

U.S.EPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

FIELD SAMPLING GUIDANCE DOCUMENTS #1229

TRACE METAL CLEAN SAMPLING OF NATURAL WATERS

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SOP #1229

TRACE METAL CLEAN SAMPLING OF NATURAL WATERS

1.0 Scope and Application

This Standard Operating Procedure (SOP) describes collection, handling, filtration, preservation and quality control procedures for sampling natural waters. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples. Samples will be subsequently analyzed for determination of total recoverable metals and/or dissolved (<0.45 µm) metals. It is designed to prevent contaminating ambient water samples with the metal(s) of interest and to yield accurate measurement via proposed EPA analytical methods listed in Table 1. Implementation of these sampling techniques supports water quality monitoring and permitting programs administered under the Clean Water Act. This SOP is derived from EPA Method 1669, *Sampling Ambient Water for Determinations of Metals at EPA Water Quality Criteria Levels*.

This SOP is applicable to the metals listed below and other metals, metals species, and elements amenable to determination at trace levels; i.e., ambient concentrations in the part-per-trillion (ppt) to low part-per-billion (ppb) range. It is not intended for determination of metals normally found in untreated discharges from industrial facilities, in-process waters, landfill leachates, processed inorganic substances and other samples containing mid- to high-level (part-per-thousand to part-per-million) concentrations of the analytes listed below.

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium (III)	Cr ⁺³	16065-83-1
Chromium (VI)	Cr ⁺⁶	18540-29-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

This SOP includes techniques to maximize the ability of the sampling team to reliably collect samples, eliminate sample contamination, and maintain sample integrity during filtration and preservation. Procedures for manual sampling, grab sampling, continuous-flow sampling, field filtering and re-cleaning sampling equipment in the field are explained in Section 7.0. These clean techniques are based on findings of researchers collecting and performing trace metal analyses in aqueous samples from natural waters including pristine streams, large lakes, bays or oceanic waters.

For dissolved metal determinations, samples must be filtered through a 0.45 µm pore size capsule filter at

the field site. The filtering procedures are described in this method. The filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in this sampling method; whereas procedures for laboratory preservation are provided in the analytical methods referenced in Table 1. Field preservation requirements are summarized in Table 2.

It cannot be overemphasized as to the ease of contaminating ambient water samples with the metal(s) of interest and/or interfering substances. The only way to measure the performance of these clean techniques is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the methods in Table 1. Thus it is a performance based sampling method; it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before ambient water samples are collected.

The terms "clean" and "ultraclean" have been used in other Agency guidance to describe the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this sampling method due to a lack of exact definitions.

Procedures outlined below are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality control levels.

2.0 METHOD SUMMARY

This SOP describes field sampling procedures commonly referred to as "clean hands, dirty hands" techniques. Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery (pump), and for all other activities that do not involve direct contact with the sample.

The "clean hands, dirty hands" technique has been included and adapted for three methods to collect natural waters samples. **Manual sampling** is the simplest and requires the least equipment. Subsurface samples are collected by either grab immersion sampling or pumping the sample to the surface. **Grab sampling** with a specialized device can be used to collect discrete samples and can conveniently obtain samples at several depths. **Continuous flow sampling** via pump systems is used to collect numerous samples at various depths. **Field filtering** and **re-cleaning** equipment in the field are also included in this SOP since they apply to three sampling methods.

The success of trace metal clean sampling depends upon the sampling personnel. Section 4 details contamination problems, which must be acknowledged and adapted by field samplers both in the laboratory prior to arrival at the site as well as during the sampling event. *This new mind-set needs to be accepted as doctrine by the samplers* (see Section 4 & 7).

Trace metal clean sampling does not require sophisticated sampling equipment. It does require metal-free sampling apparatus and sufficient re-training of personnel to modify collection procedures to maintain sample integrity; e.g., minimize contamination sources. To achieve low detection levels in ambient water samples, personnel must complete significant preparation in the laboratory prior to travelling to the sampling site. Also, they must evaluate the environmental conditions which may affect sampling free of

contamination. For example, whenever possible, samples are collected facing upstream and upwind to minimize introduction of contamination. Another example is to manually fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter. This equipment is scrupulously cleaned to be free of metal contamination as outlined in SOP #140–Trace Metal Labware cleaning procedures.

EPA protocol calls for field filtration to collect samples for dissolved metals. Unpreserved samples are filtered through a 0.45 µm capsule filter at the field site. After filtering, the samples are double-bagged and iced immediately. Sample containers are shipped to the analytical laboratory.

Acid preservation of samples (unfiltered and filtered) can be performed either in the field or the laboratory. The sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination since it can be performed under HEPA filters inside a Class 100 clean bench. Samples can be field preserved inside a glove box designed to provide a particulate free environment.

Via SOP #140, the laboratory is responsible for generating an acceptable equipment blank to demonstrate the sampling equipment and most notably sample containers are free from trace metals contamination before used by the field sampling team. An acceptable blank is one that is free from contamination below the quantitation level (QL) specified in analytical method 1640.

Quality control samples must be collected while sampling in the field. This includes equipment blanks, field blanks, field duplicates. The laboratory or cleaning facility must prepare a large carboy or other appropriate clean container filled with reagent water for use with collection of field blanks during sampling activities. The reagent-water-filled container should be shipped to the field site and handled as all other sample containers and sampling equipment.

NOTE: Specific details for collecting aqueous mercury samples are provided in italics.

3.0 SAMPLE CONTAINERS, HANDLING, PRESERVATION AND STORAGE

Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.

Before samples are collected, all sampling devices and sample containers are cleaned in a laboratory using detergent, mineral acids, and reagent water. Most sampling devices and containers must be constructed of nonmetallic material and free from material that contains metals. Acceptable materials are high- and low-density polyethylene, polycarbonate, or polypropylene, unless mercury is the target analyte when fluoropolymers (FEP, PFA or PTFE) are required. Details on material construction can be found in section 5. Sample containers must be acid-cleaned and prepared for field use in a class 100 clean room. After cleaning, sample containers are filled with weak acid solution, individually double-bagged, and shipped to the sampling site. All sampling equipment is also bagged for storage or shipment.

Samples collected for dissolved metal determinations are to be filtered in the field (section 7.4). They can be acid preserved in the field or in the laboratory. Field preservation may introduce undesired contamination; therefore laboratory preservation is recommended.

4.0 CONTAMINATION PROBLEMS AND INTERFERENCES

Much of the historical metals data in samples from natural waters are inaccurate due to contamination from sampling methods or containers. In the mid-1970's, when analytical chemists devised new techniques and applied them to environmental sampling, then it was revealed much of the ambient waters trace metals data were erroneously high. Preventing contamination of aqueous samples during the sampling, handling and analytical process is the greatest challenge faced in accurate trace metals determinations. Thus, it is imperative samplers use forethought while considering sampling orientation at the site. Also samplers must practice extreme care to reduce contamination and avoid compromising the integrity of ambient water samples.

Thorough presentation of requirements and suggestions for controlling sample contamination are given in corresponding EPA sampling Method 1669 and EPA analytical methods (e.g., Method 1640) listed in Table 1.

Contamination Control

There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact (hair or dental work) can be a source of trace metal contamination.

Use metal-free Apparatus—When possible obtain and use equipment that is completely free of the metal(s) of interest. Only fluoropolymer (FEP, PFA), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz should come in contact with the samples. PFA is less desirable than FEP due to expense. Regardless of construction, all materials that will directly or indirectly contact the sample must be cleaned prior to use (see SOP 140).

Avoiding contamination—Avoid exposure of the sample and sampling apparatus by performing operations in an area known to be free from contamination. Two of the most important factors are: (1) awareness of potential sources of contamination and (2) strict attention to work being performed.

Minimize exposure—Contact or expose samples or blanks only in a clean room, under a clean bench, inside a glove box, or clean plastic bag, so that exposure to atmospheric inputs is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean, colorless zip-type bags (most convenient).

Wear gloves—Personnel must wear clean, nontalc gloves (Section 5.0) while handling the Apparatus, samples and blanks. If another object or substance is touched, the glove(s) must be changed before handling the Apparatus again.

Contamination by carryover—At sites where more than one sample will be collected, the sample known or expected to contain the lowest concentration of metals should be collected first with the sample containing the highest levels collected last (Section 7). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. Without prior knowledge of the waterbody,

sampling team should rinse the collection equipment with dilute acid and reagent water between samples and then collect a field blank (Section 7.5).

Contamination by indirect contact—Apparatus that may not directly contact samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

Contamination by airborne particulate matter—Samples may easily be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or nearby roads; and even human breath (mercury amalgam in dental fillings). Muddy rain gear has the potential to contaminate samples, so it must be free of dirt and particulate matter prior to sampling. This is also true of dried sediment particles inside a boat, wash the boat prior to sampling whenever possible. Areas where nearby soil is bare and subject to wind erosion should be avoided.

Contamination by samples—This *sampling method is not intended for application to samples containing high concentrations (part per thousand to part per million) of metals* such as untreated effluents, landfill leachates, in-process waters. Such high level samples must NOT be collected, processed, or shipped with ambient samples being collected for trace metals determinations.

Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 11 of this sampling SOP. Additional techniques are described in analytical methods in Table 1.

5.0 EQUIPMENT/APPARATUS

All sampling equipment and sample containers must be pre-cleaned in a laboratory or cleaning facility, before they are shipped to the field site. Cleaning procedures are described in SOP# 140; or more briefly in Section 3.0. Clean equipment should be packaged and arranged to minimize field preparation. Here is a quick checklist of sampling apparatus; additional comments for most items appear later in this section.

Sample Bottles—pre-cleaned, of either polyethylene or fluoropolymer construction material

Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; wrist and or shoulder-length

Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes)

Plastic Wrap—Clean, colorless polyethylene

Double bagged ice packs—to keep samples chilled in the cooler during shipment

Cooler—Clean, nonmetallic, with white interior for shipping samples

Filter—0.45 μm , 15 mm diameter or larger, encapsulated filters, OR

Filters—0.4 μm , 47 mm polycarbonate Nuclepore (or equivalent) used with vacuum filtration setup

Filter holder—plastic material with plastic clamps, for mounting filter to the gunwale of the boat

Pump and Pump Apparatus—peristaltic or submersible type for continuous flow sampling
Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, or equivalent
Tubing and connectors—sufficient length and extra "barbed" straight connectors
Carboy—for collection and storage of dilute waste acids used to store bottles
Eppendorf auto pipet and colorless pipet tips—(optional) for acid preservation in field
Fluoropolymer wash bottles—one filled with DI water, one with high-purity 10% HCl for rinsing
Metal-free sampling pole—for extension of sampling tubing away from the boat gunwhales
Field-Portable Glove Bag—portable, non-metallic or equivalent, covered with inexpensive polyethylene bag.

When possible obtain and use equipment that is completely free of the metal(s) of interest. Only fluoropolymer, conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz should come in contact with the samples. *Fluoropolymer* (FEP, PFA, or PTFE) *or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of other materials, resulting either in contamination or low-biased results (Reference 3).* Avoid use of Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, avoid material such as highly colored plastics, paper cap liners, pigments (used to mark increments on plastics and rubber) all of which contain trace levels of metals. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 6).

Materials such as gloves, storage bags, and plastic wrap, may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either a different supplier must be obtained or the materials must be cleaned.

Sample Bottles—Fluoropolymer (FEP, PFA), conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL or 1 L with lids. *If mercury is a target analyte, FEP bottles must be used.* Previously cleaned sample bottles (SOP# 140) should be filled with 0.1% HCl (v/v); individually stored in double plastic bags. In most cases, it may be possible to empty the weak acid solution from the sample bottle immediately prior to transport to the field site.

Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.

The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 14). Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials *unless mercury* is a target analyte.

An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination.

Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by continuous-flow pumping of water into a sample bottle (new Figure 3).

Pump and Pump Apparatus—peristaltic or submersible type. Required for use with the jar sampling system (Section 6.5.1) or the continuous-flow system (Section 6.5.2). Peristaltic pump; 115 V a.c., 12 V d.c., internal battery, variable-speed, single-head, Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent.

Peristaltic pumps do not require cleaning; however, touching the metal head and metal controls necessitates changing of gloves before touching the Apparatus. If a submersible pump is used, a large volume of sample should be pumped to clean the stainless steel shaft (hidden behind the impeller) that comes in contact with the sample. Pumps with metal impellers should not be used.

Flexible tubing—for use with peristaltic pump. SEBS resin, approximately 3/8 in. i.d. by approximately 3 ft, Cole-Parmer size 18, Cat. No. G-06464-18, or approximately 1/4 in. i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent. Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

Hard case Tubing—For connection to peristaltic flexible pump tubing. Fluoropolymer, 3/8 or 1/4 in. o.d., in lengths as required to reach the point of sampling. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required.

Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.

Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.

Continuous-flow sampler—(depicted in new Figure 3), consists of a peristaltic or submersible pump and one or more lengths of precleaned fluoropolymer or styrene/ethylene/butylene/ silicone (SEBS) tubing. A filter is added to the sampling train immediately prior to sampling for dissolved metals. Easy to use, more work required prior to arriving at field site.

Advantages of this flow-through sampling system include (1) all wetted surfaces are fluoropolymer or SEBS and can be readily cleaned; (2) the suction device is located in the boat, isolated from the sample bottle; (3) the sample does not travel through long lengths of tubing that are difficult to clean and keep clean; and (4) in-line filtration is possible, minimizing field handling requirements for dissolved metals samples.

Boat--For most sampling situations (i.e., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping. Immediately before use, the boat should be

washed to remove any dust or dirt accumulation. All samples should be collected upstream of boat movement and upwind of any fossil fuel exhaust.

When sampling for mercury, a fiberglass boat with battery-powered engine and wooden or fiberglass oars is preferred. Before first use, the boat should be washed and stored in an area that minimizes exposure to dust and atmospheric particles. If motor engine is required (remember that gasoline or diesel motor exhaust can be a source of contamination), it should be shut off at a distance far enough from the sampling point to avoid contamination, then the sampling team should manually propel the boat to the sampling point. Personnel may wear an unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber to prevent mercury adsorbed onto cotton or other clothing materials from contaminating samples. (See Method 1631 or 1669 for more explanation.)

6.0 REAGENTS

"Trace-metal grade" reagents must be used in place of "reagent grade" chemicals because acids, bases and other materials labeled "reagent grade" contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

- 6.1 Reagent Water—Water in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method used for analysis of samples. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other techniques that remove the metal(s) and potential interferent(s). A large carboy or other appropriate container filled with reagent water must be available for the collection of field blanks.
- 6.2 Hydrochloric acid—Dilute (10%), trace-metal grade, shipped with sampling kit for cleaning equipment between samples.
- 6.3 Nitric acid—Dilute (10%), trace-metal grade, shipped with sampling kit for cleaning equipment between samples.

7.0 PROCEDURES

Site Selection--Overview of Sampling Considerations

Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.

Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are

vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples.

To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow.

The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.

When sampling from a boat, the bow of the boat should be oriented into the current (the boat will be pointed upstream). Ideally, the team should approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the boat or equipment. All sampling activity should occur from the bow, preferably pointed upwind and upstream.

If the samples are being collected from a boat, it is recommended that the sampling team create a stable workstation by arranging the cooler or shipping container as a work table on the upwind side of the boat, covering this worktable and the upwind gunnel with plastic wrap or a plastic tablecloth, and draping the wrap or cloth over the gunnel. If necessary, duct tape is used to hold the wrap or cloth in place.

Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may require a good deal of coordination and practice. For example, "dirty hands" must open the box or cooler containing the sample bottle and unzip the outer bag; clean hands must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place it in a cooler.

All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (if the sample is not directly collected in the bottle) are handled by the individual designated as "clean hands." "Dirty hands" is responsible for all activities that do not involve direct contact with the sample; e.g., sample documentation.

Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. *For mercury sampling, samplers should avoid breathing directly on the sample.*

Before heading off to the sampling site, the sampling team should consider the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface

samplers). Sufficient sample volume should be collected to allow for necessary quality control analyses, such as sample duplicates, matrix spike/matrix spike duplicate analyses and various blanks (Section 9). This SOP describes three sampling procedures: manual collection, grab sampling with device, and continuous flow sampling, i.e., with pumps.

7.1 Manual Sampling--collection of surface samples directly into the sample bottle

At the site, all sampling personnel must put on clean gloves (Section 5) before commencing sample collection activity. Note that "clean hands" should put on shoulder-length polyethylene gloves and "dirty hands" should put on wrist length PVC gloves.

If samples are to be analyzed for mercury, the sampling team must also put their precleaned wind suits on at this time.

7.1.1 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

7.1.2 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

7.1.3 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes (Section 5) or discards the reagent water directly into the water body.

7.1.4 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.

7.1.5 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

7.1.6 "Dirty hands" zips the outer bag.

7.1.7 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedure described in Section 7.4.

7.1.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

7.2 Grab Sampling--collection with grab sampling device

The following steps detail sample collection using the grab sampling device shown in Figure 1. The procedure is indicative of the "clean hands/dirty hands" technique that must also be used with alternative grab sampling devices.

The sampling team puts on gloves. Ideally, a sample bottle will have been preattached to the sampling device in the laboratory. If it is necessary to attach a bottle to the device in the field, "clean hands" performs this operation inside the field-portable glove bag.

- 7.2.1 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.
 - 7.2.2 "Clean hands" opens the inside polyethylene bag and removes the sampling device.
 - 7.2.3 "Clean hands" changes gloves.
 - 7.2.4 "Dirty hands" submerges the sampling device to the desired depth and pulls the fluoropolymer pull cord to bring the seal plate into the middle position so that water can enter the bottle.
 - 7.2.5 When the bottle is full (i.e., when no more bubbles appear), "dirty hands" pulls the fluoropolymer cord to the final stop position to seal off the sample and removes the sampling device from the water.
 - 7.2.6 "Dirty hands" returns the sampling device to its large inner plastic bag, "clean hands" pulls the bottle out of the collar, unscrews the bottle from the sealing device, and caps the bottle. "Clean hands" and "dirty hands" then return the bottle to its double-bagged storage.
 - 7.2.7 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the grab sampler, rinses the device with reagent water (Section 6.1), places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.
 - 7.2.8 Sampling device—"Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.
 - 7.2.9 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedure described in Section 7.4.
 - 7.2.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.
- 7.3 Continuous Flow Sampling**--uses peristaltic pump to pump sample through the pre-cleaned tubing on to boat, shore, or dock to collect sample.
- 7.3.1 Before putting on wind suits or gloves, the sampling team removes the bags containing the pump, SEBS-resin tubing, batterie), gloves, plastic wrap, wind suits, and, if samples are to be filtered, the filtration apparatus from the coolers or storage containers in which they are packed.
 - 7.3.2 "Clean hands" and "dirty hands" put on PVC gloves.
 - 7.3.3 "Dirty hands" removes the pump from its storage bag, and opens the bag containing the SEBS-

resin tubing.

- 7.3.4 "Clean hands" installs the tubing while "dirty hands" holds the pump. "Clean hands" immerses the inlet end of the tubing in the sample stream.
- 7.3.5 Both "clean hands" and "dirty hands" change gloves. "Clean hands" also puts on shoulder length polyethylene gloves.
- 7.3.6 "Dirty hands" turns the pump on and allows the pump to run for 5-10 minutes or longer to purge the pump and tubing.
- 7.3.7 If the sample is to be filtered, "clean hands" installs the pre-cleaned cartridge filter at the end of the tubing, and "dirty hands" sets up the filter holder on the gunwale as shown in Figure 4.

NOTE: *The filtration apparatus is not attached while flushing the sample tubing with ambient water, rather wait until immediately before sampling to prevent buildup of particulates from clogging the filter.*

- 7.3.8 The sample is collected by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.
- 7.3.9 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

7.4 Field Filtering

Sample Filtration—The filtration procedure described below is used for samples collected using the manual or grab collection systems. This setup describes, in-line filtration using the peristaltic pump or continuous-flow approach because this setup is optimal for reducing contamination. One cartridge can be used for numerous samples although the tubing may need to be either cleaned or exchanged for each new piece.

Because of the risk of contamination, it is recommended that samples for mercury be shipped unfiltered by overnight courier and filtered when received at the laboratory.

- 7.4.1 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.
- 7.4.2 "Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 8.2.5.2 through 8.2.5.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.
- 7.4.3 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.
- 7.4.4 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle

and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.

- 7.4.5 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.
- 7.4.6 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.
- 7.4.7 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle (final volume 500 mL). If preservation is required, the sample is acidified at this point.
- 7.4.8 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."
- 7.4.9 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

7.5 RE-CLEANING EQUIPMENT IN THE FIELD

- 7.5.1 Ideally sampling activity can be planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals collected last. In this manner, cleaning of the sampling equipment between samples is unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment should be provided for each sampling event.
- 7.5.2 If samples are collected from adjacent sites (e.g., immediately upstream or downstream), rinsing of the sampling Apparatus with water that is to be sampled should be sufficient.
- 7.5.3 If it is necessary to cross a gradient (i.e., going from a high-concentration sample to a low-concentration sample), such as might occur when collecting at a second site, the following procedure may be used to clean the sampling equipment between samples:
 - 7.5.3.1 Inside the glove bag, use the "clean hands/dirty hands" procedure to process the dilute nitric acid solution (Section 7.2) through the Apparatus.
 - 7.5.3.2 Dump the spent dilute acid in the waste carboy or in the waterbody away from the sampling point.
 - 7.5.3.3 Process 1 L of reagent water through the Apparatus to rinse the equipment and discard the spent water.
 - 7.5.3.4 Collect a field blank as described in Section 9.2.
 - 7.5.3.5 Rinse the Apparatus with copious amounts of the ambient water sample and proceed with sample collection.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

The sampling team shall employ a strict quality assurance/ quality control (QA/QC) program. The team **MUST** collect equipment blanks and field replicates. It is also desirable to include equipment and field collection blanks and QC samples.

The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks.

9.1 Equipment Blanks

Before using any sampling equipment at a given site, the laboratory is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device, then an equipment blank must be run on both pieces of equipment. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

Equipment blanks are generated in the laboratory by processing reagent water through the equipment using the same procedures that are used in the field (Section 7.0). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory. Sampling personnel must collect a clean equipment blank before performing on-site field activities.

Detailed procedures for collecting equipment blanks are given in the analytical methods referenced in Table 1. If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank at the minimum level specified in the referenced method, the source of contamination/interference must be identified and removed.

9.2 Field Blank

To demonstrate that sample contamination has not occurred during field sampling and sample processing, at least one field blank must be generated for every 10 samples that are collected at a given site. Field blanks are collected before sample collection.

Field blanks are generated by filling a large carboy or other appropriate container with reagent water (Section 7.1) in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis in accordance with the method(s) referenced in Table 1. For example, manual grab sampler field blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler field blanks are collected by immersing the tubing into the water and pumping water into a sample container.

Filter the field blanks using the procedures described in Section 7.4.

If it is necessary to acid clean the sampling equipment between samples (Section 7.5), a field blank should be collected after the cleaning procedures but before the next sample is collected.

9.3 Field Duplicate

To assess the precision of the field sampling and analytical processes, at least one field duplicate sample must be collected for every 10 samples that are collected at a given site.

The field duplicate is collected either by splitting a larger volume into two aliquots in the glove box, by using a sampler with dual inlets that allows simultaneous collection of two samples, or by collecting two samples in rapid succession. Field duplicates for dissolved metals determinations must be processed using the procedures in Section 7.4.

9.4 MS/MSD—The sampling team must prepare one matrix spike (MS) and one matrix spike duplicate MSD for a 10% minimum of aqueous field samples.

If, through historical data, the background concentration of the sample can be estimated, the MS and MSD samples should be spiked at a level of one to five times the background concentration.

If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 µm filter as described in Section 7.4.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA and specific health and safety procedures.

Decontamination can pose hazards under certain circumstances even though performed to protect health and safety. Hazardous substances may be incompatible with decontamination methods. For example, the decontamination solution or solvent may react with contaminants to produce heat, explosion, or toxic products. Decontamination methods may be incompatible with clothing or equipment; some solvents can permeate or degrade protective clothing. Also, decontamination solutions and solvents may pose a direct health hazard to workers through inhalation or skin contact, or if they combust.

TABLE 1. ANALYTICAL METHODS, METALS, AND CONCENTRATION LEVELS APPLICABLE TO METHOD 1669

Method	Technique	Metal	MDL (µg/L) ¹	ML (µg/L) ²
1631	Oxidation/Purge & Trap/CVAFS	Mercury	0.0002	0.0005
1632	Hydride AA	Arsenic	0.003	0.01
1636	Ion Chromatography	Chromium(VI)	0.23	0.5
1637	CC/STGFAA	Cadmium	0.0075	0.02
		Lead	0.036	0.1
1638	ICP/MS	Antimony	0.0097	0.02
		Cadmium	0.013	0.1
		Copper	0.087	0.2
		Lead	0.015	0.05
		Nickel	0.33	1
		Selenium	0.45	1
		Silver	0.029	0.1
		Thallium	0.0079	0.02
		Zinc	0.14	0.5
1639	STGFAA	Antimony	1.9	5
		Cadmium	0.023	0.05
		Chromium(III)	0.10	0.2
		Nickel	0.65	2
		Selenium	0.83	2
		Zinc	0.14	0.5
1640	CC/ICP/MS*	Antimony	0.01*	
		Arsenic	0.15	
		Beryllium	0.015	
		Cadmium	0.004	
		Chromium	0.03	
		Cobalt	0.004	
		Copper	0.02	
		Lead	0.005	
		Nickel	0.01	
		Selenium	0.015	
		Thallium	0.005	
		Vanadium	0.02	
		Zinc	0.2	

¹ Method Detection Limit as determined by 40 CFR Part 136, Appendix B.

² Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50, etc., in accordance with procedures used by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

*MDL for Method 1640 based upon laboratory work by county environmental lab using “metal clean” seawater as reagent water. Values represent reasonable and achievable MDL levels.

TABLE 2. ANALYTES, PRESERVATION REQUIREMENTS, AND CONTAINERS

Metal	Preservation Requirements	Acceptable Containers
Antimony Arsenic Cadmium Copper Lead Nickel Selenium Silver Thallium Zinc	Add 5 mL of 10% HNO ₃ to 1-L sample; preserve on-site or immediately upon laboratory receipt.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (III)	Add 1 mL chromium (III) extraction solution to 100 mL aliquot, vacuum filter through 0.4 μm membrane, add 1 mL 10% HNO ₃ ; preserve on-site immediately after collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (VI)	Add 50% NaOH; preserve immediately after sample collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Mercury	Total: Add 0.5% high-purity HCl or 0.5% BrCl to pH < 2; Total & Methyl: Add 0.5% high-purity HCL; preserve on-site or immediately upon laboratory receipt	Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps

Addendum: Details for collection and field preservation of aqueous chromium (III) samples

Reagents –

6.4 Sodium Hydroxide – Concentrated, 50% solution for use when field-preserving samples for *hexavalent chromium* determinations (Section 8.4.5).

6.5 For field-processing aliquots for **trivalent chromium** determinations:

Nitric Acid, Ultrapure – For use when field-preserving samples for trivalent chromium determinations

Ammonium Iron (II) Sulfate Solution (0.01M) – Used to prepare the chromium (III) extraction solution (Section 7.4.3) necessary for field preservation of samples for trivalent chromium (Section 8.4.4). Prepare the ammonium iron (II) sulfate solution by adding 3.92 g ammonium iron (II) sulfate (ultrapure grade) to a 1 L volumetric flask. Bring to volume with reagent water. Store in a clean polyethylene bottle.

Chromium (III) extraction solution – For use when field-preserving samples for trivalent chromium determinations (Section 8.4.4). Prepare this solution by adding 100 mL of ammonium iron (II) sulfate solution (Section 7.4.2) to a 125 mL polyethylene bottle. Adjust 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.

Hydrochloric acid – High-purity, 10% solution, shipped with sampling kit in fluoropolymer wash bottles for cleaning trivalent chromium sample preservation equipment between samples.

Chromium stock standard solution (1000 µg/mL) – Prepared by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid. Store in polyethylene bottle. A commercially available standard solution may be substituted.

Standard chromium spike solution (1000 µg/L) – Used to spike sample aliquots for matrix spike/matrix spike duplicate (MS/MSD) analysis and to prepare ongoing precision and recovery standards. Prepared by spiking 1 mL of the chromium stock standard solution (Section 7.4.5) into a 1 L flask. Dilute to volume with 1% HCl. Store in a polyethylene bottle.

Ongoing precision and recovery (OPR) standard (25 µg/L) – Prepared by spiking 2.5 mL of the standard chromium spike solution (Section 7.4.6) into a 100 mL flask. Dilute to volume with 1% HCl. One OPR is required for every 10 samples.

Additional QC for Collection of Trivalent Chromium Aliquots

Method blank – The sampling team must prepare one method blank for every ten or fewer field samples. Each method blank is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on a 100 mL aliquot of reagent water (Section 7.1). Do not use the procedures in Section 8.3 to process the method blank through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

Ongoing precision and recovery (OPR) – The sampling team must prepare one OPR for every ten or fewer field samples. The OPR is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on the OPR standard (Section 7.4.7). Do not use the procedures in Section 8.3 to process the OPR through the 0.45

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σω' ,ΥΥ;ςΩ, κφ 'θ'κΥ'θ 'θ'Ω υ'Υ'Υρε'ω"φυ Υ'ωφΥ'Ωφ"Υ'κωφ κ, "φρφω'φε 'θ'Ω ΦΩ Υφυ ΦΩρ ,ΥΥ;ςΩ, ,θ'ω"ςυ υ'Ω ,;κρ'Ωυ Υ' Υ'Υ'Ω'Ως ωω θK µg/L.

Prepare the matrix spike sample by spiking a 100-mL aliquot of sample with 2.5 mL of the standard chromium spike solution (Section 7.4.6), and processing the MS through the steps in Sections 8.4.4.1 through 8.4.4.6.

Prepare the matrix spike duplicate sample by spiking a second 100-mL aliquot of the same sample with 2.5 mL of the standard chromium spike solution, and processing the MSD through the steps in Sections 8.4.4.1 through 8.4.4.6.

If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 µm filter as described in Section 8.3.