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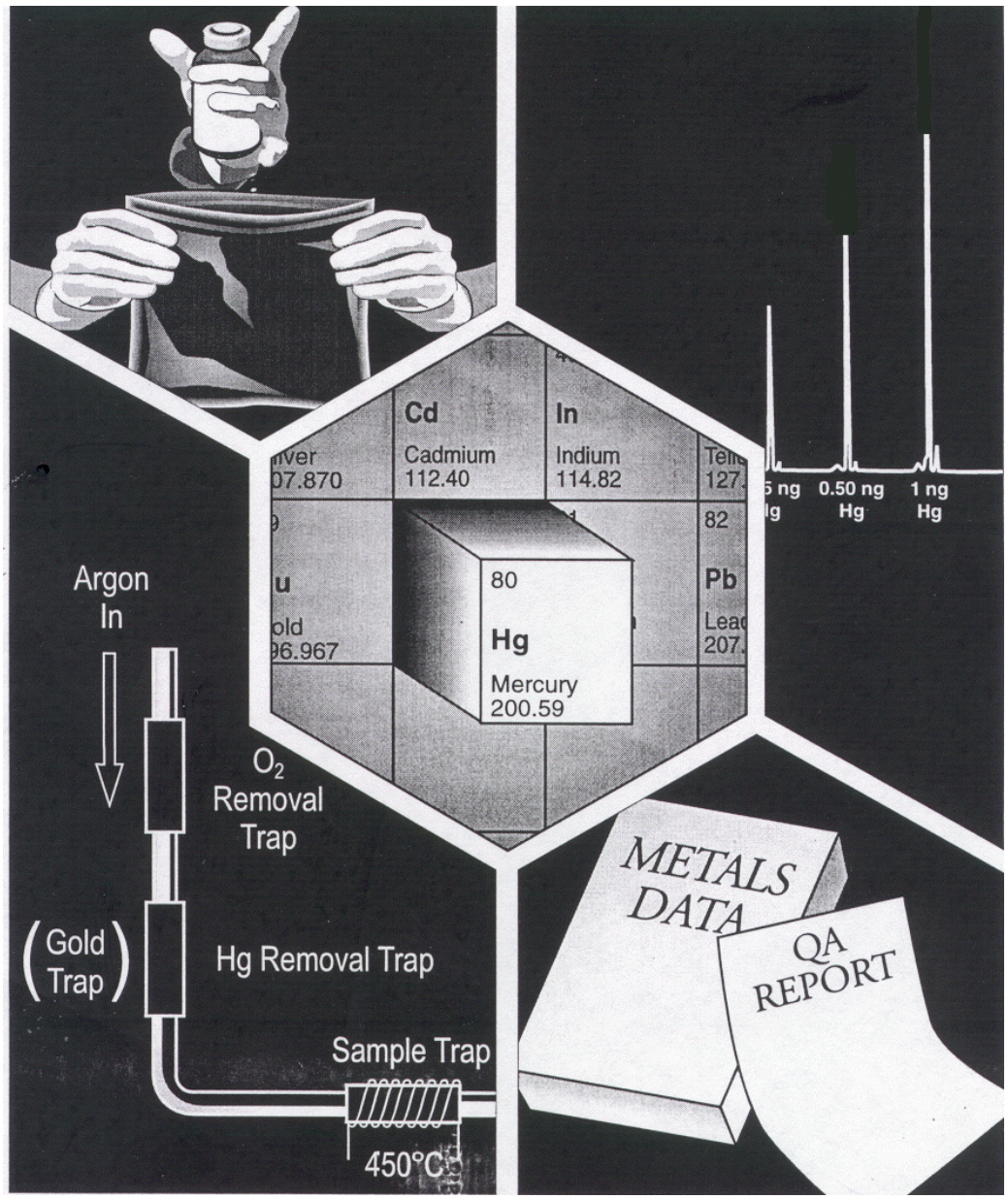
Method 1631, Revision C: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry



Acknowledgments

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Disclaimer

This Method has been reviewed and approved for publication by the Analytical Methods Staff within EPA's Engineering and Analysis Division. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Introduction

Method 1631 (the "Method") supports water quality monitoring programs authorized under the Clean Water Act (CWA; the "Act"). CWA Section 304(a) requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

CWA Section 303 requires each State to set a water quality standard for each body of water within its boundaries. A State water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by CWA Sections 301(b) and 306.

In defining water quality standards, a State may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to CWA required States to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, ambient water quality criteria (WQC) are as much as 280 times lower than levels measurable using approved EPA methods available in the mid-1990s and required to support technology-based permits. EPA developed new sampling and analysis methods to specifically address State needs for measuring toxic metals at WQC levels, when such measurements are necessary to protect designated uses in State water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (58 FR 60848) and the Stay of Federal Water Quality Criteria for Metals (60 FR 22228). These rules include water quality criteria for 13 metals, and it is these criteria that the new sampling and analysis methods address. Method 1631 was specifically developed to provide reliable measurements of mercury at EPA WQC levels.

In developing methods for determination of trace metals, EPA found that one of the greatest difficulties was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. Method 1631 is designed to preclude contamination in nearly all situations. It also contains procedures necessary to produce reliable results at the lowest WQC levels published by EPA. In recognition of the variety of situations to which this Method may be applied, and in recognition of continuing technological advances, Method 1631 is performance based. Alternative procedures may be used so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this Method should be directed to:

U.S. EPA NCEPI
11209 Kenwood Road
Cincinnati, OH 45242
513/489–8190

Note: This Method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this Method are met. The laboratory may not omit any quality control tests. The terms "shall" and "must" define procedures required for producing reliable data at water quality criteria levels. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this Method.

Method 1631, Revision C

Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry

1.0 Scope and Application

1.1 Method 1631, Revision C (the "Method") is for determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). This Method is for use in EPA's data gathering and monitoring programs associated with the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, and the Safe Drinking Water Act. The Method is based on a contractor-developed method (Reference 1) and on peer-reviewed, published procedures for the determination of mercury in aqueous samples, ranging from sea water to sewage effluent (References 2–5).

1.2 This Method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (Sampling Method). The Sampling Method guidance document is recommended to preclude contamination during the sampling process.

1.3 This Method is for determination of Hg in the range of 0.5–100 ng/L and may be extended to higher levels by selection of a smaller sample size.

1.4 The ease of contaminating ambient water samples with mercury and interfering substances cannot be overemphasized. This Method includes suggestions for improvements in facilities and analytical techniques that should minimize contamination and maximize the ability of the laboratory to make reliable trace metals determinations. Section 4.0 gives these suggestions.

1.5 The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrumental limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for Hg has been determined to be 0.2 ng/L when no interferences are present. The minimum level of quantitation (ML) has been established as 0.5 ng/L. An MDL as low as 0.05 ng/L can be achieved for low Hg samples by using a larger sample volume, a lower BrCl level (0.2%), and extra caution in sample handling.

1.6 Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this Method because they lack an exact definition. However, the information provided in this Method is consistent with the summary guidance on clean and ultraclean techniques (References 6-7).

1.7 This Method follows the EPA Environmental Methods Management Council's "Guidelines and Format for Methods to Be Proposed at 40 CFR, part 136 or part 141."

1.8 This Method is "performance based." The laboratory is permitted to modify the Method to overcome interferences or lower the cost of measurements if all performance criteria are met. Section 9.1.2 gives the requirements for establishing method equivalency.

1.9 Any modification of this Method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.10 This Method should be used only by analysts experienced in the use of CVAFS techniques and who are trained thoroughly in the sample handling and instrumental techniques described in this Method. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.11 This Method is accompanied by a data verification and validation guidance document, *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for CWA Compliance Monitoring* (Reference 8), that can be used for verification and validation of the data obtained.

2.0 Summary of Method

2.1 A 100- to 2000-mL sample is collected directly into a specially cleaned, pretested, fluoropolymer bottle using sample handling techniques specially designed for collection of mercury at trace levels (Reference 9).

2.2 For dissolved Hg, the sample is filtered through a 0.45-µm capsule filter.

2.3 The sample is preserved by adding either 5 mL/L of pretested 12N HCl or 5 mL/L BrCl solution. If a sample will also be used for the determination of methyl mercury, it should be preserved with 5 mL/L HCl solution only.

2.4 Prior to analysis, a 100-mL sample aliquot is placed in a specially designed purge vessel, and 0.2N BrCl solution is added to oxidize all Hg compounds to Hg(II).

2.5 After oxidation, the sample is sequentially prereduced with $NH_2OH{\cdot}HCl$ to destroy the free halogens, then reduced with $SnCl_2$ to convert Hg(II) to volatile Hg(0).

2.6 The Hg(0) is separated from solution by purging with nitrogen onto a gold-coated sand trap (Figure 1).

2.7 The trapped Hg is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg(0) into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection (Figure 2).

2.8 Quality is assured through calibration and testing of the oxidation, purging, and detection systems.

3.0 Definitions

3.1 Total mercury—all BrCl-oxidizable mercury forms and species found in an unfiltered aqueous solution. This includes, but is not limited to, Hg(II), Hg(0), strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg, and several tested covalently bound organo-mercurials (e.g., CH_3HgCl, $(CH_3)_2Hg$, and $C_6H_5HgOOCCH_3$). The recovery of Hg bound within microbial cells may require the additional step of UV photo-oxidation. In this Method, total mercury and total recoverable mercury are synonymous.

3.2 Dissolved mercury—all BrCl-oxidizable mercury forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45 micron filter.

3.3 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 that come in contact with the sample and therefore require careful cleaning will be referred to collectively as the Apparatus.

3.4 Definitions of other terms used in this Method are given in the glossary at the end of the Method.

4.0 Contamination and Interferences

4.1 Preventing ambient water samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, marine chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.2 Samples may become contaminated by numerous routes. Potential sources of trace metals contamination during sampling include: metallic or metal-containing labware (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned or stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples directly exposed to exhalation (Reference 9).

4.3 Contamination Control

4.3.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain mercury.

4.3.1.1 The integrity of the results produced cannot be compromised by contamination of samples. This Method and the Sampling Method give requirements and suggestions for control of sample contamination.

4.3.1.2 Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace metals measurements. This Method gives requirements and suggestions for protecting the laboratory.

4.3.1.3 Although contamination control is essential, personnel health and safety remain the highest priority. The Sampling Method and Section 5 of this Method give suggestions and requirements for personnel safety.

4.3.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means

performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being done. Therefore, it is imperative that the procedures described in this Method be carried out by well-trained, experienced personnel.

4.3.3 Use a clean environment—The ideal environment for processing samples is a class-100 clean room. If a clean room is not available, all sample preparation should be performed in a class-100 clean bench or a nonmetal glove box fed by mercury- and particle-free air or nitrogen. Digestions should be performed in a nonmetal fume hood situated, ideally, in a clean room.

4.3.4 Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere 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 zip-type bags. Minimizing the time between cleaning and use will also minimize contamination.

4.3.5 Clean work surfaces—Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water.

4.3.6 Wear gloves—Sampling personnel must wear clean, nontalc gloves during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.3.7 Use metal-free Apparatus—All Apparatus used for determination of mercury at ambient water quality criteria levels must be nonmetallic, free of material that may contain metals, or both.

4.3.7.1 Construction materials—Only fluoropolymer or borosilicate glass (if Hg is the only target analyte) containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of other materials, resulting in results that are biased low or high. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures in this Method and must be known to be clean and mercury free before proceeding.

4.3.7.2 Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to introduction into the instrument. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected.

4.3.7.3 The laboratory or cleaning facility is responsible for cleaning the Apparatus used by the sampling team. If there are any indications that the Apparatus is not clean when received by the sampling team (e.g., ripped storage bags), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.3.8 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.3.8.1 Contamination by carryover—Contamination may occur when a sample containing a low concentration of mercury is processed immediately after a sample containing a relatively high concentration of mercury. When an unusually concentrated sample is encountered, a bubbler blank should be analyzed immediately following the sample to check for carryover. Samples known or suspected to contain the lowest concentration of mercury should be analyzed first followed by samples containing higher levels.

4.3.8.2 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other undiluted samples containing concentrations of mercury greater than 100 ng/L are processed and analyzed. Samples known or suspected to contain Hg concentrations greater than 100 ng/L should be diluted prior to bringing them into the clean room or laboratory dedicated for processing trace metals samples.

4.3.8.3 Contamination by indirect contact—Apparatus that may not directly come in contact with the 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. It is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of water samples be thoroughly cleaned (Section 6.1.2).

4.3.8.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample processing and analysis should occur as far as possible from sources of airborne contamination.

4.3.8.5 Contamination from reagents— Contamination can be introduced into samples from method reagents used during processing and analysis. Reagent blanks must be analyzed for contamination prior to use (see Section 9.4.2). If reagent blanks are contaminated, a new batch of reagents must be prepared (see Section 9.4.2.3).

4.4 Interferences

4.4.1 At the time of promulgation of this method, gold and iodide were known interferences. At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent. At iodide concentrations greater than 3 mg/L, the sample should be pre-reduced with $SnCl_2$ (to clarify the brown color), and additional $SnCl_2$ should be added to the bubbler. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4 N HCl after the analysis (Reference 10).

4.4.2 The potential exists for destruction of the gold traps if free halogens are purged onto them, or if they are overheated (>500 °C). When the instructions in this Method are followed, neither of these outcomes is likely.

4.4.3 Water vapor may collect in the gold traps and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by predrying the gold trap, and by discarding those traps that tend to absorb large quantities of water vapor.

4.4.4 The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms. The dual amalgamation technique eliminates quenching due to trace gases, but it remains the laboratory's responsibility to ensure high purity inert carrier gas and a leak-free analytical train.

5.0 Safety

5.1 The toxicity or carcinogenicity of each chemical used in this Method has not been precisely determined; however, each compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.1.1 Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. Organo-mercurials may cause permanent brain damage. Because of the toxicological and physical properties of Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and the associated risks.

5.1.2 It is recommended that the laboratory purchase a dilute standard solution of the Hg in this Method. If primary solutions are prepared, they shall be prepared in a hood, and a NIOSH/MESA-approved toxic gas respirator shall be worn.

5.2 This Method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current file of OSHA regulations for safe handling of the chemicals specified in this Method. OSHA rules require that a reference file of material safety data sheets (MSDSs) must be made available to all personnel involved in these analyses (29 CFR 1917.28, appendix E). It also is suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this Method and that the results of this monitoring be made available to the analyst. Personal hygiene monitoring should be performed using OSHA or NIOSH approved personal hygiene monitoring methods. Additional information on laboratory safety can be found in References 11-14. The references and bibliography at the end of Reference 14 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 Samples suspected to contain concentrations of Hg at μg/L or higher levels are handled using essentially the same techniques employed in handling radioactive or infectious materials. Well-ventilated, controlled access laboratories are required. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or Labor, many of which have an industrial health service. Each laboratory must develop a safety program for handling Hg.

5.3.1 Facility—When samples known or suspected of containing high concentrations of mercury are handled, all operations (including removal of samples from sample containers, weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leaktight or in a fume hood demonstrated to have adequate airflow. Gross losses to the laboratory ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in an accident.

5.3.2 Protective equipment—Disposable plastic gloves, apron or lab coat, safety glasses or mask, and a glove box or fume hood adequate for radioactive work should be used. During analytical operations that may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters.

5.3.3 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.4 Personal hygiene—Hands and forearms should be washed thoroughly after each manipulation and before breaks (coffee, lunch, and shift).

5.3.5 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.

5.3.6 Effluent vapors—The effluent from the CVAFS should pass through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react mercury vapors.

5.3.7 Waste handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.

5.3.8 Decontamination

5.3.8.1 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.

5.3.8.2 Glassware, tools, and surfaces—Sulfur powder will react with mercury to produce mercuric sulfide, thereby eliminating the possible volatilization of Hg. Satisfactory cleaning may be accomplished by dusting a surface lightly with sulfur powder, then washing with any detergent and water.

5.3.9 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons that convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. If the launderer knows of the potential problem, the

clothing may be put into a washer without contact. The washer should be run through a cycle before being used again for other clothing.

5.3.10 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by this Method can achieve a limit of detection of less than 1 ng per wipe. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

6.0 Apparatus and Materials

Disclaimer: The mention of trade names or commercial products in this Method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Equivalent performance may be achievable using apparatus, materials, or cleaning procedures other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.

6.1 Sampling equipment

6.1.1 Sample collection bottles-Fluoropolymer or borosilicate glass, 125- to 1000-mL, with fluoropolymer or fluoropolymer-lined cap.

6.1.2 Cleaning

6.1.2.1 New bottles are cleaned by heating to 65–75 °C in 4 N HCl for at least 48 h. The bottles are cooled, rinsed three times with reagent water, and filled with reagent water containing 1% HCl. These bottles are capped and placed in a clean oven at 60-70 °C overnight. After cooling, they are rinsed three more times with reagent water, filled with reagent water containing 0.4% (v/v) HCl, and placed in a mercury-free class-100 clean bench until the outside surfaces are dry. The bottles are tightly capped (with a wrench), double-bagged in new polyethylene zip-type bags until needed, and stored in wooden or plastic boxes until use.

6.1.2.2 Used bottles known not to have contained mercury at high (>100 ng/L) levels are cleaned as above, except for only 6–12 h in hot 4 N HCl.

6.1.2.3 Bottle blanks should be analyzed as described in Section 9.4.4.1 to verify the effectiveness of the cleaning procedures.

6.1.3 Filtration Apparatus

6.1.3.1 Filter—0.45-µm, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent)

6.1.3.2 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).

6.1.3.3 Tubing—styrene/ethylene/butylene/silicone (SEBS) resin for use with peristaltic pump, approx 3/8-in ID by approximately 3 ft (Cole-Parmer size 18, Catalog No. G-06424-18, or approximately 1/4-in OD, Cole-Parmer size 17, Catalog No. G-06424-17, or equivalent). Tubing is cleaned by soaking in 5–10% HCl solution for 8–24 h, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

6.2 Equipment for bottle and glassware cleaning

6.2.1 Vat, 100–200 L, high-density polyethylene (HDPE), half filled with 4 N HCl in reagent water.

6.2.2 Panel immersion heater, 500-W, all-fluoropolymer coated, 120 vac (Cole-Parmer H-03053-04, or equivalent)

WARNING: *Read instructions carefully!! The heater will maintain steady state, without temperature feedback control, of 60–75°C in a vat of the size described. However, the equilibrium temperature will be higher (up to boiling) in a smaller vat. Also, the heater plate MUST be maintained in a vertical position, completely submerged and away from the vat walls to avoid melting the vat or burning out!*

6.2.3 Laboratory sink—in class-100 clean area, with high-flow reagent water (Section 7.1) for rinsing.

6.2.4 Clean bench—class-100, for drying rinsed bottles.

6.2.5 Oven—stainless steel, in class-100 clean area, capable of maintaining ± 5°C in the 60–70°C temperature range.

6.3 Cold vapor atomic fluorescence spectrometer (CVAFS): The CVAFS system used may either be purchased from a supplier, or built in the laboratory from commercially available components.

6.3.1 Commercially available CVAFS—Tekran (Toronto, ON) Series 2600 CVAFS, or Brooks-Rand (Seattle, WA) Model III CVAFS, or equivalent

6.3.2 Custom-built CVAFS (Reference 15). Figure 2 shows the schematic diagram. The system consists of the following:

6.3.2.1 Low-pressure 4-W mercury vapor lamp

6.3.2.2 Far UV quartz flow-through fluorescence cell—12 mm x 12 mm x 45 mm, with a 10-mm path length (NSG Cells, or equivalent).

6.3.2.3 UV-visible photomultiplier (PMT)—sensitive to < 230 nm. This PMT is isolated from outside light with a 253.7-nm interference filter (Oriel Corp., Stamford, CT, or equivalent).

6.3.2.4 Photometer and PMT power supply (Oriel Corp. or equivalent), to convert PMT output (nanoamp) to millivolts

6.3.2.5 Black anodized aluminum optical block—holds fluorescence cell, PMT, and light source at perpendicular angles, and provides collimation of incident and fluorescent beams (Frontier Geosciences Inc., Seattle, WA, or equivalent).

6.3.2.6 Flowmeter—with needle valve capable of reproducibly keeping the carrier gas flow rate at 30 mL/min

6.4 Hg purging system—Figure 2 shows the schematic diagram for the purging system. The system consists of the following:

6.4.1 Flow meter/needle valve—capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min.

6.4.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm OD fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm OD fluoropolymer tubing because of its greater flexibility.

6.4.3 Acid fume pretrap—10-cm long x 0.9-cm ID fluoropolymer tube containing 2–3 g of reagent grade, nonindicating, 8–14 mesh soda lime chunks, packed between wads of silanized glass wool. This trap is cleaned of Hg by placing on the output of a clean cold vapor generator (bubbler) and purging for 1 h with N_2 at 350 mL/min.

6.4.4 Cold vapor generator (bubbler)—200-mL borosilicate glass (15 cm high x 5.0 cm diameter) with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Frontier Geosciences, Inc. or equivalent).

6.5 The dual-trap Hg(0) preconcentrating system

6.5.1 Figure 2 shows the dual-trap amalgamation system (Reference 5).

6.5.2 Gold-coated sand traps—10-cm long x 6.5-mm OD x 4-mm ID quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand (Frontier Geosciences Inc., Seattle, WA, or equivalent). The ends are plugged with quartz wool.

6.5.2.1 Traps are fitted with 6.5-mm ID fluoropolymer friction-fit sleeves for making connection to the system. When traps are not in use, fluoropolymer end plugs are inserted in trap ends to eliminate contamination.

6.5.2.2 At least six traps are needed for efficient operation, one as the "analytical" trap, and the others to sequentially collect samples.

6.5.3 Heating of gold-coated sand traps—To desorb Hg collected on a trap, heat for 3.0 min to 450–500 °C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a potential of 10-14 vac. Potential is applied and finely adjusted with an autotransformer.

6.5.4 Timers—The heating interval is controlled by a timer-activated 120-V outlet (Gralab, or equivalent), into which the heating coil autotransformer is plugged. Two timers are required, one each for the "sample" trap and the "analytical" trap.

6.5.5 Air blowers—After heating, traps are cooled by blowing air from a small squirrel-cage blower positioned immediately above the trap. Two blowers are required, one each for the "sample" trap and the "analytical" trap.

6.6 Recorder—Any multi-range millivolt chart recorder or integrator with a range compatible with the CVAFS is acceptable. By using a two pen recorder with pen sensitivity offset by a factor of 10, the dynamic range of the system is extended to 10^3.

6.7 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10 µL to 5.0 mL.

6.8 Analytical balance capable of weighing to the nearest 0.01 g

7.0 Reagents and Standards

7.1 Reagent water—18-MÙ minimum, ultrapure deionized water starting from a prepurified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

7.2 Air—It is very important that the laboratory air be low in both particulate and gaseous mercury. Ideally, mercury work should be conducted in a new laboratory with mercury-free paint on the walls. Outside air, which is very low in Hg, should be brought directly into the class-100 clean bench air intake. If this is not possible, air coming into the clean bench can be cleaned for mercury by placing a gold-coated cloth prefilter over the intake.

7.2.1 Gold-coated cloth filter: Soak 2 m^2 of cotton gauze in 500 mL of 2% gold chloride solution at pH 7. In a hood, add 100 mL of 30% $NH_2OH{\cdot}HCl$ solution, and homogenize into the cloth with gloved hands. The material will turn black as colloidal gold is precipitated. Allow the mixture to set for several hours, then rinse with copious amounts of deionized water. Squeeze-dry the rinsed cloth, and spread flat on newspapers to air-dry. When dry, fold and place over the intake prefilter of the laminar flow hood.

CAUTION: *Great care should be taken to avoid contaminating the laboratory with gold dust. This could cause interferences with the analysis if gold becomes incorporated into the samples or equipment. The gilding procedure should be done in a remote laboratory if at all possible.*

7.3 Hydrochloric acid—trace-metal purified reagent-grade HCl containing less than 5 pg/mL Hg. The HCl should be preanalyzed for Hg before use.

7.4 Hydroxylamine hydrochloride—Dissolve 300 g of $NH_2OH{\cdot}HCl$ in reagent water and bring to 1.0 L. This solution may be purified by the addition of 1.0 mL of $SnCl_2$ solution and purging overnight at 500 mL/min with Hg-free N_2.

7.5 Stannous chloride—Bring 200 g of $SnCl_2{\cdot}2H_2O$ and 100 mL concentrated HCl to 1.0 L with reagent water. Purge overnight with mercury-free N_2 at 500 mL/min to remove all traces of Hg. Store tightly capped.

7.6 Bromine monochloride (BrCl)—In a fume hood, dissolve 27 g of reagent grade KBr in 2.5 L of low-Hg HCl. Place a clean magnetic stir bar in the bottle and stir for approximately 1 h in the fume hood. Slowly add 38 g reagent grade $KBrO_3$ to the acid while stirring. When all of the $KBrO_3$ has been added, the solution color should change from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid.

WARNING: *This process generates copious quantities of free halogens (Cl_2, Br_2, BrCl), which are released from the bottle. Add the $KBrO_3$ slowly in a fume hood!*

7.7 Stock mercury standard—NIST-certified 10,000-ppm aqueous Hg solution (NIST-3133). This solution is stable at least until the NIST expiration date.

7.8 Secondary Hg standard—Add approx 0.5 L of reagent water and 5 mL of BrCl solution (Section 7.6) to a 1.00-L class A volumetric flask. Add 0.100 mL of the stock mercury standard (Section 7.7) to the flask and dilute to 1.00 L with reagent water. This solution contains 1.00 μg/mL (1.00 ppm) Hg. Transfer the solution to a fluoropolymer bottle and cap tightly. This solution is considered stable until the NIST expiration date.

7.9 Working Hg Standard A—Dilute 1.00 mL of the secondary Hg standard (Section 7.8) to 100 mL in a class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 7.6). This solution contains 10.0 ng/mL and should be replaced monthly.

7.10 Working Hg Standard B—Dilute 0.10 mL of the secondary Hg standard (Section 7.8) to 1000 mL in a class A volumetric flask with reagent water containing 0.5% by volume BrCl solution (Section 7.6). This solution contains 0.10 ng/mL and should be replaced monthly.

7.11 IPR and OPR solutions—Using the working Hg standard A (Section 7.9), prepare IPR and OPR solutions at a concentration of 5 ng/L Hg in reagent water.

7.12 Nitrogen—Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap.

7.13 Argon—Grade 5.0 (ultra high-purity, GC grade) that has been further purified by the removal of Hg using a gold-coated sand trap.

8.0 Sample Collection, Preservation, and Storage

8.1 Before samples are collected, consideration should be given to the type of data required, (i.e., dissolved or total), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately before aliquotting for processing or direct analysis to ensure the sample has been properly preserved.

8.2 Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Borosilicate glass bottles may be used if Hg is the only target analyte. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Reference 4). Polyethylene sample bottles must not be used (Reference 15).

8.3 Collect samples using guidance provided in the Sampling Method (Reference 9). Procedures in the Sampling Method are based on rigorous protocols for collection of samples for mercury (References 4 and 15).

NOTE: *Discrete samplers have been found to contaminate samples with Hg at the ng/L level. Therefore, great care should be exercised if this type of sampler is used to collect samples. It may be necessary for the sampling team to use other means of sample collection if samples are found to be contaminated using the discrete sampler.*

8.4 Sample filtration—For dissolved Hg, samples and field blanks are filtered through a 0.45-µm capsule filter (Section 6.1.3.1). The Sampling Method gives the filtering procedures.

8.5 Preservation—Samples are preserved by adding either 5 mL/L of pretested 12N HCl or 5 mL/L BrCl solution. If a sample will be used also for the determination of methyl mercury, it should be preserved with 5 mL/L HCl solution only. Acid- and BrCl-preserved samples are stable for a period of 28 days.

8.5.1 Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, and (4) maintained at 0–4°C from the time of collection until preservation. The samples must be acid-preserved within 48 h after sampling.

8.5.2 Samples that are acid-preserved may lose Hg to coagulated organic materials in the water or condensed on the walls (Reference 16). The best approach is to add BrCl directly to the sample bottle at least 24 hours before analysis. If other Hg species are to be analyzed, these aliquot must be removed prior to the addition of BrCl. If BrCl cannot be added directly to the sample bottle, the bottle must be shaken vigorously prior to sub-sampling.

8.5.3 Handling of the samples in the laboratory should be undertaken in a mercury-free clean bench, after rinsing the outside of the bottles with reagent water and drying in the clean air hood.

NOTE: *Because of the potential for contamination, it is recommended that filtration and preservation of samples be performed in the clean room in the laboratory. However, if circumstances in the field prevent overnight shipment of samples, samples should be filtered and preserved in a designated clean area in the field in accordance with the procedures given in Sampling Method 1669 (Reference 9).*

8.6 Storage—Sample bottles should be stored in clean (new) polyethylene bags until sample analysis. Sample storage and holding time requirements are given at 40 CFR 136.3(e) Table II.

9.0 Quality Control

9.1 Each laboratory that uses this Method is required to operate a formal quality assurance program (Reference 17). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of matrix spikes (MS) and matrix spike duplicates (MSD) to assess accuracy and precision. Laboratory performance is compared to established performance criteria to determine that the results of analyses meet the performance characteristics of the Method.

9.1.1 The laboratory shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this Method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve results or lower the cost of measurements. These options include automation of the dual-amalgamation system, single-trap amalgamation (Reference 18), direct electronic data acquisition, calibration using gas-phase elemental Hg standards, changes in the bubbler design (including substitution of a flow-injection system), or changes in the detector (i.e., CVAAS) when less sensitivity is acceptable or desired. Changes in the principle of the determinative technique, such as the use of colorimetry, are not allowed. If an analytical technique other than the CVAFS technique specified in this Method is used, that technique must have a specificity for mercury equal to or better than the specificity of the technique in this Method.

9.1.2.1 Each time this Method is modified, the laboratory is required to repeat the procedure in Section 9.2 to demonstrate that an MDL (40 CFR Part 136, Appendix B) less than or equal to one-third the regulatory compliance level or less than or equal to the MDL of this Method, whichever is greater, can be achieved. If the change will affect calibration, the instrument must be recalibrated according to Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this Method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and the quality control officer who witnessed and will verify the analyses and modification

9.1.2.2.2 A narrative stating the reason(s) for the modification(s)

9.1.2.2.3 Results from all quality control (QC) tests comparing the modified method to this Method, including the following:

(a) Calibration (Section 10)
(b) Initial precision and recovery (Section 9.2)
(c) Analysis of blanks (Section 9.4)
(d) Matrix spike/matrix spike duplicate analysis (Section 9.3)
(e) Ongoing precision and recovery (Section 9.5)
(f) Quality control sample (Section 9.6)
(g) Method detection limit (Section 9.2.1)

9.1.2.2.4 Data that will allow an independent reviewer to validate each determination by tracking the instrument output to the final result. These data are to include the following:

(a) Sample numbers and other identifiers
(b) Processing dates
(c) Analysis dates
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Copies of logbooks, chart recorder, or other raw data output
(g) Calculations linking raw data to the results reported

9.1.3 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision and to monitor matrix interferences. Section 9.3 describes the procedure and QC criteria for spiking.

9.1.4 Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 9.4 describes the procedures and criteria for analyzing blanks.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control. Sections 9.5 and 9.6 describe these procedures, respectively.

9.1.6 The laboratory shall maintain records to define the quality of the data that are generated. Sections 9.3.7 and 9.5.3 describe the development of accuracy statements.

9.1.7 The determination of Hg in water is controlled by an analytical batch. An analytical batch is a set of samples oxidized with the same batch of reagents, and analyzed during the same 12-hour shift. A batch may be from 1 to as many as 20 samples. Each batch must be accompanied by at least three bubbler blanks (Section 9.4), an OPR sample, and a QCS. In addition, there must be one MS and one MSD sample for every 10 samples (a frequency of 10%).

9.2 Initial demonstration of laboratory capability

9.2.1 Method detection limit—To establish the ability to detect Hg, the laboratory shall achieve an MDL that is less than or equal to the MDL listed in Section 1.5 or one-third the regulatory compliance limit, whichever is greater. The MDL shall be determined according to the procedure at 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this Method. This MDL shall be used for determination of laboratory capability only, and should be determined when a new operator begins work or whenever, in the judgment of the laboratory, a change in instrument hardware or operating conditions would dictate reevaluation of capability.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations:

9.2.2.1 Analyze four replicates of the IPR solution (5 ng/L, Section 7.10) according to the procedure beginning in Section 11.

9.2.2.2 Using the results of the set of four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for Hg.

9.2.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test (Section 9.2.2.1).

9.3 Matrix spike (MS) and matrix spike duplicate (MSD)—To assess the performance of the Method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (1 sample in 10) from a given sampling site or, if for compliance monitoring, from a given discharge.

Therefore, an analytical batch of 20 samples would require two pairs of MS/MSD samples (four spiked samples total).

9.3.1 The concentration of the spike in the sample shall be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of Hg in the sample is being checked against a regulatory compliance limit, the spiking level shall be at that limit or at 1–5 times the background concentration of the sample (as determined in Section 9.3.2), whichever is greater.

9.3.1.2 If the concentration of Hg in a sample is not being checked against a limit, the spike shall be at 1–5 times the background concentration or at 1-5 times the ML in Table 2, whichever is greater.

9.3.2 To determine the background concentration (B), analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established a priori.

9.3.2.1 If necessary, prepare a standard solution to produce an appropriate level in the sample (Section 9.3.1).

9.3.2.2 Spike two additional sample aliquots with the spiking solution and analyze these aliquots as described in Section 11.1.2 to determine the concentration after spiking (A).

9.3.3 Calculate the percent recovery (R) in each aliquot using the following equation:

$$\%\ R \quad 100\ \frac{(A\ \ B)}{T}$$

where:

A *Measured concentration of analyte after spiking*
B *Measured concentration of analyte before spiking*
T *True concentration of the spike*

9.3.4 Compare percent recovery (R) with the QC acceptance criteria in Table 2.

9.3.4.1 If results of the MS/MSD are similar and fail the acceptance criteria, and recovery for the OPR standard (Section 9.5) for the analytical batch is within the acceptance criteria in Table 2, an interference is present and the results may not be reported or otherwise used for permitting or regulatory compliance purposes. If the interference can be attributed to sampling, the site or discharge should be resampled. If the interference can be attributed to a method deficiency, the laboratory must modify the method, repeat the test required in Section 9.1.2, and repeat analysis of the sample and MS/MSD. However, during the development of Method 1631, very few interferences have been noted in the determination of Hg using this Method. (See Section 4.4 for information on interferences.)

9.3.4.2 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be not in control, and the results may

not be reported or used for permitting or regulatory compliance purposes. The laboratory must identify and correct the problem and reanalyze all samples in the sample batch.

9.3.5 Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD results according to the following equation using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.3.3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

$$RPD \quad 200 \times \frac{(|D1 \;\; D2|)}{(D1 \;\; D2)}$$

Where:
D1 *concentration of Hg in the MS sample*
D2 *concentration of Hg in the MSD sample*

9.3.6 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 2. If the criterion is not met, the system is judged to be out of control. The problem must be identified and corrected immediately, and the analytical batch reanalyzed.

9.3.7 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records maintained. After analyzing five samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (R_a) and the standard deviation of the percent recovery (s_r). Express the accuracy assessment as a percent recovery interval from $R_a - 2s_r$ to $R_a + 2s_r$. For example, if $R_a = 90\%$ and $s_r = 10\%$ for five analyses, the accuracy interval is expressed as 70–110%. Update the accuracy assessment regularly (e.g., after every five to ten new accuracy measurements).

9.4 Blanks—Blanks are critical to the reliable determination of Hg at low levels. The sections below give the minimum requirements for analysis of blanks. However, it is suggested that additional blanks be analyzed as necessary to pinpoint sources of contamination in, and external to, the laboratory.

9.4.1 Bubbler blanks—Bubbler blanks are analyzed to demonstrate freedom from system contamination. At least three bubbler blanks must be run per analytical batch. One bubbler blank must be analyzed following each OPR. The mean bubbler blank for an analytical batch, if within acceptance criteria, is subtracted from all raw data for that batch prior to the calculation of results.

9.4.1.1 Immediately after analyzing a sample for Hg, place a clean gold trap on the bubbler, purge and analyze the sample a second time using the procedure in Section 11, and determine the amount of Hg remaining in the system.

9.4.1.2 If the bubbler blank is found to contain more than 50 pg Hg, the system is out of control. The problem must be investigated and remedied, and the samples run on that bubbler must be reanalyzed. If the blanks from other bubblers contain less than 50 pg Hg, the data associated with those bubblers remain valid.

9.4.1.3 The mean result for all bubbler blanks (from bubblers passing the specification in Section 9.4.1.2) in an analytical batch (at least three bubbler blanks) is calculated at the end of the batch. The mean result must be < 25 pg with a standard

deviation of < 10 pg for the batch to be considered valid. If the mean is < 25 pg, the average peak measurement value is subtracted from all raw data before results are calculated.

9.4.1.4 If Hg in the bubbler blank exceeds the acceptance criteria in Section 9.4.1.3, the system is out of control, and the problem must be resolved and the samples reanalyzed. Usually, the bubbler blank is too high for one of the following reasons:

(a) Bubblers need rigorous cleaning;
(b) Soda-lime is contaminated; or
(c) Carrier gas is contaminated.

9.4.2 Reagent blanks—The Hg concentration in reagent blanks must be determined on solutions of reagents by adding these reagents to previously purged reagent water in the bubbler.

9.4.2.1 Reagent blanks are required when the batch of reagents (bromine monochloride plus hydroxylamine hydrochloride) are prepared, with verification in triplicate each month until a new batch of reagents is needed.

9.4.2.2 Add aliquots of BrCl (0.5 mL), NH_2OH (0.2 mL) and $SnCl_2$ (0.5 mL) to previously purged reagent water in the bubbler. Samples high in organic materials may require additional BrCl. In order to evaluate the reagents as a potential source of contamination, the amount of reagent added to the reagent blank(s) must be the same as the amount of reagent added to the sample(s).

9.4.2.3 The presence of more than 25 pg of Hg indicates a problem with the reagent solution. The purging of certain reagent solutions, such as $SnCl_2$ or NH_2OH with mercury-free nitrogen or argon can reduce Hg to acceptable levels. Because BrCl cannot be purified, a new batch should be made from different reagents and should be tested for Hg levels if the level of Hg in the BrCl solution is too high.

9.4.3 Field blanks

9.4.3.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples). Analyze the blank immediately before analyzing the samples in the batch.

9.4.3.2 If Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 2), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.

9.4.3.3 Alternatively, if sufficient multiple field blanks (a minimum of three) are collected, and the average concentration (of the multiple field blanks) plus two standard deviations is equal to or greater than the regulatory compliance limit or equal to or greater than one-half of the level in the associated sample, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.

9.4.3.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.

9.4.4 Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks to demonstrate that the sampling equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampler check blanks.

9.4.4.1 Bottle blanks—After undergoing the cleaning procedures in this Method, bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to pH <2 and allowed to stand for a minimum of 24 h. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that the sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If a bottle shows contamination at or above the level specified for the field blank (Section 9.4.3), the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles recleaned.

9.4.4.2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing sampler check blanks at the laboratory or cleaning facility.

9.4.4.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.1) and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method, Reference 9). For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing a submersible pump or intake tubing into the water and pumping water into a sample container.

9.4.4.2.2 The sampler check blank must be analyzed using the procedures in this Method. If mercury or any potentially interfering substance is detected in the blank at or above the level specified for the field blank (Section 9.4.3), the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from mercury and interferences before the equipment may be used in the field.

9.4.4.2.3 Sampler check 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 a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

9.5 Ongoing precision and recovery (OPR)—To demonstrate that the analytical system is within the performance criteria of this Method and that acceptable precision and accuracy is being maintained within each analytical batch, the laboratory shall perform the following operations:

9.5.1 Analyze the OPR solution (5 ng/L, Section 7.11) followed by a bubbler blank prior to the analysis of each analytical batch according to the procedure beginning in Section 11. An OPR also must be analyzed at the end of an analytical run or at the end of each 12-hour shift. Subtract the peak height (or peak area) of the bubbler blank from the peak height (or area) of the OPR and calculate the concentration for the blank-subtracted OPR.

9.5.2 Compare the concentration recovery with the limits for ongoing precision and recovery in Table 2. If the recovery is in the range specified, the analytical system is control and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not in control. Correct the problem and repeat the ongoing precision and recovery test. All reported results must be associated with an OPR that meets the Table 2 performance criteria at the beginning and end of each batch.

9.5.3 The laboratory should add results that pass the specification in Section 9.5.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory also should develop a statement of laboratory data quality by calculating the average percent recovery (R_a) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from $R_a - 2s_r$ to $R_a + 2s_r$. For example, if $R_a = 95\%$ and $s_r = 5\%$, the accuracy is 85–105%.

9.6 Quality control sample (QCS)—The laboratory must obtain a QCS from a source different from the Hg used to produce the standards used routinely in this Method (Sections 7.7–7.10). The QCS should be analyzed as an independent check of system performance.

9.7 Depending on specific program requirements, the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 20%. If the RPD of the field duplicates exceeds 20%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

10.0 Calibration and Standardization

10.1 Establish the operating conditions necessary to purge Hg from the bubbler and to desorb Hg from the traps in a sharp peak. Further details for operation of the purge and trap and desorption and analysis systems is given in Sections 11.3 and 11.4, respectively. The entire system is calibrated using standards traceable to NIST standard reference material, as follows:

10.1.1 Calibration

10.1.1.1 The calibration must contain five or more non-zero points and the results of analysis of two bubbler blanks. The lowest calibration point must be at the Minimum Level (ML).

10.1.1.2 Standards are analyzed by the addition of aliquots of Hg working standard A (Section 7.9) and Hg working standard B (Section 7.10) directly into the bubblers. Add 0.50 mL of working standard B and 0.5 mL $SnCl_2$ to the bubbler. Swirl to produce a standard of 0.5 ng/L. Purge under the optimum operating conditions (Section 10.1). Sequentially follow with the addition of aliquots of 0.05, 0.25, 0.50 and 1.0 mL of working standard A plus 0.5 mL $SnCl_2$ to produce standards of 5.0, 25.0, 50.0 and 100.0 ng/L.

10.1.1.3 For each point, subtract the mean peak height or area of the bubbler blanks for the analytical batch from the peak height or area for the standard. Calculate the calibration factor (CF_x) for Hg in each of the five standards using the mean bubbler-blank-subtracted peak height or area and the following equation:

$$CF_x = \frac{(A_x)\ (A_{BB})}{(C_x)}$$

Where:

A_x = *peak height or area for Hg in standard*
A_{BB} = *peak height or area for Hg in bubbler blank*)
C_x = *concentration of standard analyzed* (*ng/L*)

10.1.1.4 Calculate the mean calibration factor (CF_m), the standard deviation of the calibration factor (SD), and the relative standard deviation (RSD) of the calibration factor, where RSD = 100 x SD/CF_m.

10.1.1.5 If RSD ≤ 15%, calculate the recovery for the lowest standard (0.5 ng/L) using CF_m. If the RSD ≤ 15% and the recovery of the lowest standard is in the range of 75-125%, the calibration is acceptable and CF_m may be used to calculate the concentration of Hg in samples. If RSD > 15% or if the recovery of the lowest standard is not in the range of 75-125%, recalibrate the analytical system and repeat the test.

10.2 Ongoing precision and recovery—Perform the ongoing precision and recovery test (Section 9.5) to verify calibration prior to and after analysis of samples in each analytical batch.

11.0 Procedure

NOTE: *The following procedures for analysis of samples are provided as guidelines. Laboratories may find it necessary to optimize the procedures, such as drying time or potential applied to the Nichrome wires, for the laboratory's specific instrumental set-up.*

11.1 Sample Preparation

11.1.1 Pour a 100-mL aliquot from a thoroughly shaken, acidified sample, into a 125-mL fluoropolymer bottle. If BrCl was not added as a preservative (Section 8.5), add the amount of BrCl solution (Section 7.6) given below, cap the bottle, and digest at room temperature for a 12 h minimum.

11.1.1.1 For clear water and filtered samples, add 0.5 mL of BrCl; for brown water and turbid samples, add 1.0 mL of BrCl. If the yellow color disappears because of

consumption by organic matter or sulfides, more BrCl should be added until a permanent (12-h) yellow color is obtained.

11.1.1.2 Some highly organic matrices, such as sewage effluent, will require high levels of BrCl (i.e., 5 mL/100 mL of sample), and longer oxidation times, or elevated temperatures (i.e.; place sealed bottles in oven at 50 °C for 6 h). The amount of reagent (including BrCl) added to a sample must be the same as the amount added to a blank to detect contamination in the reagents (see Section 9.4.2.2). The oxidation must be continued until it is complete. Complete oxidation can be determined by either observation of a permanent yellow color remaining in the sample or the use of starch iodide indicating paper to test for residual free oxidizer.

11.1.2 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour two additional 100-mL aliquots from a randomly selected sample, spike at the level specified in Section 9.3, and process in the same manner as the samples. There should be 2 MS/MSD pairs for each analytical batch of 20 samples.

11.2 Hg reduction and purging—Place 100 mL of reagent water in each bubbler, add 1.0 mL of $SnCl_2$, and purge with Hg-free N_2 for 20 min at 300–400 mL/min (Figure 1).

11.2.1 Connect a gold sand trap to the output of the soda lime pretrap, and purge the water another 20 min to obtain a bubbler blank.

11.2.2 Add 0.2 mL of 30% NH_2OH to the BrCl-oxidized sample in the 125-mL fluoropolymer bottle. Cap the bottle and swirl the sample. The yellow color will disappear, indicating the destruction of the BrCl. Allow the sample to react for 5 min with periodic swirling to be sure that no traces of halogens remain.

NOTE: *Purging of free halogens onto the gold trap will result in damage to the trap and low or irreproducible results.*

11.2.3 After discarding the water from the standards, connect a fresh trap to the bubbler, pour the reduced sample into the bubbler, add 0.5 mL of 20% $SnCl_2$ solution, and purge the sample onto a gold sand trap with N_2 for 20 min.

11.2.4 When analyzing Hg samples, the recovery is quantitative, and organic interferents are destroyed. Thus, standards, bubbler blanks, and small amounts of high-level samples may be run directly in the water of previously purged samples. After very high samples, a small degree of carryover (<0.01%) may occur. Bubblers that contain such samples should be blanked prior to proceeding with low level samples.

11.3 Desorption of Hg from the gold trap

11.3.1 Remove the sample trap from the bubbler, place the Nichrome wire coil around the trap and connect the trap into the analyzer train between the incoming Hg-free argon and the second gold-coated (analytical) sand trap (Figure 2).

11.3.2 Pass argon through the sample and analytical traps at a flow rate of approximately 30 mL/min for approximately 2 min to drive off condensed water vapor.

11.3.3 Apply power to the coil around the sample trap for 3 minutes to thermally desorb the Hg (as Hg(0)) from the sample trap onto the analytical trap.

11.3.4 After the 3-min desorption time, turn off the power to the Nichrome coil, and cool the sample trap using the cooling fan.

11.3.5 Turn on the chart recorder or other data acquisition device to start data collection, and apply power to the Nichrome wire coil around the analytical trap. Heat the analytical trap for 3 min (1 min beyond the point at which the peak returns to baseline).

11.3.6 Stop data collection, turn off the power to the Nichrome coil, and cool the analytical trap to room temperature using the cooling fan.

11.3.7 Place the next sample trap in line and proceed with analysis of the next sample.

NOTE: *Do not heat a sample trap while the analytical trap is still warm; otherwise, the analyte may be lost by passing through the analytical trap.*

11.4 Peaks generated using this technique should be very sharp and almost symmetrical. Mercury elutes at approximately 1 minute and has a width at half-height of about 5 seconds.

11.4.1 Broad or asymmetrical peaks indicate a problem with the desorption train, such as improper gas flow rate, water vapor on the trap(s), or an analytical trap damaged by chemical fumes or overheating.

11.4.2 Damage to an analytical trap is also indicated by a sharp peak, followed by a small, broad peak.

11.4.3 If the analytical trap has been damaged, the trap and the fluoropolymer tubing downstream from it should be discarded because of the possibility of gold migration onto downstream surfaces.

11.4.4 Gold-coated sand traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded.

12.0 Data Analysis and Calculations

12.1 Calculate the mean peak height or area for bubbler blanks, "BB" (n = at least 3)

12.2 Calculate the concentration of Hg in ng/L (parts-per-trillion; ppt) in each sample according to the following equation:

$$[Hg]\ (ng/L) \quad \frac{A_s \quad A_{BB}}{CF_m}$$

where:

A_s *peak height (or area) for Hg in sample*

A_{BB} *peak height (or area) for Hg in bubbler blank*

CF_m *mean calibration factor (Section 10.1.1.5)*

12.3 Calculate the concentration of Hg in the reagent blank (C_{RB}), in ng/L, using the equation in Section 12.2 and substituting the peak height or area resulting from the reagent blank for A_s. If the Hg in the reagent blank is attributable to Hg in the BrCl, correct the concentration of Hg in the reagent blank by the volume of BrCl used for the particular sample (Section 11.1.1.2) using the following correction factor:

$$C_{RB} = \frac{V_{BS}}{V_{BRB}}$$

where:
V_{BS} = *volume of BrCl solution used in sample* (*Section* 11.1.1.2)
V_{BRB} = *volume of BrCl solution used in reagent blank* (*Section* 9.4.2.2)

12.4 Reporting

12.4.1 Report results for Hg at or above the ML, in ng/L, to three significant figures. Report results for Hg in samples below the ML as <0.5 ng/L, or as required by the regulatory authority or in the permit. Report results for Hg in reagent blanks and field blanks at or above the ML, in ng/L, to three significant figures. Report results for Hg in reagent blanks or field blanks below the ML but at or above the MDL to two significant figures. Report results for Hg not detected in reagent blanks or field blanks as <0.2 ng/L, or as required by the regulatory authority or in the permit.

12.4.2 Report results for Hg in samples, reagent blanks and field blanks separately. In addition, if blank correction is requested or required by a regulatory authority or in a permit, subtract the concentration of Hg in the reagent blank or the field blank from the concentration of Hg in the test sample to obtain the net Hg concentration in the test sample.

12.4.3 Results from tests performed with an analytical system that is not in control must not be reported or otherwise used for permitting or regulatory compliance purposes, but does not relieve a discharger or permittee of reporting timely results.

13.0 Method Performance

13.1 This method was tested in 12 laboratories using reagent water, freshwater, marine water and effluent (Reference 19). The quality control acceptance criteria listed in Table 2 were verified by data gathered in the interlaboratory study, and the method detection limit (MDL) given in Section 1.5 was verified in all 12 laboratories. In addition, the techniques in this Method have been intercompared with other techniques for low-level mercury determination in water in a variety of studies, including ICES-5 (Reference 20) and the International Mercury Speciation Intercomparison Exercise (Reference 21).

13.2 Precision and recovery data for reagent water, freshwater, marine water, and secondary effluent are given in Table 3.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option. The acids used in this Method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this Method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

14.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872–4477.

15.0 Waste Management

15.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

15.2 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

15.3 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

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17.0 Glossary

The definitions and purposes below are specific to this Method, but have been conformed to common usage as much as possible.

17.1 **Ambient Water**—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

17.2 **Analytical Batch—**A batch of up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include at least three bubbler blanks, an OPR, and a QCS. In addition, MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).

17.3 **Bubbler Blank**—Analyzed to demonstrate freedom from system contamination. Immediately after analyzing a sample, water in the bubbler is purged and analyzed using the same procedure as for the samples to determine Hg. The blank is somewhat different between days, and a minimum of three bubbler blanks must be analyzed per analytical batch. The average of the results for the three bubbler blanks is subtracted from the result of analysis of each sample to produce a final result.

17.4 **Intercomparison Study**—An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.

17.5 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**—Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for these background concentrations.

17.6 **May**—This action, activity, or procedural step is allowed but not required.

17.7 **May not**—This action, activity, or procedural step is prohibited.

17.8 **Minimum Level (ML)**—The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to (1, 2, or 5) x 10^n, where n is an integer.

17.8 **Must**—This action, activity, or procedural step is required.

17.9 **Quality Control Sample (QCS)**—A sample containing Hg at known concentrations. The QCS is obtained from a source external to the laboratory, or is prepared from a source of standards different from the source of calibration standards. It is used as an independent check of instrument calibration.

17.10 **Reagent Water**—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MÙ ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as trip and field blanks, and in the preparation of standards and reagents.

17.11 **Regulatory Compliance Limit**—A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory authority.

17.12 **Shall**—This action, activity, or procedure is required.

17.13 **Should**—This action, activity, or procedure is suggested, but not required.

17.14 **Stock Solution**— A solution containing an analyte that is prepared from a reference material traceable to EPA, NIST, or a source that will attest to the purity and authenticity of the reference material.

17.15 **Ultraclean Handling**— A series of established procedures designed to ensure that samples are not contaminated during sample collection, storage, or analysis.

18.0 Tables and Figures

Table 1

Lowest Ambient Water Quality Criterion for Mercury and the Method Detection Limit and Minimum Level of Quantitation for EPA Method 1631

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[2]	ML[3]
Mercury (Hg)	1.3 ng/L	0.2 ng/L	0.5 ng/L

1. Lowest water quality criterion for the Great Lakes System (Table 4, 40 CFR 132.6). The lowest Nationwide criterion is 12 ng/L (40 CFR 131.36).
2. Method detection limit (40 CFR 136, Appendix B)
3. Minimum level of quantitation (see Glossary)

Table 2

Quality Control Acceptance Criteria for Performance Tests in EPA Method 1631

Acceptance Criteria	Section	Limit (%)
Initial Precision and Recovery (IPR)	9.2.2	
Precision (RSD)	9.2.2.3	21
Recovery (X)	9.2.2.3	79-121
Ongoing Precision and Recovery (OPR)	9.5.2	77-123
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	9.3	
Recovery	9.3.4	71-125
Relative Percent Difference (RPD)	9.3.5	24

Table 3

Precision and Recovery for Reagent Water, Fresh Water, Marine Water, and Effluent Water Using Method 1631

Matrix	*Mean Recovery (%)	*Precision (% RSD)
Reagent Water	98.0	5.6
Fresh Water (Filtered)	90.4	8.3
Marine Water (Filtered)	92.3	4.7
Marine Water (Unfiltered)	88.9	5.0
Secondary Effluent (Filtered)	90.7	3.0
Secondary Effluent (Unfiltered)	92.8	4.5

*****Mean percent recoveries and RSDs are based on expected Hg concentrations.

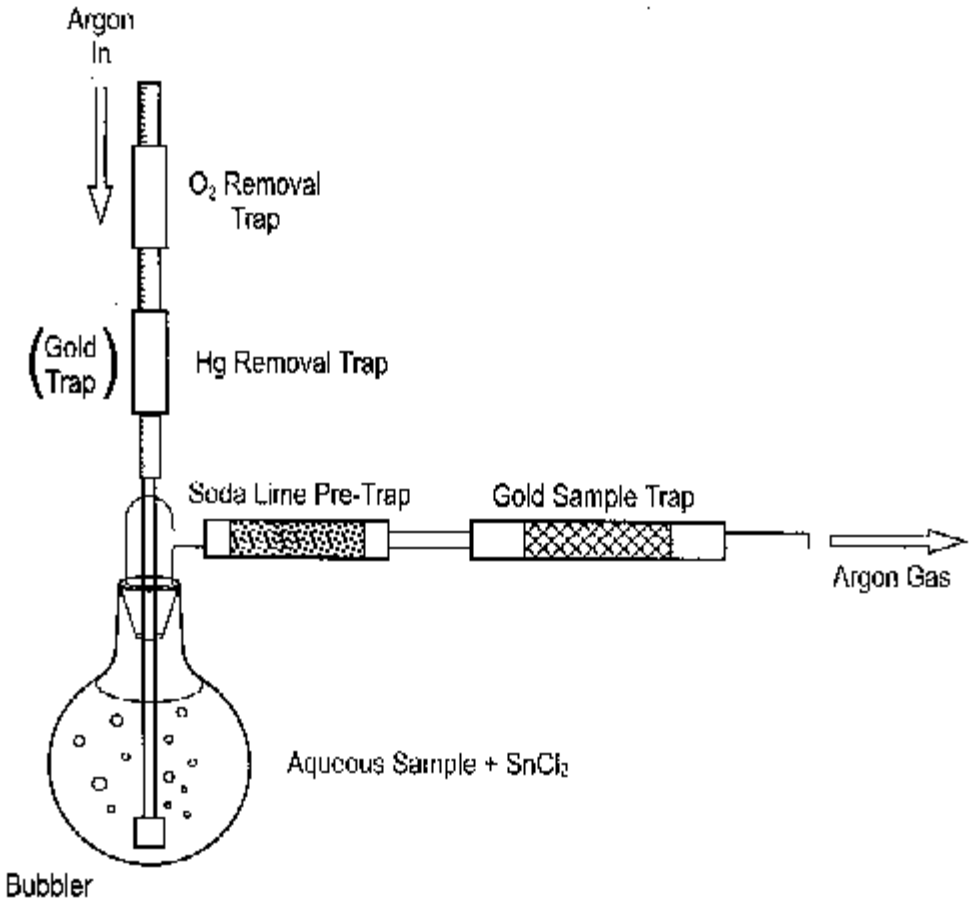

Figure 1. Schematic Diagram of Bubbler Setup

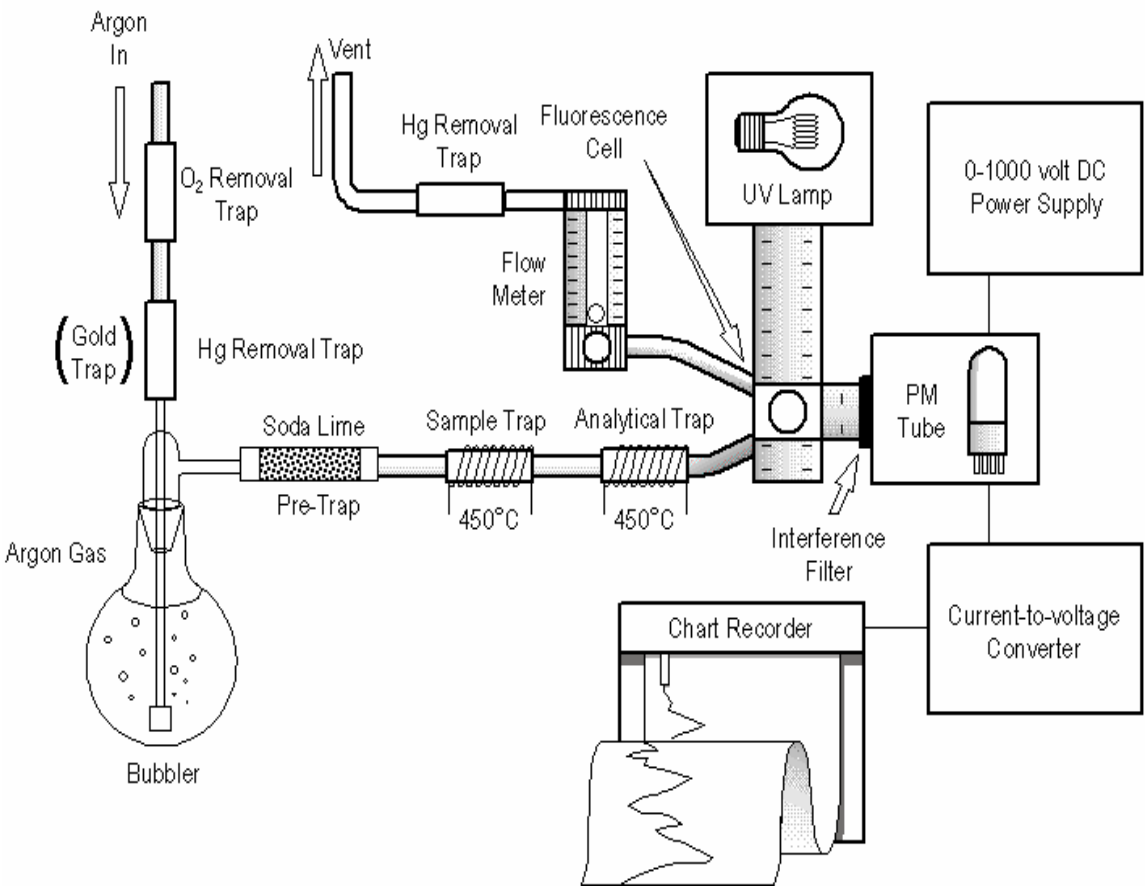

Figure 2. Schematic Diagram of the Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) System