

## **FS 8200. Clean Sampling for Ultratrace Metals in Surface Waters**

Use in conjunction with:

- FA 1000 Regulatory Scope and Administrative Procedures for Use of DEP SOPs
- FD 1000 Documentation Procedures
- FM 1000 Field Planning and Mobilization
- FQ 1000 Field Quality Control Requirements
- FS 1000 General Sampling Procedures
- FS 2000 General Aqueous Sampling
- FS 2100 Surface Water Sampling

### **1. INTRODUCTION AND SCOPE**

This procedure is designed for the collection of ambient water samples for the determination of total and dissolved metals at concentrations listed in Table FS 8200-1 and for the collection of other metals and metal species amenable to determination at ultratrace levels. Use these protocols only when the “clean hands, dirty hands” sampling procedures are specifically stipulated in the permit, consent order or as part of the project data quality objectives. This method is not intended for determination of metals normally found in treated and untreated discharges from industrial facilities. Actual concentration ranges to which this guidance is applicable will depend on the sample matrix, dilution levels and other laboratory operating conditions.

1.1. Filter samples for dissolved metal determinations through a 0.45 µm capsule filter at the field site.

1.2. The ease of contamination of ambient waters with metals cannot be over emphasized. Follow this method closely to avoid contamination. It is based on EPA Method 1669.

1.3. This procedure is “performance-based”, and emphasizes that the modification of procedure or technique is allowed as long as neither samples nor blanks are artificially contaminated when using the modified procedures. Thoroughly evaluate any modifications by demonstrating effective collection of field samples.

1.3.1. Modify the procedures below as applicable to the level of effort required for the analytical objectives of the project. Ensure that the modified procedures have been approved by all parties to the project, including DEP permitting or other regulatory authorities.

1.3.2. Document the collection of uncontaminated samples, equipment blanks and other applicable quality control samples using the modified procedures.

1.4. The procedures in this SOP are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality levels. Documentation of training must be kept on file and readily available for review.

### **2. CONTAMINATION AND INTERFERENCES**

#### **2.1. Contamination Problems in Ultratrace Metals Analysis**

2.1.1. Take extreme care to avoid contamination when collecting water samples for ultratrace metals.

2.1.2. Potential sources of contamination during field activities include metallic or metal-containing equipment or containers (e.g., talc gloves that contain high levels of zinc), decontamination reagents including analyte-free water, improperly cleaned and stored equipment, and atmospheric inputs such as dirt, dust, automobile exhaust, cigarette smoke and nearby structures (roads, bridges, wires, poles).

## 2.2. Avoiding Contamination

Avoid exposing the sample and sampling apparatus to contamination by being acutely aware of potential sources of contamination and paying strict attention to work being performed.

2.2.1. To minimize atmospheric input open or expose all equipment that will contact samples or blanks in a clean room, clean bench, glove box or clean plastic bag. Keep the amount of time between cleaning and use as short as possible. When not in use, cover equipment with clean plastic wrap, store in the clean bench or in a plastic box or glove box, or bag in clean, colorless zip-type bags.

2.2.2. Field personnel must wear clean non-talc gloves during all activities involving handling of sampling equipment. Change gloves that are contaminated by touching an unclean object or substance. Consider wearing multiple pairs of gloves to allow stripping of the outer pair to facilitate the sampling operation.

### 2.2.3. Approved Construction Materials of Sampling Equipment

2.2.3.1. Use only materials and equipment of approved construction (see FS 8210).

2.2.3.2. Do not allow the following materials to come in contact with the sample or be used to hold liquids that come in contact with the sample: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon or Vycor. Do not use highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber, all contain trace levels of metals.

### 2.2.4. Sources of Contamination

2.2.4.1. Collect samples from expected lowest concentrations to the highest concentrations where this information is known.

2.2.4.2. Do not collect, process or ship samples containing high levels of metals at the same time as samples being collected for ultratrace metals determinations.

2.2.4.3. Collect sample as far as possible from airborne contamination. Avoid if possible or take precautions in areas of bare soil subject to wind erosion, airborne dust or dirt, particulate matter, or vapors from automobile, small engines or cigarette smoke as well as nearby bridges, pipes, poles or wires.

2.2.5. Sample Interferences: If a sample is suspected of containing substances that interfere with the analyses of trace metals at these levels, collect sufficient sample to allow the laboratory to identify and overcome the interference problems.

2.2.6. Decontaminate sampling equipment according to procedures detailed in FS 8220.

## **FS 8210. EQUIPMENT AND SUPPLIES**

All equipment (sample containers, dippers, tubing, etc.) coming in direct contact with the sample must be free of the metal(s) of interest. Use materials constructed of fluoropolymers such as fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE), conventional or linear polyethylene, polycarbonate, polypropylene or ultrapure quartz.

Package and arrange the equipment to minimize field preparations. Any preparations or cleaning done in the field must be done in a way that minimizes the possibility of contamination. See FS 8200, section 2.2.

### **1. SAMPLE CONTAINERS**

1.1. Fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene construction material. Use fluoropolymer or glass containers if mercury is a target analyte.

1.2. Decontaminated sample containers must be filled with 0.1% hydrochloric acid (volume/volume, v/v). Prior to shipping to the field site the acid may be emptied and the containers filled with reagent water.

### **2. SUPPORT EQUIPMENT**

- Gloves: Clean, non-talc polyethylene, latex, vinyl or polyvinylchloride (PVC).
- Shoulder-length gloves: Clean, non-talc polyethylene, latex, vinyl or PVC.
- Plastic wrap: Clean, colorless polyethylene.
- Storage bags: Plastic, colorless, reclosable.
- Cooler: Non-metallic.
- Ice to keep samples chilled during storage.
- Carboy for collection and storage of dilute waste acids, if necessary.
- Boom: A PVC or plastic rod, pole or other extension used to support or guide the sampling apparatus to the sampling location.
- Field portable glove bag or a field glove box constructed of a non-metallic frame and a cover for the frame of inexpensive, disposable, non-metallic material.

### **3. SAMPLING EQUIPMENT**

3.1. Filtration apparatus: Required when collecting samples for dissolved metals. In line 0.45 micron, 15 mm diameter or larger, tortuous path capsule filters.

#### **3.2. Pump and Pump Apparatus**

3.2.1. Required for use with the jar sampling system or the continuous flow system. Use a peristaltic or equivalent pump. Equivalent pumps include rotary vacuum, submersible, or other pumps free from metals and suitable to meet the site-specific depth sampling needs.

#### **3.2.2. Tubing**

3.2.2.1. Tubing for use with peristaltic pump: Styrene/ethylene/butylene/silicone (SEBS) resin.

3.2.2.2. Tubing for connection to peristaltic pump tubing – fluoropolymer in lengths required to reach the sampling point, taking into consideration the distance required if a boom is used.

3.2.2.3. Tubing connectors: Appropriately sized PVC, clear polyethylene, or fluoropolymer barbed straight connectors used to connect multiple lengths of tubing.

3.3. Grab sampler: Used where depth profiling is not a concern.

3.3.1. Polyethylene pole with a fluoropolymer collar to hold the sample container. A fluoropolymer closing mechanism threaded on to the sample container triggered by a Teflon string that allows opening and closing the container underwater avoiding surface contamination. Components must be made of other acceptable construction materials as detailed in the opening paragraph of this section.

3.3.2. A grab sampler that allows the collection of a discrete water sample and is constructed so that a capped clean sample container can be submerged, the cap removed, and the bottle recapped at a selected depth. This device eliminates contact with conventional sampling devices and eliminates carry over from previous samples.

3.4. Subsurface sampling devices: Appropriate for use in lakes and low flow river systems where depth profiling is necessary.

3.4.1. Jar Sampler

3.4.1.1. Consists of a heavy fluoropolymer 1 liter jar with a fluoropolymer lid equipped with two fluoropolymer fittings. Sample enters the jar by pumping on fluoropolymer tubing attached to one fitting causing the sample to be drawn through the other fitting. A thick fluoropolymer plate supports the jar and allows for attachment of a fluoropolymer torpedo weight.

3.4.1.2. Advantages to the jar sampler:

- The suction device is located in an area remote from the sampling jar.
- The sampling jar can be rinsed with sample.
- There is not a long length of tubing, eliminating the need for decontamination.
- Eliminates atmospheric contact with the sample.

3.4.2. Continuous Flow Sampler

3.4.2.1. Consists of a peristaltic or submersible pump and associated fluoropolymer tubing. A boom may be used to separate the sampling personnel from the equipment and sampling location. Add a filter is added to the sampling train when collecting dissolved metals.

3.4.2.2. Advantages to the continuous flow sampler:

- Surfaces are easily decontaminated.
- Pump is isolated from the sample bottle.
- In-line filtration is possible.

## **FS 8220. EQUIPMENT DECONTAMINATION PROCEDURES**

### **1. INTRODUCTION AND SCOPE**

- 1.1. Strictly follow the procedures outlined in this SOP to ensure that the equipment, reagents, and sample containers brought and used in the field for the purpose of collecting samples for ultratrace metals analyses have been properly decontaminated.
- 1.2. Take care with the storage of the decontaminated equipment. If you notice any indications that the equipment is not clean and an assessment indicates that there has been the possibility the apparatus is contaminated, immediately stop sampling and return the affected equipment for decontamination.
- 1.3. If equipment and field blanks produced from a less rigorous protocol than those detailed in this SOP show no levels of analytes above the method detection limit (MDL) or other source of interference, then these alternative protocols may be used. Maintain complete documentation of the procedure and demonstration of its effectiveness.

### **2. GENERAL REQUIREMENTS**

- 2.1. Clean all sampling equipment and sample containers in a designated cleaning area that has been demonstrated to be free of trace element contaminants. This area may be a class 100 clean room, clean benches or a designated equipment cleaning area.
- 2.2. Use new gloves, storage bags and plastic wrap without additional cleaning unless evidence from the blanks indicates they are a source of contamination. In such a case, find an alternative supplier or decontaminate the materials.
- 2.3. After decontamination store each piece of sampling equipment in a clean, single polyethylene zip-type polyethylene bag. Use a second polyethylene bag if shipment is required.
- 2.4. Periodically monitor all cleaning solutions and acid baths for accumulation of metals. When the levels become too high change the solutions and baths and neutralize and discard in compliance with local, state and federal regulations.

## **FS 8221. *Decontamination Equipment and Supplies***

### **1. EQUIPMENT**

- 1.1. Buckets or Basins: 5 to 50 L capacity for acid soaking of equipment.
- 1.2. Gloves: Non-talc polyethylene, latex or vinyl. Wear heavy gloves should be worn when working in the acid baths since baths will contain hot, strong acids.
- 1.3. Tongs: For removal of sampling equipment from acid baths. Do not use coated metal tongs.
- 1.4. Brushes: Non-metallic for scrubbing equipment.
- 1.5. Wash bottles: FEP (fluorinated ethylene propylene) or equivalent with screw closure.
- 1.6. Storage bags: Zip-type, non-vented, colorless polyethylene.
- 1.7. Plastic wrap: Clean, colorless polyethylene.

2. REAGENTS: Use only trace metal grade acids for cleaning equipment and supplies. If the purity of a reagent is in question, it must be analyzed and the concentration determined to be below the method detection limit.

- 2.1. Nitric acid: Concentrated (specific gravity 1.41).
- 2.2. Diluted nitric acid: Used for field decontamination.
- 2.3. Nitric acid (1+1): Add 500 mL concentrated nitric acid to 400 mL of reagent grade water and dilute to 1 L with reagent grade water.
- 2.4. Hydrochloric acid: 1N and 4N.
- 2.5. Hydrochloric acid: 0.1% (v/v) ultrapure grade.
- 2.6. Hydrochloric acid: 1% and 0.4% (v/v).
- 2.7. Hydrochloric acid: 10% by weight, trace metal grade.
- 2.8. Alkaline detergent: Liquinox, Alconox or equivalent.

**FS 8222.**     *Decontamination Protocols for Sampling Equipment and Sample Containers*

1. DECONTAMINATION IN DESIGNATED CLEANING AREAS

1.1. Sampling Equipment

- 1.1.1. Fill a precleaned bucket or basin with a sufficient quantity of 0.5% solution of liquid detergent. Completely immerse each piece of equipment. Soak for 30 minutes.
- 1.1.2. Thoroughly scrub down all materials with the detergent using a pair of clean gloves and a clean non-metallic brush.
- 1.1.3. Change gloves and place the scrubbed equipment in another precleaned bucket or basin. Rinse all equipment (inside and out) with reagent grade water until there is no sign of detergent residue.
- 1.1.4. Change gloves and place the equipment in a hot bath (50-60°C) of concentrated nitric acid. Allow to soak for 2 hours.
- 1.1.5. Use clean gloves and tongs to remove the equipment and thoroughly rinse with reagent grade water.
- 1.1.6. Change gloves and immerse the equipment in a hot (50-60°C) bath of 1N trace metal grade hydrochloric acid. Soak for 48 hours.
- 1.1.7. Thoroughly rinse all equipment with analyte-free water.
- 1.1.8. Air dry in a class 100 clean bench or other designated clean area.
- 1.1.9. Wrap each piece of equipment in two layers of polyethylene film.

1.2. Sample Containers (all metals except mercury)

- 1.2.1. After cleaning (steps 1.1.1-1.1.8 of this section), fill each bottle with 0.1% (v/v) ultrapure hydrochloric acid and cap tightly.
- 1.2.2. Double bag each bottle in a zip-type polyethylene bag and store at room temperature.

1.3. Procedures for Mercury Sample Containers

- 1.3.1. Clean new bottles by heating at 65-75°C in 4N hydrochloric acid for at least 48 hours.

1.3.2. Cool and rinse bottles three times with analyte-free water and fill with 1% hydrochloric acid solution.

1.3.3. Cap the bottles, place in an oven at 60-70°C and leave overnight.

1.3.4. Cool the bottles, rinse three more times in analyte-free water and fill the bottles with 0.4% (v/v) hydrochloric acid. Place the bottles in a mercury-free class 100 clean bench or other designated clean area until dry.

1.3.5. Tightly cap the bottles, double bag in new polyethylene zip-type bags and store in wooden or plastic boxes.

1.3.6. Bottles may be reused only if it is known that they have not contained mercury at high levels. The procedure in 1.3.1-1.3.5 of this section must be used for cleaning except that the bottles have to remain in the hot 4N hydrochloric acid for only 6-12 hours.

1.4. Polyethylene bags (cleaning is required only if blank contamination is associated with the bags)

1.4.1. Partially fill with cold, 1+1 nitric acid.

1.4.2. Rinse with analyte-free water.

1.4.3. Dry by hanging upside down from a plastic line using a plastic clip.

1.5. Tubing: Rinse with 10% hydrochloric acid by weight and thoroughly flush with water from the site. Soak tubing used for the analysis of mercury samples for at least 8 hours in the 10% Hydrochloric acid solution and dry with metal-free air or nitrogen in a designated clean area.

1.6. Extension Pole: Use a non-metallic brush to scrub the pole with analyte-free water. Wipe down the pole with 0.1% (V/V) ultrapure hydrochloric acid and wrap the pole in polyethylene film.

## 2. RECLEANING THE APPARATUS BETWEEN SAMPLES

If possible, bring enough precleaned equipment to the field for the entire sampling event. If this is not possible follow the following field cleaning protocols:

2.1. In the glove bag using the clean hands/dirty hands procedure rinse the sampling apparatus with diluted nitric acid. See FS 8221, section 2.2.

2.2. Dump the spent diluted acid in the waste carboy.

2.3. Rinse the sampling equipment with analyte-free water and discard the spent water.

2.4. Rinse the sampling apparatus with ambient water.

## FS 8230. SAMPLING PROCEDURES

### 1. GENERAL PROTOCOLS

1.1. Designate one member of the sampling team as clean hands and the other as dirty hands. Clean hands is responsible for all operations involving contact with the sample and/or sample bottle. Dirty hands is responsible for all other activities that do not involve direct contact with the sample or sample bottle. The proper collection of a sample requires a great deal of coordination between clean hands and dirty hands. Each sampler must know and understand his role and if possible the team has experience together.

1.2. Begin sample collection at sites of lower concentrations and continue to sites of higher concentrations. This procedure minimizes carryover between sites. To prevent carryover when the relative concentrations of metals are not known for each site, use new equipment (tubing, dippers, etc.) for each site.

1.3. Approach the sampling site from downstream and downwind, when possible. If samples are being collected from a boat, samplers must approach from down current and sample from the bow of the boat. When sampling from shore, it is best to approach the site from downwind.

1.4. The sampling team puts on a clean pair of gloves with clean hands donning shoulder length gloves. All sampling personnel must wear clean, powder-free gloves at all times. Furthermore, when personnel come in contact with equipment that has not been precleaned, they must stop and put on a clean pair of gloves. Dirty hands personnel must help clean hands personnel to put on a clean pair of gloves whenever needed.

## 2. SAMPLE COLLECTION DIRECTLY INTO THE SAMPLE BOTTLE

2.1. Dirty hands removes the double-bagged sample bottle from storage and unzips the outer bag.

2.2. Clean hands opens the inside bag containing the sample bottle, removes the sample bottle and reseals the inner bag. Dirty hands then reseals the outer bag.

2.3. Clean hands removes the cap, while holding the cap upside down, discards the acid into a waste container or the reagent water into the water body.

2.4. Clean hands submerges the sample bottle allowing it to partially fill, then screws the cap on the bottle, shakes the bottle several times, and empties the rinse water away from the site. Clean hands repeats the rinses of the sample container two more times following the same procedure. Clean hands then completely fills the sample bottle with sample and, with the bottle still inverted underwater, replaces the bottle cap. The sample has never contacted the air.

2.5. Dirty hands reopens the outer plastic bag and clean hands opens the inside bag, places the bottle inside and zips the bag, dirty hands places the inside bag containing the sample container inside the outer bag and zips the outer bag.

## 3. SAMPLE COLLECTION WITH GRAB SAMPLING DEVICE

3.1. If necessary, clean hands attaches a bottle to the sampling device inside the field portable glove bag. Ideally this was already accomplished in a clean area before arriving on site.

3.2. Dirty hands removes the sampling device and opens the outer polyethylene bag.

3.3. Clean hands opens the inside polyethylene bag and removes the sampling device and then changes gloves.

3.4. Dirty hands submerges the sampling device and proceeds to fill the sample container.

3.5. When the bottle is full (when no more bubbles appear), dirty hands seals off the sample container and removes the sampling device from the water.

3.6. Dirty hands returns the sampling device to the inner plastic bag and clean hands removes and caps the bottle.

- 3.7. Dirty hands reopens the outer plastic bag, and clean hands opens the inside bag, places the bottle inside it, and zips the inner bag. Dirty hands zips the outer bag.
4. SAMPLE COLLECTION USING A JAR SAMPLING DEVICE
- 4.1. The sample team puts on gloves and handles bottles as with manual collection.
- 4.2. Dirty hands removes the jar sampling device from its storage container and opens the outer polyethylene bag. Clean hands opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally the apparatus was assembled inside a clean area at the laboratory. However, if assembly is required in the field, clean hands must perform this operation inside the field portable glove bag.
- 4.3. While dirty hands is holding the jar sampling apparatus, clean hands connects the pump to the flush line and dirty hands lowers the sampler to the sampling depth.
- 4.4. Dirty hands turns on the pump allowing > 2 L of water to pass through the system. Dirty hands stops the pump, pulls up the sampling device and places it into a larger clean plastic bag. Both clean hands and dirty hands change gloves.
- 4.5. Following the procedures in sections 2.2 – 2.3 above, the sampling team gets a sample container and clean hands places the bottle into a glove bag.
- 4.6. Clean hands tips the sampling jar and dispenses the sample through the short length of tubing into the sample container.
- 4.7. Clean hands replaces the bottle cap, places the bottle in the inside polyethylene bag and closes the bag. Clean hands places the inside bag in the outside polyethylene bag held by dirty hands and dirty hands closes the bag.
5. CONTINUOUS FLOW SAMPLING: The continuous flow sampling system uses a peristaltic pump and tubing to obtain the sample.
- 5.1. The sampling team removes the sampling equipment and puts on gloves.
- 5.2. Dirty hands removes the pump from its storage bag and opens the bag containing the tubing.
- 5.3. Clean hands installs the tubing while dirty hands holds the pump. Clean hands places the tubing in the sample stream. Both parties change gloves.
- 5.4. Dirty hands turns the pump on and allows the pump to run for 5-10 minutes to purge the pump and tubing.
- 5.5. If dissolved metals are to be collected, clean hands places the filter at the end of the tubing.
- 5.6. After rinsing the sample container three times, clean hands fills the bottle.
6. OTHER TYPES OF SURFACE WATER SAMPLING EQUIPMENT
- 6.1. Sampling equipment types not included in this SOP but discussed in the Surface Water SOP, FS 2100, may be used for collecting samples for ultratrace metal analyses if they are constructed of acceptable materials as described in FS 8210 and as long as an acceptable equipment blank can be obtained with the subject equipment.
- 6.2. The clean hands/dirty hands procedures as described in number 3 of this section (Sample Collection with a Grab Sampling Device) must be used when these sample collection devices are used.

## **FS 8240. DOCUMENTATION**

1. Immediately following sample collection, identify each sample container with a unique field identification code.
2. Record sampling information specific to the site while still at the site and meet all of the requirements specified in FD 1000.

## **FS 8250. SAMPLE PRESERVATION**

Preserve all samples in a designated clean area or in the glove bag. Personnel must wear gloves and conduct the process as quickly as possible to eliminate particulate contamination.

1. Preservation of Samples for Metals other than Trivalent Chromium, Hexavalent Chromium and Mercury
  - 1.1. Reagents: nitric acid, ultrapure – 10% (v/v) solution.
  - 1.2. Preservation Protocol: Maintained at 0–4°C from the time of collection until preservation.
    - 1.2.1. If the samples are not preserved immediately upon collection, they must be acid-preserved within 48 hours after sampling.
    - 1.2.2. Using a precleaned, disposable, plastic pipet add 5 mL of the nitric acid solution per liter of sample. Preserve the sample to a pH of <2.
2. PRESERVATION OF SAMPLES FOR THE ANALYSIS OF TRIVALENT CHROMIUM: the clean area for the preservation of trivalent chromium must be large enough to hold the vacuum filtration apparatus and an area established for the setup of the wrist-action shaker.
  - 2.1. Reagents
    - 2.1.1. Nitric acid, ultrapure
    - 2.1.2. Chromium (III) extraction solution: Prepare this solution by adding 100 mL of ammonium iron (II) sulfate solution to a 125 mL polyethylene bottle. Adjust the pH to 8 with approximately 2 mL of ammonium hydroxide solution. Cap and shake on a wrist-action shaker for 24 hours. This solution is stable for 30 days.
    - 2.1.3. Ammonium Iron (II) sulfate solution (0.01M): Used to prepare the chromium (III) extraction solution. Prepare by adding 3.92 g ammonium iron (II) sulfate solution to a 125 mL polyethylene bottle. Adjust the pH to 8 with approximately 2 mL of ammonium hydroxide solution. Cap and shake on a wrist-action shaker for 24 hours. This iron (III) hydroxide solution is stable for 30 days.
    - 2.1.4. 10% (v/v) high purity hydrochloric acid solution: Shipped in fluoropolymer wash bottles for cleaning preservation equipment between samples.
    - 2.1.5. Stock chromium standard solution (1000 µg/mL): Prepare by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid or using a commercially prepared solution. Store in a polyethylene bottle.
    - 2.1.6. Chromium spike solution (1000 µg/L): Prepare by adding 1 mL of the chromium stock standard solution to a 1 L flask and dilute to volume with 1% hydrochloric acid. Store in a polyethylene bottle.

2.1.7. On-going precision and recovery standard (OPR): Prepare by spiking 2.5 mL of the chromium spike solution into a 100 mL flask and bringing to volume with 1% hydrochloric acid.

## 2.2. Preservation Protocol

2.2.1. Decant 100 mL of the sample into a clean polyethylene bottle.

2.2.2. Clean an Eppendorf pipet by pipeting 1 mL of 10% hydrochloric acid followed by 1 mL of reagent water. Use the rinsed pipet to add 1 mL of chromium (III) extraction solution to each sample and blank.

2.2.3. Place each sample into a clean polyethylene bag and shake on a wrist-action shaker for 1 hour.

2.2.4. Remove the sample from the shaker and vacuum filter through a 0.4  $\mu$ m, pretreated membrane filter using fluoropolymer forceps to handle the membrane. Rinse the filtration apparatus with 15 mL of reagent water.

2.2.5. Fold the membrane into quarters using the forceps, taking precautions not to touch the filter to any surfaces. Transfer the filter to a 30 mL fluoropolymer vial containing 1 mL of ultrapure nitric acid. If the acid was not previously added to the vial, add it with a pipet that has been rinsed with 1 mL of 10% hydrochloric acid and 1 mL of reagent water.

2.2.6. Cap the vial and double bag it for shipment to the laboratory.

## 3. PRESERVATION OF SAMPLES FOR HEXAVALENT CHROMIUM

### 3.1. Reagents

3.1.1. 10% (v/v) ultrapure hydrochloric acid solution: Shipped in fluoropolymer wash bottles for cleaning preservation equipment between samples.

3.1.2. Sodium hydroxide: Concentrated, 50% solution for field-preserving samples for hexavalent chromium analyses.

### 3.2. Preservation Protocol

3.2.1. Decant 125 mL of sample into a clean polyethylene bottle.

3.2.2. Clean an Eppendorf pipet by pipeting 1 mL of 10% hydrochloric acid followed by 1 mL of reagent water. Use the rinsed pipet to add 1 mL of sodium hydroxide to each 125 mL aliquot.

## 4. PRESERVATION OF SAMPLES FOR MERCURY

### 4.1. Reagents

4.1.1. Hydrochloric Acid: Trace-metal purified reagent-grade hydrochloric acid containing less than 5 pg/mL mercury. The hydrochloric acid should be preanalyzed for Hg before use.

4.1.2. Bromine Monochloride (BrCl): In a fume hood dissolve 27 g of reagent grade potassium bromide (KBr) in 2.5 L of low-mercury HCl. Stir for approximately 1 hour in a fume hood. Slowly add 38 g reagent-grade potassium bromate (KBrO<sub>3</sub>) to the acid while stirring. When all the potassium bromate has been added, the solution color should change from yellow to red to orange. **(Warning: This process generates copious quantities of free halogens. Add the potassium chromate slowly in a fume hood.)** Loosely cap the bottle and continue to stir for 1 hour before tightening the lid.

#### 4.2. Preservation Protocol

4.2.1. Samples are preserved by either adding 5 mL/L of hydrochloric acid or 5 mL/L bromine monochloride.

4.2.2. Samples may be shipped to the laboratory unpreserved if they are:

- Collected in fluoropolymer bottles.
- Filled to the top with no headspace.
- Capped tightly.
- Maintained at 0–4°C from the time of collection until preservation.

4.2.3. If the samples are not preserved immediately upon collection, they must be acid-preserved within 48 hours after sampling.

4.2.4. Samples that are acid-preserved may lose mercury to coagulated organic materials in the water or condensed on the walls. The best approach is to add bromine monochloride directly to the sample bottle at least 24 hours before analysis. If Bromine monochloride cannot be added directly to the sample bottle, the bottle must be shaken vigorously prior to sub-sampling.

### **FS 8260.            QUALITY CONTROL**

1. Equipment blanks must be collected as required in FQ 1000. Follow the clean hands/dirty hands protocol when preparing blanks.

2. Training programs must require sampling personnel to collect a clean equipment blank before performing field activities.

3. The equipment must be demonstrated to be free from the metals of interest before use in the field.

4. Collect the equipment blanks by:

4.1. Filling a large carboy with reagent water in the laboratory and transporting the filled container to the sample site.

4.2. Processing the reagent water through each of the sampling processing steps and equipment (including any filtration equipment if applicable) that will be used in the field.

4.3. Collecting and preserving a blank in one of the project sample containers and transporting it to the laboratory in the same fashion as the other samples.

5. ADDITIONAL QC FOR COLLECTION OF TRIVALENT CHROMIUM ALIQUOTS

5.1. Prepare one method blank on a 100 mL aliquot of analyte-free water for every 10 or fewer samples preserving the sample of analyte-free water using the steps in FS 8250, section 2.2. For dissolved metals do not filter the blank.

5.2. On-going Precision and Recovery (OPR) Sample

5.2.1. Reagents

5.2.1.1. Stock Chromium Standard Solution (1000 µg/mL): Prepare by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid or using a commercially prepared solution. Store in a polyethylene bottle.

5.2.1.2. Chromium Spike Solution (1000 µg/L): Prepare by adding 1 mL of the chromium stock standard solution to a 1L flask and diluting to volume with 1% hydrochloric acid. Store in a polyethylene bottle.

5.2.1.3. On-going Precision and Recovery Standard: Prepare by spiking 2.5 mL of the standard chromium spike solution into a 100 mL flask and bringing to volume with 1% hydrochloric acid.

5.2.2. The sampling team must prepare one on-going precision and recovery standard for every ten or fewer samples. Preserve the OPR standard following the steps in FS 8250, section 2.2.

5.3. Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

5.3.1. Reagents

5.3.1.1. Stock Chromium Standard Solution (1000 µg/mL): Prepare by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid or using a commercially prepared solution. Store in a polyethylene bottle.

5.3.1.2. Chromium Spike Solution (1000 µg/L): Prepare by adding 1 mL of the chromium stock standard solution to a 1 L flask and diluting to volume with 1% hydrochloric acid. Store in a polyethylene bottle.

5.3.2. If the background of the sample is known through historical data, spike the MS and MSD at a level of 1 to 5 times the background concentration.

5.3.3. If the background concentration is unknown, spike the MS and MSD at 25 µg/L.

5.3.4. Prepare the MS/MSD by spiking a 100 mL aliquot of the sample with 2.5 mL of the standard chromium spike solution and preserve the MS/MSD by following the steps in FS 8250, section 2.2.

5.3.5. The sampling team must prepare one MS and one MSD for every ten or fewer samples.

**APPENDIX FS 8200**  
**Tables, Figures and Forms**

Table FS 8200-1 Analytical Methods, Metals, and Concentration Levels Applicable to Clean Sampling

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FS 8200 Clean Sampling For Ultratrace Metals in Surface Waters

Table FS 8200-1

Analytical Methods, Metals, and Concentration Levels Applicable to Clean Sampling

| Method | Technique                    | Metal        | MDL (µg/L) |
|--------|------------------------------|--------------|------------|
| 1631   | Oxidation/Purge & Trap/CVAFS | Mercury      | 0.0002     |
| 1632   | Hydride AA                   | Arsenic      | 0.003      |
| 1636   | Ion Chromatography           | Chromium VI  | 0.23       |
| 1637   | CC/STGFAA                    | Cadmium      | 0.0075     |
|        |                              | Lead         | 0.036      |
| 1638   | ICP/MS                       | Antimony     | 0.0097     |
|        |                              | Cadmium      | 0.013      |
|        |                              | Copper       | 0.087      |
|        |                              | Lead         | 0.015      |
|        |                              | Nickel       | 0.33       |
|        |                              | Selenium     | 0.45       |
|        |                              | Silver       | 0.029      |
|        |                              | Thallium     | 0.0079     |
|        |                              | Zinc         | 0.14       |
| 1639   | STGFAA                       | Antimony     | 1.9        |
|        |                              | Cadmium      | 0.023      |
|        |                              | Chromium III | 0.1        |
|        |                              | Nickel       | 0.65       |
|        |                              | Selenium     | 0.83       |
|        |                              | Zinc         | 0.14       |
| 1640   | CC/ICP/MS                    | Cadmium      | 0.0024     |
|        |                              | Copper       | 0.024      |
|        |                              | Lead         | 0.0081     |
|        |                              | Nickel       | 0.029      |