and allow to stand for 4 days.
2. After 4 days, rinse the filter using 20 filter volumes of reagent-grade water.
3. Refill the filter with hydrochloric acid and immerse it in a 10-percent (v/v) solution of hydrochloric acid at room temperature. Soak for 3 days.
4. Empty the hydrochloric acid from the filter. Rinse the filter by sequentially filling it with 20 filter volumes of fresh reagent-grade water.
5. Fill the filter with reagent-grade water, cap it securely to prevent leakage, and double bag the filter until filtration.

USGS projects are advised to use the capsule filters that are precleaned and supplied by the WDML, if possible.

Sample Collection

To minimize the potential for sample contamination, collect samples using the least complex sampling method possible that results in a representative sample and meets study objectives. The potential for sample contamination increases with the increasing complexity of sampling methods. Follow the sampling procedures described below. If specific study objectives or site conditions necessitate procedure modifications, ensure that the modifications are well documented in field notes.

- **For surface-water sites with flowing water,** the selection of a sampling method depends on stream-mixing conditions and stream access.
  - **Well-mixed stream site**
    - Collect a dip sample (NFM 4.1.1.B) at the centroid of flow using an FP or PETG bottle of appropriate size (table 5-9).
    - Specific bottle requirements for surface-water dip samples are discussed below under "Sample Processing" and in table 5-9.
  - **Poorly mixed stream site**
    - Collect an isokinetic sample (NFM 4.1.1) using an appropriate isokinetic sampler.
    - Use a sampling device with an FP bottle, cap, and nozzle.
  - **Sites with boat access only**
    - Collect a dip sample or isokinetic sample, as appropriate for site conditions and study objectives.
    - Approach the sampling location from downstream; avoid collecting samples in water that has been disturbed by boat traffic.
    - In streams with slow velocities, sample from the bow of the boat while heading slowly upstream.

- **For surface-water sites with still water,** collect samples using either the dip-sampling, point-sampling, or pump-sampling method, depending on the site conditions and study objectives.

  If sampling an area with floating vegetation or detritus, pass the sampler beneath these materials before collecting a sample. In the case of a dip sample, open the bottle once it is submerged beneath these materials, and cap the bottle securely before removing it from the water.

  — **Dip-sampling method** (NFM 4.1.1.B): collect samples using either FP or PETG bottles. Specific bottle requirements for surface-water dip samples are discussed below under "Sample Processing" and in table 5-9.

    - Head upwind while sampling, if possible.
    - If samples are collected while wading, then collect the sample while slowly moving away from the area of disturbed bottom sediment.
    - If samples are collected from a boat, then sample from the bow of the boat, moving slowly away from the water disturbed by the boat.

  — **Pump- and point-sampling methods**: To collect samples at depth, use either a peristaltic pump with FP tubing, an FP weight, and C-Flex® pump-head tubing, or use an FP thief-type sampling device (NFM 4.1.2).

    - When using the pump-sampling method, run the pump for 5 to10 minutes to purge the tubing before collecting the sample.
    - Use clean (NFM 3.2.1) Kevlar rope to avoid sample contamination.

- **For ground-water sites,** the type of sampling system and method selected depends on the type of well and depth to water from land surface.
  - Follow standard guidelines for well purging and sample collection (NFM 4.2).
  - Peristaltic pumps with FP tubing and an FP weight are recommended for sampling shallow wells (for example, depth to water is less than about 25 feet or 9 meters). Use clean (NFM 3.2.1) Kevlar rope to attach the weight to the tubing.
  - Wells with a depth to water exceeding 25 feet can be sampled using an FP bladder pump and FP tubing. Use clean (NFM 3.2.1) Kevlar rope.
  - Avoid using a submersible, metallic pump wherever possible. If using a submersible, metallic pump, clean the pump following prescribed guidelines (NFM 3.3.9.A) and collect a pump-blank sample (NFM 4.3) well in advance of collecting environmental samples to assess the potential for contamination.

Sample Processing

Samples can be processed on-site, in a District laboratory, or at the WDML, but processing must be done within 24 hours of collection and under appropriately clean conditions. By prior agreement, the WDML can filter and acidify samples upon request, if samples are received via overnight courier.

- When processing samples on-site, minimize the potential for contamination.
  - The processing chamber should be fitted with a clean, clear plastic bag in which to work (NFM 2.2.2).
  - Work away from traffic, dusty roadways, or any other source of dust or other potential airborne contaminants.
  - Never work in vehicles in which mercury has been transported.
  - Avoid contact with metal work surfaces.
  - Wear lint-free, non-shedding clothing, a disposable Tyvek suit or a clean nylon wind suit.
  - Wear shoulder-length polyethylene gloves under disposable, wrist-length powderless (nitrile or latex) gloves.

- Use a 500-mL FP sample bottle for unfiltered total mercury (UTHg) and filtered total mercury (FTHg) samples. Use a 250-mL FP sample bottle for unfiltered methylmercury (UMHg) and filtered methylmercury (FMHg) samples.
- Use CH/DH techniques (NFM 4.0.1) when filling the FP sample bottles.
  - Discard the 1-percent hydrochloric acid contained in the FP sample bottles, before rinsing the sample bottles.
  - Triple rinse the bottles with small amounts (10 to 20 mL) of the water to be sampled.
  - Fill bottle to shoulder, leaving approximately 20 mL of headspace for later addition of preservative and laboratory reagents.
  - Cap bottle securely, dry off the bottle, and rebag until sample preservation.
- **If the sample will be processed off-site**, label outer sample bag with (a) site name and site number, (b) date and time of sample collection, and (c) type of analysis being requested.

To process samples for unfiltered total mercury and methylmercury analysis *(the processing method to be used depends on how samples are collected)**:***

Surface-water dip samples

1. Collect samples directly into the appropriate FP sample bottle.

Surface-water point samples

1. Dispense sample directly from an FP thief-type sampler into the appropriate FP sample bottle or FP churn.
2. If compositing the sample in a churn:
   a. Following sample collection, rebag the churn and place it in the churn carrier until sample splitting.
   b. Split the sample into FP sample bottles following guidelines for the churn splitter (NFM 5.1.1.A).

Surface-water pumped samples

1. Using a peristaltic pump and FP tubing, direct the sample flow into the appropriate FP sample bottle.

Isokinetic samples

1. Composite isokinetic samples in an FP churn. Rebag churn and place it into the churn carrier until sample splitting.
2. Split the sample into FP sample bottles following guidelines for the churn splitter (NFM 5.1.1.A).

Ground-water samples

1. Direct the sample flow into the appropriate FP sample bottle.

To process aqueous samples for filtered total mercury and methylmercury analyses *(the sample-processing method used depends on the choice of filter type and filtration equipment, as well as on the sample-collection method)**:***

- **Capsule-Filter Method**. Use an acid-resistant 0.45-µm polypropylene capsule filter, precleaned as previously described. When filtering the sample using the capsule filter and a peristaltic pump, follow the guidelines in NFM 5.2.1.A ("To filter a composite sample"), but implement the following modifications to that standard procedure:

  1. Using CH/DH techniques and a sample-processing chamber, remove capsule filter from plastic bag; uncap and discard reagent-grade water from capsule filter, shaking the filter to expel entrained water.
  2. Load the peristaltic pump head with precleaned C-Flex® pump-head tubing obtained from the WDML.
  3. Discard appropriately the 1-percent hydrochloric acid solution contained in the clean sample bottles. Triple rinse the sample bottles with small amounts (10 to 20 mL) of sample filtrate before collecting the sample.
  4. Fill bottles to shoulder with the sample filtrate, leaving approximately 20 mL of headspace for later addition of preservative and laboratory reagents.
  5. Cap each bottle securely, then dry off and rebag it until ready for sample preservation.

- **Vacuum-Filtration Method**. An alternative filtration method uses a vacuum filtration chamber, FP filtration assembly (for example, a Savillex® PFA/PFTE filtration assembly to hold a quartz fiber filter), and a 47-mm 0.7-µm precombusted quartz fiber filter (QFF) (described below in "*To filter samples for particulate mercury analysis*"). **The vacuum filtration method is recommended if collecting samples for both filtered and particulate mercury analysis.**

Surface-water dip samples

1. Collect samples directly in 1-L FP bottles or 1-L PETG bottles, after triple rinsing bottles with water to be sampled.
2. Fill bottles to the top. Cap bottles securely and rebag until ready for filtration.
3. Filter samples using either a capsule filter or vacuum filtration.

Surface-water point samples

1. Dispense samples directly from a thief-type sampler into 1-L FP or 1-L PETG bottles.
2. Fill bottles to the top. Cap bottles securely and rebag until filtration.
3. Filter samples using either a capsule filter or vacuum filtration.

Surface-water pumped samples

- **For on-site sample filtration**, connect a 0.45-µm WDML capsule filter in-line and follow filtration guidelines described above under "Capsule-Filter Method."
- **For off-site filtration**:
  1. Direct sample flow into either 1-L FP or 1-L PETG bottles and fill bottles to the top.
  2. Cap bottles securely and rebag until filtration.
  3. Use either the capsule-filter or vacuum-filtration method to filter samples off-site.

Surface-water isokinetic samples

1. Composite subsamples in an FP churn (NFM 4.1.1.A). Rebag churn and place into churn carrier until sample filtration.
2. Filter the sample using either the capsule-filter or the vacuum-filtration method.
   a. If using a capsule filter, then filter directly from the churn.
   b. If using vacuum filtration, then follow guidelines for the churn splitter (NFM 5.1.1.A), splitting the sample into either 1-L FP or 1-L PETG bottles before filtration and then capping the bottles securely and rebagging until the samples can be filtered.

Ground-water samples

1. Connect a 0.45-µm WDML capsule filter in-line with the pump and follow filtration guidelines described above under "Capsule-Filter Method."

To process aqueous samples for particulate total mercury and methylmercury analyses:

- Collect samples or split samples into 1-L FP or PETG bottles, as previously described in "Sample Collection."
- A 1-L sample is required for each particulate total mercury (PTHg) or particulate methylmercury (PMHg) analysis.
- Particulate total mercury and particulate methylmercury are processed using a vacuum-desiccator filtration chamber, an FP filtration assembly, and a 47-mm 0.7-µm pre-combusted QFF (figs. 1 and 2).
- Depending on study requirements for filter pore size, the filtrate for particulate mercury can be collected for filtered total mercury (FTHg) and filtered methylmercury (FMHg) samples.
- USGS projects are advised to obtain all filtration supplies from the WDML, if possible.

Figure 1. Vacuum-desiccator filtration chamber with a modified Savillex® PFA/PFTE filtration assembly attached.
(Photograph by Michael E. Lewis)

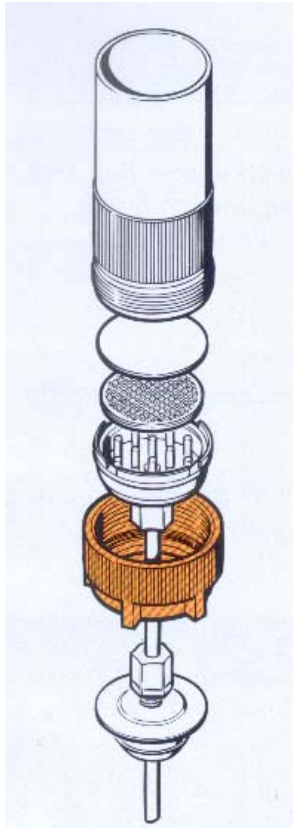


Figure 2. Savillex® PFA/PTFE filtration assembly. (From Savillex Corporation. Published with permission.)

To filter samples for particulate mercury analysis:

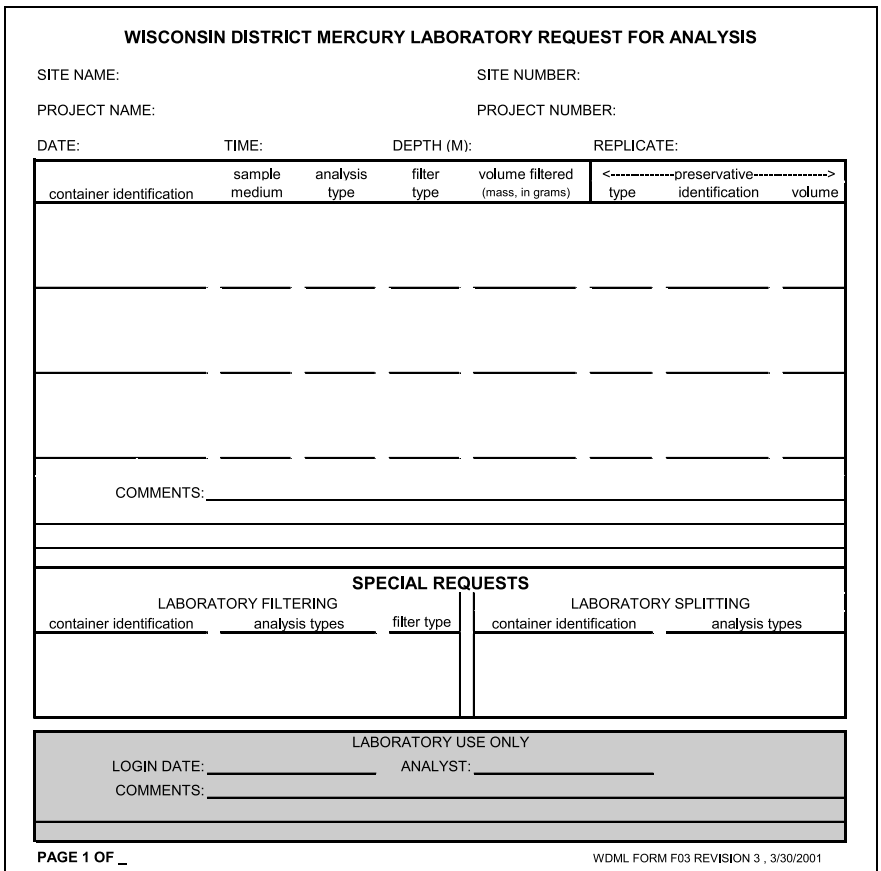
- If the particulate concentration is very low, evidenced by little or no slowing of the filtration rate, then filter an entire 1-L sample for total mercury (PTHg) and an entire 1-L sample for methylmercury (PMHg).
- At modest particle concentrations, evidenced by a slowing filtration rate, filtering approximately 500 mL of sample is sufficient.
- High particle-concentration water may require several filter changes to collect sufficient volumes for filtered-water sample analysis (for example, 500 mL for FTHg and 250 mL for FMHg). In such cases, retain only one filter for PTHg and one filter for PMHg, recording the volume of water filtered through each filter. **Do not calculate sample volumes that pass through the subsequent filters after the PTHg and PMHg filters have been collected.**

1. Weigh the bottled 1-L samples, recording mass in grams.
2. Filter each sample in a sample-processing chamber that is fitted with a clean plastic covering (NFM 2.2.2). Use CH/DH techniques. The chamber must be large enough to contain the vacuum filtration unit (approximately 16 inches in height) and allow enough room to pour water into the top of the filter reservoir. A chamber height of 24 inches is suggested; however, existing chambers of 21 to 23 inches should suffice.
3. Using CH/DH techniques, prepare the vacuum filtration chamber (fig. 1). Using a clean FP filtration assembly (fig. 2), insert a ¼-inch FP tube into the vacuum-desiccator filtration chamber (see fig. 1). Place the inverted orange nut on top of the chamber. Attach the filter support. Using FP forceps, place a quartz fiber filter (random pattern facing up) onto the filter support. Place the filtration-assembly reservoir on the filter and secure it with the orange nut, holding the reservoir firmly to avoid tearing the filter.
4. If processing samples for filtered total mercury, discard the 1-percent HCl solution from the 500-mL FP bottle for FTHg analysis. Place the open 500-mL FTHg bottle inside the vacuum desiccator, positioned directly beneath the FP tube. Close the filtration chamber. Attach the vacuum pump line and turn on the vacuum pump.

5. Agitate each 1-L sample bottle to keep the sample well mixed (do this frequently during the filtration process), and begin pouring small volumes of water into the top of the filter chamber.
6. Filter the sample into the 500-mL FTHg bottle, triple rinsing the bottle with small amounts (10 to 20 mL) of filtrate before filling the bottle to the shoulder. Leave about 20 mL of headspace for the addition of preservative and laboratory reagents; decant excess water if necessary.
7. If a noticeable particle load has collected on the filter, evidenced by a slowing filtration rate, remove the PTHg filter and place it into an FP petri dish. For low particle loads, filter the remaining water in the first 1-L sample. It is acceptable to overflow the filtered-water bottle that is inside the vacuum chamber in order to filter sufficient water volume for the particulate sample.
8. Label the outer bag with all sample information.
9. When filtration is complete, re-weigh the 1-L sample bottle; calculate and record the mass of water (in grams) that passed through the filter. Place the filter in its FP petri dish and cover with a stackable petri dish. Record on the laboratory request form (fig. 3) all the necessary sample information, including the calculated mass (in grams) of water that passed through the filter (volume filtered).
10. Remove the FTHg bottle from the chamber, securely capping, drying off, and bagging the bottle until sample preservation.
11. **PMHg and FMHg samples:** Repeat steps 1-10 above. Save the filter for PMHg, recording the sample mass (in grams—see step 9 above) that passed through the filter.
12. **Particulate mercury samples:** When filtration is complete and the quartz fiber filters are stacked in their petri dishes, tape the petri dishes together to prevent separation during sample storage and shipping. Place petri dishes in zip-seal bag(s). Ensure that all sample information is recorded on the bags. Place bagged filters into a cooler stocked with dry ice or frozen, bagged blue-ice packs. **Do not use wet ice.** Keep particulate-mercury filters frozen or chilled in the field. Upon return to the office, store the bagged filters in a freezer until all mercury sampling is complete. Every petri dish has two corresponding bar codes with the petri dish identification. Place one bar code on the Request for Analysis form; retain the other bar code with the petri dish in the inner bag.

13. When filtration is complete, empty any water that has spilled in the filtration chamber. The FP filtration-assembly reservoir and filter support (fig. 2) must be cleaned rigorously before use, as previously described in "Equipment, Supplies, and Equipment-Cleaning Procedures". All other components of the vacuum filtration apparatus, including the vacuum chamber, can be cleaned utilizing standard procedures for inorganic constituents (NFM 3.2.1).

14. Place used FP filtration parts into a bag to be returned to the WDML for cleaning and reuse.



WISCONSIN DISTRICT MERCURY LABORATORY REQUEST FOR ANALYSIS

SITE NAME: SITE NUMBER:

PROJECT NAME: PROJECT NUMBER:

DATE: TIME: DEPTH (M): REPLICATE:

container identification	sample medium	analysis type	filter type	volume filtered (mass, in grams)	<----------preservative----------> type	identification	volume

COMMENTS:

SPECIAL REQUESTS

LABORATORY FILTERING container identification	analysis types	filter type	LABORATORY SPLITTING container identification	analysis types

LABORATORY USE ONLY

LOGIN DATE: ANALYST:

COMMENTS:

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Figure 3. Wisconsin District Mercury Laboratory (USGS) request-for-analysis form (available on the Internet at http://infotrek.er.usgs.gov/doc/mercry/doc/Analysis_Request_Form.pdf).

Sample Preservation, Storage, and Shipment

Preserve unfiltered and filtered total and methylmercury samples with trace-pure 6 *N* hydrochloric acid preservative as soon after collection as practical, **but ensure that the acid treatment is added to the samples within 24 hours of filtration.**

Sample preservation is the most susceptible step in sample processing, with respect to the potential for sample contamination.

- The WDML provides the ultra-trace hydrochloric acid and the measurement vial. Wear appropriate protective eyewear, gloves, and clothing when handling the 6 *N* hydrochloric acid.
- If multiple sites are to be sampled per day, all samples should be preserved at the same time to minimize the number of times the hydrochloric acid preservative is opened.

To preserve samples for mercury analyses:

1. Prepare a clean workspace. Using CH/DH procedures, prepare a sample-processing chamber with a new plastic cover.
2. Rinse the measurement vial three times with small volumes of 6 *N* hydrochloric acid. Collect the waste in a clean, sturdy, sealable plastic container. Neutralize and dispose of the used hydrochloric acid solution appropriately and in accordance with local regulations.
3. Fill the vial to the 10-mL mark with hydrochloric acid. Pour 10 mL of the hydrochloric acid into each of the 500-mL FTHg and UTHg bottles.
4. Fill each vial to the 5-mL mark. Pour 5 mL into each of the 250-mL FMHg and UMHg bottles.
5. Reseal all bottles as tightly as possible by hand. Rebag bottles in their zip-seal bags, leaving one sample bar code label in the bottom of the inner bag with the sample bottle.
6. Save at least 30 mL of the hydrochloric acid because the WDML must analyze the remaining solution to assess potential preservative contamination. Return the hydrochloric acid and the measurement vial to the WDML along with the samples.
7. Record on the WDML laboratory request form (fig. 3) the identification number of the hydrochloric acid preservative that was used with each sample.

To store and (or) ship samples:

Do not store or ship samples on ice. Ice meltwater invariably invades the sealed bags, potentially compromising a bottle's clean environment. **Do not expose samples to light or heat.**

1. Enter all sample-header data (site name, date, time, sample depth, medium code, sample type) on the WDML laboratory request-for-analysis form (fig. 3).
2. Place bar codes from the outer bag of the double-bagged sample bottles on the WDML request-for-analysis form under "container identification" (fig. 3).
3. Transport and store preserved water samples in a cool, dark environment, such as in a clean cooler. Line the cooler with a clean plastic bag. **Do not store samples on ice.** If field conditions are particularly warm, use bagged and sealed frozen blue-ice packs to keep samples cool.
4. Fill out the cooler inventory form for all samples to be shipped to WDML (fig. 4). Consolidate and ship samples to WDML when sampling is completed; **samples must be shipped within 14 days of collection.**
5. Enclose the WDML laboratory request-for-analysis form (fig. 3) and cooler inventory form (fig. 4) in a sealed plastic bag in the cooler with the samples.
6. Notify WDML of sample shipment via e-mail mercury@usgs.gov.

Samples for low-level mercury analysis must be shipped to the laboratory within 14 days of collection.

COOLER INVENTORY FORM

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USGS -- WISCONSIN DISTRICT
MERCURY LABORATORY
8505 RESEARCH WAY
MIDDLETON, WI 53562

PROJECT:

SAMPLERS:

SITE NAME	DATE	TIME	DEPTH	SAMPLE MEDIA	TOTAL NUMBER OF CONTAINERS	125 ML TEFLON	250 ML TEFLON	500 ML TEFLON	1 L TEFLON	2 L TEFLON	5 L TEFLON	PETRI DISHES	40 ML GLASS	SEDIMENT VIAL			LABORATORY CHECK-IN COMMENTS

Relinquished by:	date/time:	Received by:	date/time:	COMMENTS:
Relinquished by:	date/time:	Received by:	date/time:	
Relinquished by:	date/time:	Received by:	date/time:	

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Figure 4. Wisconsin District Mercury Laboratory (USGS) cooler inventory form (available on the Internet at http://infotrek.er.usgs.gov/doc/mercury/doc/Cooler_Inventory_Form.pdf)

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