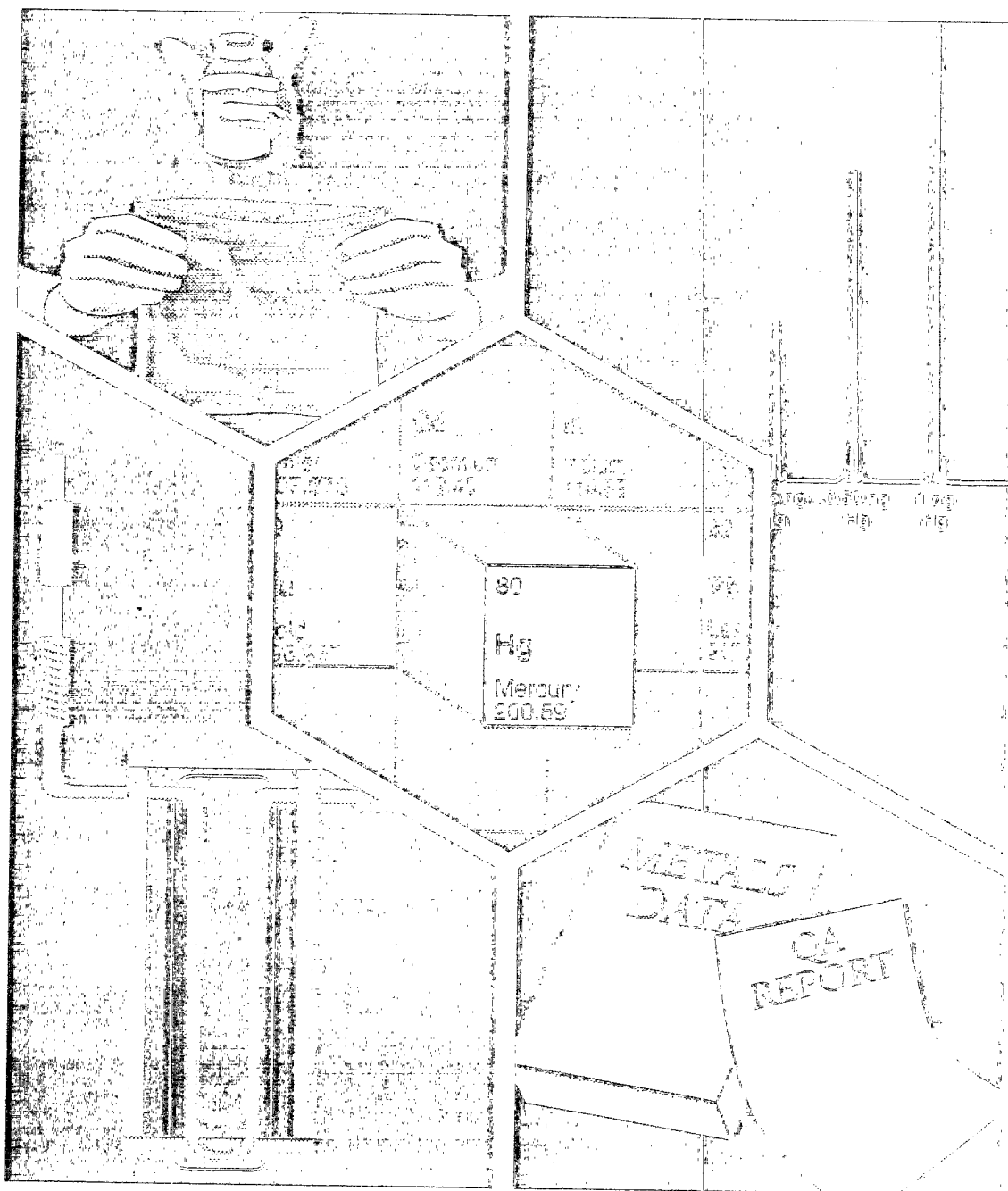




# Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry







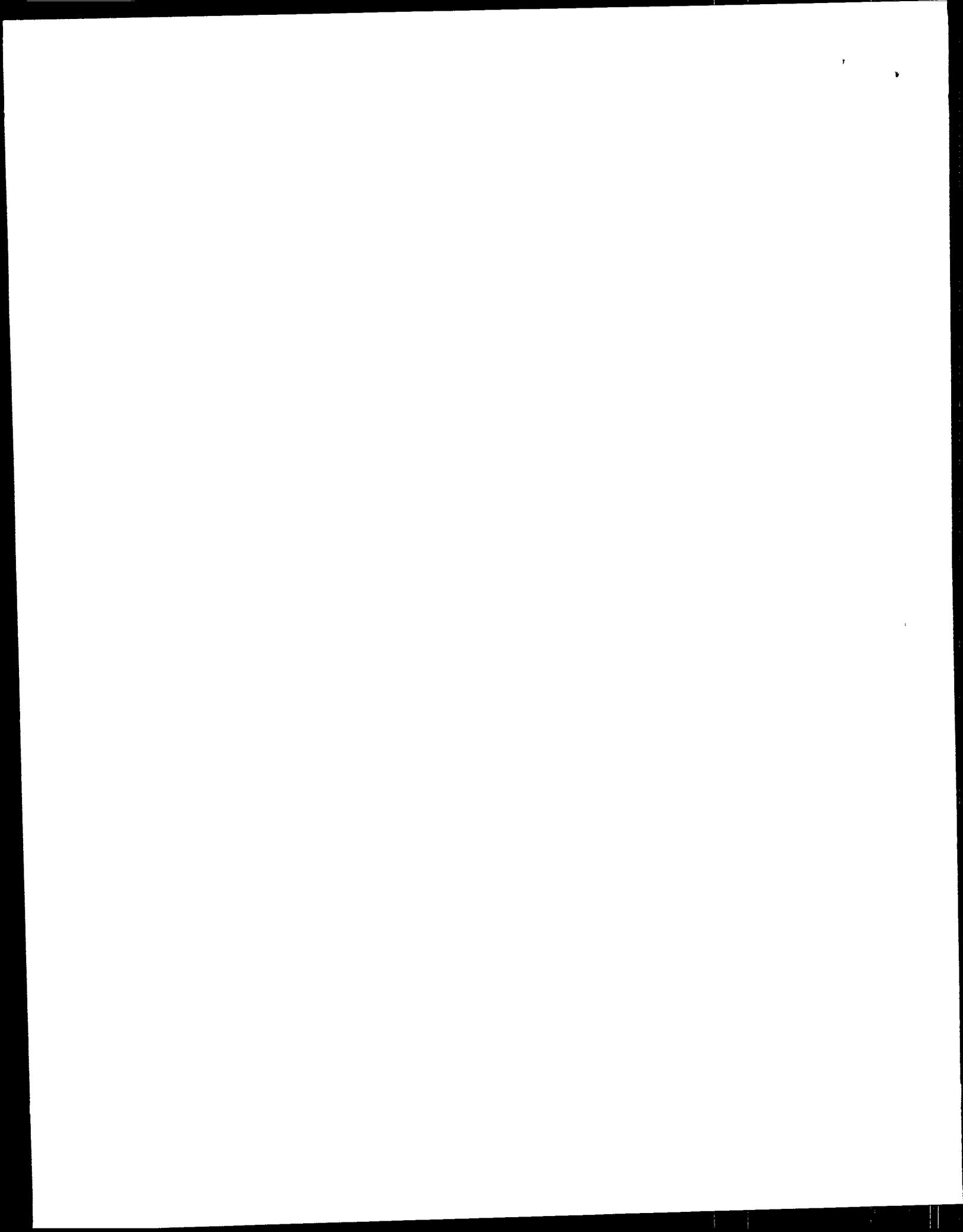
**EPA**

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## Acknowledgments

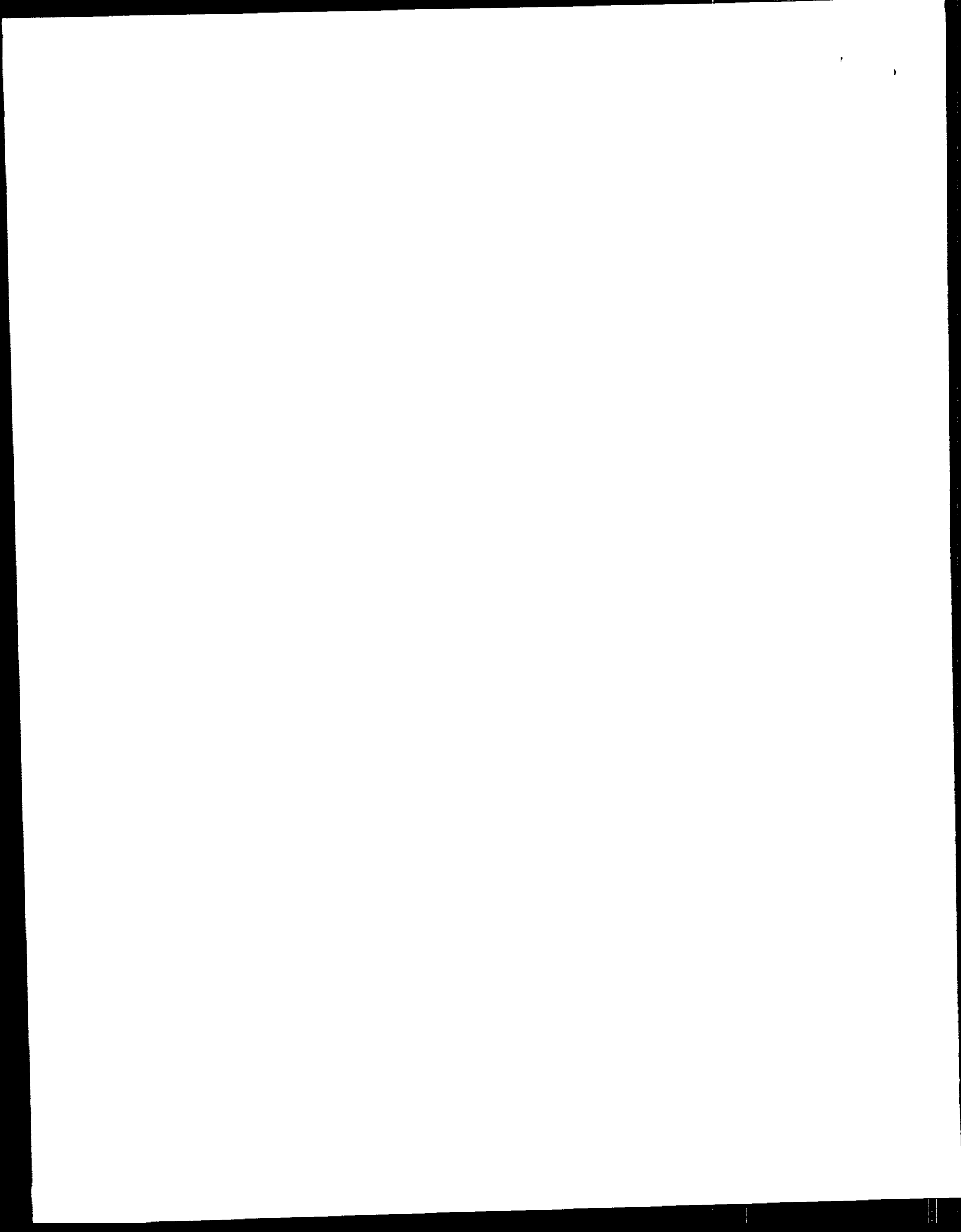
This method was prepared under the direction of William A. Telliard of the Engineering and Analysis Division (EAD) within the U.S. Environmental Agency's (EPA's) Office of Science and Technology (OST). The method was prepared by Nicholas Bloom of Frontier GeoSciences under EPA Contract 68-C3-0337 with the DynCorp Environmental Programs Division. Additional assistance in preparing the method was provided by Interface, Inc.

## Disclaimer

This sampling method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Questions concerning this method or its application should be addressed to:

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## Introduction

This analytical method supports water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act 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.

Section 303 of the Clean Water Act requires states 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 Sections 301(b) and 306 of the Clean Water Act.

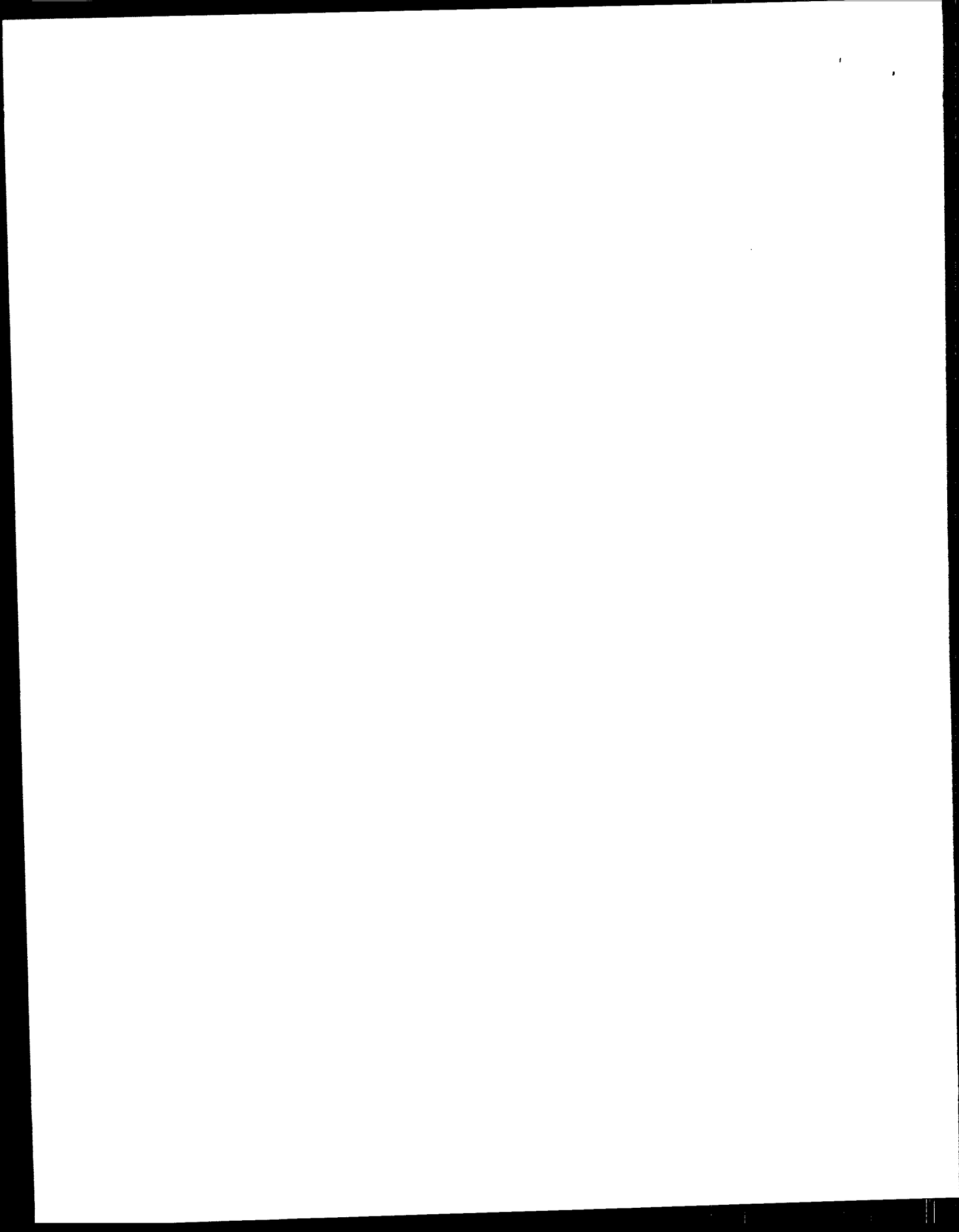
In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other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

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, EPA developed new sampling and analysis methods to specifically address state needs for measuring toxic metals at water quality criteria 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 (57 FR 60848). This rule includes water quality criteria for 13 metals, and it is these criteria on which the new sampling and analysis methods are based. Method 1631 was specifically developed to provide reliable measurements of mercury at EPA WQC levels.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This analytical method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance based. Alternative procedures may be used as 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 intended to be performance based, and the laboratory is permitted to omit any step or modify any procedure provided that all performance requirements set forth in this method are met. The laboratory is not allowed to omit any quality control analyses. The terms "must," "may," and "should" are included throughout this method and are intended to illustrate the importance of the procedures in producing verifiable data at water quality criteria levels. The term "must" is used to indicate the steps that are critical to production of reliable results; however, these procedures may be modified or omitted if the laboratory can demonstrate data quality is not affected.



# Method 1631

## Total Mercury in Water by Oxidation, Purge and Trap, and CVAFS

### 1.0 Scope and Application

- 1.1 This method is for determination of total mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence detection. 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 and 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 is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process.
- 1.3 This method is designed for measurement of total Hg in the range of 0.2–100 ng/L and may be extended to higher levels by selection of a smaller sample size. This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400–500) typically limit concentrations in industrial discharges to the part-per-billion (ppb) range, whereas ambient mercury concentrations are normally in the low part-per-trillion (ppt) range.
- 1.4 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes suggestions for improvements in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metals determinations and minimize contamination. Section 4.0 gives these suggestions.
- 1.5 The detection limits and quantitation levels in this method are usually dependent on the level of background elements rather than instrumental limitations. The method detection limit (MDL; 40 *CFR* 136, Appendix B) for total mercury has been estimated to be 0.05 ng/L when no background elements or interferences are present. The minimum level (ML) has been established as 0.2 ng/L.
- 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.

- 1.7 This method follows the EPA Environmental Methods Management Council's "Format for Method Documentation."
- 1.8 This method is "performance based." The analyst 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 who are experienced in the use of CVAF analysis and who are thoroughly trained in the sample handling and instrumental techniques described in this method. Each analyst who 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*. Data users should state data quality objectives (DQOs) required for a project before this method is used.

## 2.0 Summary of Method

- 2.1 A 100–2000 mL sample is collected directly into specially cleaned, pretested, fluoropolymer bottle(s) using sample handling techniques specially designed for collection of mercury at trace levels (Reference 6).
- 2.2 The sample is either field- or laboratory-preserved by the addition of 5 mL of pretested 12 N HCl per liter of sample, depending on the time between sample collection and arrival at the laboratory.
- 2.3 Sample preparation and analysis are conducted laboratory facilities specially designed for determination of mercury at 0.2–100 ng/L concentration. At this facility, a 100-mL sample aliquot is placed in a specially designed purge vessel.
- 2.4 Before analysis, 0.2 N BrCl solution is added to oxidize all Hg compounds to Hg(II).

- 2.5 After oxidation, the sample is sequentially prereduced with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to destroy the free halogens, and then reduced with  $\text{SnCl}_2$  to convert  $\text{Hg(II)}$  to volatile  $\text{Hg(0)}$ .
- 2.6 The  $\text{Hg(0)}$  is separated from solution by purging with nitrogen onto a gold-coated sand trap.
- 2.7 The trapped  $\text{Hg}$  is thermally desorbed from the gold trap into an inert gas stream that carries the released  $\text{Hg(0)}$  into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection.
- 2.8 Quality is ensured through calibration and testing of the oxidation, purging, and detection systems.

### 3.0 Definitions

- 3.1 Total mercury as defined by this method means all  $\text{BrCl}$ -oxidizable mercury forms and species found in aqueous solution. This includes but is not limited to  $\text{Hg(II)}$ ,  $\text{Hg(0)}$ , strongly organocomplexed  $\text{Hg(II)}$  compounds, adsorbed particulate  $\text{Hg}$ , and several tested covalently bound organomercurials (i.e.,  $\text{CH}_3\text{HgCl}$ ,  $(\text{CH}_3)_2\text{Hg}$ , and  $\text{C}_6\text{H}_5\text{HgOOCCH}_3$ ). The recovery of  $\text{Hg}$  bound within microbial cells may require the additional step of UV photo-oxidation. In this context, "total" mercury refers to the forms and species of mercury, not to the total recoverable or dissolved fraction normally determined in an unfiltered or filtered sample, respectively. In this method, the total recoverable fraction will be referred to as "total recoverable" or "unfiltered."
- 3.2 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 analytical 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 and 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 that are directly exposed to exhalation (Reference 5).

#### 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 metals.

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 requirements and suggestions 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 (Section 6.1.1). 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 the 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 (Section 6.9.7) 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 metals 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 containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of the other materials, resulting either in contamination or low-biased results. 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 metal 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 injection 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 low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. To reduce carryover, the sample introduction system may be rinsed between samples with dilute acid and reagent water. When an unusually concentrated sample is encountered, it is followed by analysis of a laboratory blank to check for carryover. Samples known or suspected to contain the lowest concentration of metals 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 samples containing high concentrations of inorganic substances are processed and analyzed. This method is not intended for application to these samples, and samples containing high concentrations should not be permitted into the clean room and 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. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of ambient water samples be cleaned as specified in Section 11.
- 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.

#### 4.4 Interferences

- 4.4.1 Because all forms of Hg are oxidized in the BrCl oxidation step, there are no observed interferences with this method.
- 4.4.2 The potential exists for destruction of the gold trap if it is exposed to free halogens or if the trap is overheated ( $> 500^{\circ}\text{C}$ ).
- 4.4.3 Water vapor may collect in the gold trap 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 fluorescence intensity is susceptible to the presence of foreign species in the carrier gas, which may cause "quenching" of the excited Hg atoms. The dual-trap technique in this method eliminates some quenching due to impurities in the carrier gas, but it remains the analyst'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.

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

5.5.1.2 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 when high concentrations are handled.

- 5.2 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in these analyses. It is also 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. Additional information on laboratory safety can be found in References 7-10. The references and bibliography at the end of Reference 10 are particularly comprehensive in dealing with the general subject of laboratory safety.

- 5.3 Samples suspected to contain high concentrations of Hg 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 strict 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 who 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 and materials other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.*

### 6.1 Sampling equipment

- 6.1.1 Sample collection bottles—Fluoropolymer, 125- to 1000-mL, with fluoropolymer or fluoropolymer-lined cap.
- 6.1.2 Cleaning—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, filled with reagent water plus 0.4% (v/v) HCl, and placed in a mercury-free class 100 clean bench until dry. The bottles are then tightly capped (with a wrench) and double-bagged in new polyethylene zip-type bags until needed. After the initial cleaning, bottles are cleaned as above, except with only 6–12 h in the hot 4 N HCl step.
- 6.1.3 Filtration Apparatus
- 6.1.3.1 Filter—Gelman Supor 0.45-µm, 15-mm diameter capsule filter (Gelman 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 for use with peristaltic pump—styrene/ethylene/butylene/silicone (SEBS) resin, approx 3/8-in i.d. by approximately 3 ft (Cole-Parmer size 18, Catalog 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 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)

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**NOTE:** *Safety note: 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!*

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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  $\pm 5^{\circ}\text{C}$  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: Tekran (Toronto, ON) Model 2357 CVAFS, or Brooks-Rand (Seattle, WA) Model 3 CVAFS, or equivalent

6.3.2 Custom-built CVAFS (Reference 11). Figure 1 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
- 6.3.2.7 Ultra high-purity argon (grade 5.0)
- 6.4 Equipment for Hg purging system—Figure 2a 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 ( $\pm 50$ ) mL/min.
  - 6.4.2 Fluoropolymer fittings—Connections between components and columns are made using 6.4-mm o.d. fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm o.d. fluoropolymer tubing because of its greater flexibility.
  - 6.4.3 Acid fume pretrap—10-cm long x 0.9-cm i.d. 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 bubbler and purging for 1 h with  $N_2$  at 350 mL/min.
  - 6.4.4 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.
- 6.5 Equipment for the dual-trap Hg(0) preconcentrating system
  - 6.5.1 Figure 2b shows the schematic for the dual-trap amalgamation system (Reference 5).
  - 6.5.2 Gold-coated sand trap—10-cm x 6.5-mm o.d. x 4-mm i.d. 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 i.d. 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 preclude 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 on.
- 6.5.3 Heating of gold-coated sand traps—To blank traps and desorb Hg collected on the traps, 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 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/integrator—Any integrator with a range compatible with the CVAFS is acceptable.
- 6.7 Pipettors—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10  $\mu$ L 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—Water in which mercury is not detected by this method; 18-M $\Omega$  ultrapure deionized water starting from a prepurified (distilled, R.O., etc.) source.
- 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 impossible, 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<sup>2</sup> of cotton gauze in 500 mL of 2% gold chloride solution at pH 7. In a hood, add 100 mL of 30% NH<sub>2</sub>OH·HCl solution, and homogenize into the cloth with gloved hands. As colloidal gold is precipitated, the material will turn black. 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 your laminar flow hood.

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**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.

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- 7.3 Hydrochloric acid—trace-metal purified reagent HCl containing less than 5 pg/mL Hg.
- 7.4 Hydroxylamine hydrochloride—Dissolve 300 g of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in reagent water and bring to 1.0 L. This solution may be purified by the addition of 1.0 mL of  $\text{SnCl}_2$  solution and purging overnight at 500 mL/min with Hg-free  $\text{N}_2$ .
- 7.5 Stannous chloride—Bring 200 g of  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  and 100 mL concentrated HCl to 1.0 L with reagent water. Purge overnight with mercury-free  $\text{N}_2$  at 500 mL/min to remove all traces of Hg. Store tightly capped.
- 7.6 Bromine monochloride ( $\text{BrCl}$ )—Dissolve 27 g of reagent grade  $\text{KBr}$  in 2.5 L of low-Hg HCl. Place a clean magnetic stir bar in the bottle and stir for approximately 1 h in a fume hood. Slowly add 38 g reagent grade  $\text{KBrO}_3$  to the acid with stirring. When all of the  $\text{KBrO}_3$  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.

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**CAUTION:** This process generates copious quantities of free halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{BrCl}$ ), which are released from the bottle. Add the  $\text{KBrO}_3$  SLOWLY in a fume hood!

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- 7.7 Stock mercury standard—NIST-certified 10,000-ppm aqueous Hg solution (NBS-3133). This solution is stable at least until the NIST expiration date.
- 7.8 Secondary Hg standard—Dilute 0.100 mL of the stock solution to 1.00 L of water containing 5 mL of  $\text{BrCl}$ . This solution contains 1.00 ug/mL (1.00 ppm) Hg. Keep in a tightly closed fluoropolymer bottle. This solution is stable indefinitely.
- 7.9 Working Hg standard—Dilute 5.00 mL of the secondary Hg standard to 1.00 L in a class A volumetric flask with reagent water containing 0.5% by volume  $\text{BrCl}$  solution. This solution contains 5.0 ng/mL and should be replaced monthly.
- 7.10 Calibration solutions—Using the secondary Hg standard (Section 7.8), prepare five calibration solutions to contain Hg at a concentration of 0.2, 1.0, 5, 25, and 100 ng/L in reagent water (Section 7.1).

- 7.11 Nitrogen—Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap.
- 7.12 Argon—Grade 5.0 (ultra high-purity, GC grade) inert gas 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 recoverable), 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. If properly acid-preserved, the sample can be held up to 6 months before analysis.
- 8.2 Samples are collected only into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Reference 4). Clean bottles filled with high-purity 0.4% (v/v) HCl are dried, capped, and double bagged in new zip-type bags in the clean room, and stored in wooden or plastic boxes until use.
- 8.3 Collect samples using the Sampling Method (Reference 6). Procedures in the Sampling Method are based on rigorous protocols for collection of samples for mercury (References 4 and 11).
- 8.4 Sample filtration—For dissolved Hg, samples and field blanks are filtered through a 0.45- $\mu$ m capsule filter at the field site. The Sampling Method describes filtering procedures. For the determination of total recoverable Hg, samples are filtered before preservation.
- 8.5 Preservation—Samples may be preserved by adding 5 mL/L of concentrated HCl (to allow both total and methyl Hg determination) or 5 mL/L BrCl solution, if total mercury only is to be determined. Acid- and BrCl-preserved samples are stable for a minimum of 6 months.
  - 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 the Hg may be condensed on the walls (Reference 12). Add BrCl directly to the sample bottle at least 24 h before analysis to prevent coagulation, condensation, or both. Aliquots for determination of other Hg species must be removed before BrCl is added. If BrCl cannot be added directly to the sample bottle, the bottle should be vigorously shaken before subsampling.



8.5.3 All 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.

8.5.4 If preserved in the laboratory, preserve a blank and OPR with each sample batch.

8.6 Storage—Sample bottles should be stored in polyethylene bags at 0–4°C until analysis.

## 9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 13). 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 analyst 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 analyst is permitted certain options to improve results or lower the cost of measurements. These options include automation of the dual-amalgamation system, direct electronic data acquisition, changes in the bubbler design (including substitution of a flow-injection system) to maximize throughput, and changes in the detector (i.e., CVAAS), where 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 techniques specified in the method is used, that technique must have a specificity equal to or better than the specificity of the techniques in the method for the analytes of interest.

9.1.2.1 Each time this method is modified, the analyst is required to repeat the procedure in Section 9.2. If the change will affect the detection limit of the method, the laboratory is required to demonstrate that the MDL (40 CFR Part 136, Appendix B) is lower than one-third the regulatory compliance level or lower than the MDL of this method, whichever is higher. If the change will affect calibration, the analyst must recalibrate the instrument 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) Calibration verification (Section 9.5)
  - (c) Initial precision and recovery (Section 9.2)
  - (d) Analysis of blanks (Section 9.4)
  - (e) Accuracy assessment (Section 9.3)
  - (f) Ongoing precision and recovery (Section 9.6)
- 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 laboratory blanks are required to demonstrate acceptable levels of contamination. Section 9.4 describes the procedures and criteria for analyzing a blank.
- 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 9.6.3 describe the development of accuracy statements.

9.1.7 The determination of total 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 10 samples. Each batch must be accompanied by at least three bubbler blanks (Section 9.4), an OPR sample, and one MS and one MSD. If more than 10 samples are run during one 12-hour shift, an additional bubbler blank, OPR sample, and MS/MSD must be analyzed for each additional 10 or fewer additional samples. Reagent blanks for this determination are required when the batch of reagents (bromine monochloride plus hydroxylamine hydrochloride) are made, with verification in triplicate each month until a new batch of reagents is needed.

## 9.2 Initial demonstration of laboratory capability

9.2.1 Method detection limit—To establish the ability to detect Hg, the analyst shall determine the MDL determined according to the procedure in 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Section 1.3 or one-third the regulatory compliance limit, whichever is greater. The MDL should be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate that the MDL be redetermined.

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

9.2.2.1 Analyze four replicates of the working Hg standard (Section 7.9) 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 ( $\bar{X}$ ), and the standard deviation of the percent recovery ( $s$ ) for total Hg.

9.2.2.3 Compare  $s$  and  $\bar{X}$  with the corresponding limits for initial precision and recovery in Table 1. If  $s$  and  $\bar{X}$  meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however,  $s$  exceeds the precision limit or  $\bar{X}$  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. Blanks (e.g., field blanks) may not be used for MS/MSD analysis.

- 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 total Hg in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1–5 times higher than the background concentration of the sample (determined in Section 9.3.2), whichever concentration is higher.
  - 9.3.1.2 If the concentration of total Hg in a sample is not being checked against a limit, the spike shall be at the concentration of the low-level working standard (Section 7.9) or at 1–5 times the background concentration, whichever concentration is higher.
- 9.3.2 To determine the background concentration (B), analyze 1 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 appropriate to produce a level in the sample at the regulatory compliance limit or at 1–5 times the background concentration (Section 9.3.1).
  - 9.3.2.2 Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A).
- 9.3.3 Calculate the percent recovery (P) in each aliquot using the following equation:

$$P = 100 \frac{(A-B)}{T}$$

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 the percent recovery (P) with the QC acceptance criteria in Table 1.
- 9.3.4.1 If the results of spike fail the acceptance criteria, and recovery for the OPR standard (Section 9.6) for the analytical batch is within the acceptance criteria in Table 1, an interference may be present. The result may not be reported for 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 analyst must modify the method, repeat the test required in Section 9.1.2, and repeat analysis of the sample and MS/MSD. However, when this method was written, there were no known interferences in the determination of total Hg using this method. If such a result is observed, the analyst should investigate it thoroughly.

9.3.4.2 If the results of both the spike and the OPR test fail the acceptance criteria, the analytical system is judged to be out of control. The analyst must identify and correct the problem and reanalyze the sample batch.

9.3.5 Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD 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.

$$RPD = 200 \times \frac{(|D1 - D2|)}{(D1 + D2)}$$

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 shall meet the acceptance criterion in Table 1. If the criterion is not met, the system is judged to be out of control. The problem must immediately be identified and corrected, 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 ( $P_a$ ) and the standard deviation of the percent recovery ( $s_p$ ). Express the accuracy assessment as a percent recovery interval from  $P_a - 2s_p$  to  $P_a + 2s_p$ . For example, if  $P_a = 90\%$  and  $s_p = 10\%$  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.
- 9.4.1.1 Immediately after analyzing a sample for total Hg, place a clean gold trap on the bubbler, 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. The remedy for a contaminated bubbler usually involves cleaning the bubbler, changing the soda lime trap on the affected bubbler, or both. If the blank from another bubbler contains less than 50 pg Hg, the data associated with that bubbler remain valid.
- 9.4.1.3 The mean result for all bubbler blanks (from bubblers passing the specification in Section 9.4.2) 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 value is subtracted from all raw data before results are calculated.
- 9.4.2 Reagent blanks—Since even reagent water often contains measurable Hg, blanks must be determined on solutions of reagents by adding these reagents to previously purged reagent water in the bubbler.
- 9.4.2.1 Add aliquots of BrCl (0.5 mL),  $\text{NH}_2\text{OH}$  (0.2 mL) and  $\text{SnCl}_2$  (0.5 mL) individually to previously purged reagent water in the bubbler.
- 9.4.2.2 The presence of more than 25 pg of Hg indicates a problem with the reagent solution. The purging of reagent solutions with mercury-free nitrogen or argon can reduce Hg to acceptable levels.
- 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 1), 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 for regulatory compliance purposes.

- 9.4.3.3 Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.
- 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  $\text{pH} < 2$  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 any bottle shows signs of contamination, 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 contractor's 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). 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 the sampler 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 any metal of interest or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from the metal(s) of interest 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 analysis system is in control and that acceptable precision and accuracy is being maintained within each analytical batch, the analyst shall perform the following operations:
- 9.5.1 Analyze the low-level Hg working standard (Section 7.9) and a bubbler blank before analysis of each analytical batch according to the procedure beginning in Section 11. Subtract the peak area of the bubbler blank from the area for the standard and compute the concentration for the blank-subtracted standard.
  - 9.5.2 Compare the concentration with the limits for ongoing precision and recovery in Table 1. If the concentration is in the range specified, the analysis system is in 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.
  - 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 should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery ( $R$ ) and the standard deviation of the percent recovery ( $s_r$ ). Express the accuracy as a recovery interval from  $R - 2s_r$  to  $R + 2s_r$ . For example, if  $R = 95\%$  and  $s_r = 5\%$ , the accuracy is 85–105%.
- 9.6 Quality control sample (QCS)—It is suggested that the laboratory 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), and that the QCS be analyzed periodically to verify the concentration of these standards.
- 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 trap in a sharp peak. The system is calibrated using the external standard technique as follows:
- 10.1.1 Initial calibration—Analyze each calibration standard (Section 7.10) according to the procedure in Section 11. After the analysis of each standard, analyze a bubbler blank (Section 9.4.1) on the same bubbler used for the standard. Subtract the peak area of the bubbler blank from the area of each respective standard. Tabulate the resulting peak area against the respective concentration of each solution to form five calibration factors. Calculate the relative standard deviation (RSD) of the calibration factor over the five-point range.
- 10.1.2 Linearity—If the calibration factor is constant ( $< 20\%$  RSD) over the five-point calibration range, linearity through the origin can be assumed and the average calibration factor can be used; otherwise, a complete calibration curve must be used over the five-point range.
- 10.2 Calibration verification and ongoing precision and recovery—The ongoing precision and recovery standard (Section 9.5) is used to verify the working calibration curve or calibration factor at the beginning of each 12-hour working shift on which samples are analyzed.

## 11.0 Procedure

### 11.1 Sample Preparation

- 11.1.1 Pour a 100-mL aliquot from a thoroughly shaken, acidified sample, into a 125-mL fluoropolymer bottle. Add bromine monochloride (BrCl), cap the bottle, and digest at room temperature for 12 hs 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 oxidation always must be continued until a permanent yellow color remains.
- 11.1.2 Matrix spikes and matrix spike duplicates—For each 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.
- 11.2 Hg reduction and purging—Place 100 mL of reagent water in each bubbler, add 1.0 mL of SnCl<sub>2</sub>, and purge with Hg-free N<sub>2</sub> for 20 min at 300–400 mL/min.
  - 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. Discard the water in the bubbler.
  - 11.2.2 Add 0.2 mL of 30% NH<sub>2</sub>OH 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.

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

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- 11.2.3 Connect a fresh trap to the bubbler, pour the reduced sample into the bubbler, add 0.5 mL of 20% SnCl<sub>2</sub> solution, and purge the sample with N<sub>2</sub> for 20 min.
- 11.3 Desorption of Hg from the gold trap
  - 11.3.1 Remove the gold (sample) trap from the bubbler, place the Nichrome wire coil around the sample trap and connect the sample trap into the analyzer train between the incoming Hg-free argon and the second gold-coated (analytical) sand trap (Figure 1a).
  - 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 electrical current 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 gold trap.
  - 11.3.4 After the 3-min desorption time, turn off the current to the Nichrome coil, and cool the sample trap using the cooling fan.

- 11.3.5 Apply electrical current to the Nichrome wire coil around the analytical trap and begin data collection. Heat the analytical trap for 3 min or for 1 min beyond the point at which the peak returns to baseline, whichever is greater.
- 11.3.6 Stop data collection, turn off the current 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.

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**NOTE:** *The analytical trap must be at or near room temperature when the sample trap is heated; otherwise, Hg may be lost by passing through the analytical trap.*

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- 11.4 Peaks generated using this technique should be very sharp and almost symmetrical. Mercury elutes at approximately 1 min 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 low gas flow rate, water vapor on the trap(s), or an analytical column 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, it and the fluoropolymer tubing downstream from it should be discarded because of the possibility of gold migration on 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 Subtract the peak area of the mean of a minimum of three bubbler blanks (Section 9.4.1.3) from the peak area of each sample.
- 12.2 Using the blank-subtracted area, calculate the concentration of Hg in each sample directly from the mean calibration factor if a linear calibration is used, or from the calibration curve if the calibration factor does not meet the criterion in Section 10.1.2.
- 12.3 Reporting—Report results for samples in ng/L to three significant figures for total Hg found above the ML (Section 1.3). Report results below the ML as < 0.2 ng/L, or as required by the permitting authority or in the permit.

## 13.0 Method Performance

The data in Table 2 give an example the performance of the method under actual operating conditions by several different analysts over a period of 1 year. In addition to such data, this methodology has been intercompared with other techniques for low-level mercury determination in water under a variety of studies, including ICES-5 (Reference 14) and the International Mercury Speciation Intercomparison Exercise (Reference 15).

## 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 their waste generation. When wastes cannot be feasibly reduced 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.
- 15.2 Acids, samples at  $\text{pH} < 2$ , and  $\text{BrCl}$  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 Shift**—All of the 12-hour period during which analyses are performed. The period begins with the purging of the OPR standard and ends exactly 12 hours later. All analyses both started and completed within this 12-hour period are valid.
- 17.3 **Bubbler Blank**—The process of analyzing water in the bubbler, including purging Hg from the water, trapping the Hg purged on a sample trap, desorbing the Hg onto an analytical trap, desorbing the Hg from the analytical trap, and determining the amount of Hg present. The blank is somewhat different between days, and the average of a minimum of the results from three bubbler blanks must be subtracted from all standards and samples before reporting the results for these standards and samples.
- 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 **Must**—This action, activity, or procedural step is required.
- 17.7 **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 to check laboratory performance with test materials prepared external to the usual preparation process.
- 17.8 **Reagent Water**—Water known not to contain the analyte(s) of interest at the detection limit of this method. For this method, the Hg level is made as low as possible in mercury usually by double deionization. The reagent water is used to wash bottles and as trip and field blanks.
- 17.9 **Should**—This action, activity, or procedure is suggested, but not required.
- 17.10 **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.
- 17.11 **Ultraclean Handling**—A series of established procedures designed to ensure that samples are not contaminated for Hg during sample collection, storage, or analysis.

**TABLE 1**  
**Acceptance Criteria For Performance Test**

| <b>Acceptance Criterion</b>         | <b>Section</b> | <b>Limits</b> |
|-------------------------------------|----------------|---------------|
| Method Detection Limit              | 9.2.1          | <0.2 ng/L     |
| Initial Precision and Recovery      | 9.9.2          |               |
| Precision (s)                       | 9.2.2.3        | ± 21%         |
| Recovery (X)                        | 9.2.2.3        | 79–121%       |
| Interlaboratory Intercomparison     | 9.2.2.2        | 75–125%       |
| Matrix Spike/Matrix Spike Duplicate | 9.3            |               |
| Recovery                            | 9.3.4          | 75–125%       |
| Relative Percent Difference         | 9.3.6          | ± 24%         |
| Bubbler Blanks                      | 9.4            |               |
| Maximum                             | 9.4.1.2        | < 50 pg       |
| Mean                                | 9.4.1.3        | < 25 pg       |
| Ongoing Precision and Recovery      | 9.5            | 77–123%       |



**TABLE 2**  
**Typical QC Results for Routine Water Analysis**  
**(Frontier Geosciences Inc., February–August 1993)**

| <b>Parameter</b>         | <b>Units</b>        | <b>Mean</b> | <b>SD</b> | <b>N</b> |
|--------------------------|---------------------|-------------|-----------|----------|
| Reagent Blanks           | ng/L                | 0.14        | 0.04      | 36       |
| Matrix Spike Recoveries  | %                   | 99.6        | 6.3       | 60       |
| Laboratory Duplicates    | RPD                 | 4.9         | 6.6       | 49       |
| Field Duplicates         | RPD                 | 13.3        | 14.6      | 33       |
| Intercomparison Exercise | % Diff <sup>a</sup> | 0.0         | 13.3      | 18 la    |

Figure 1. Schematic diagram of the Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) detector

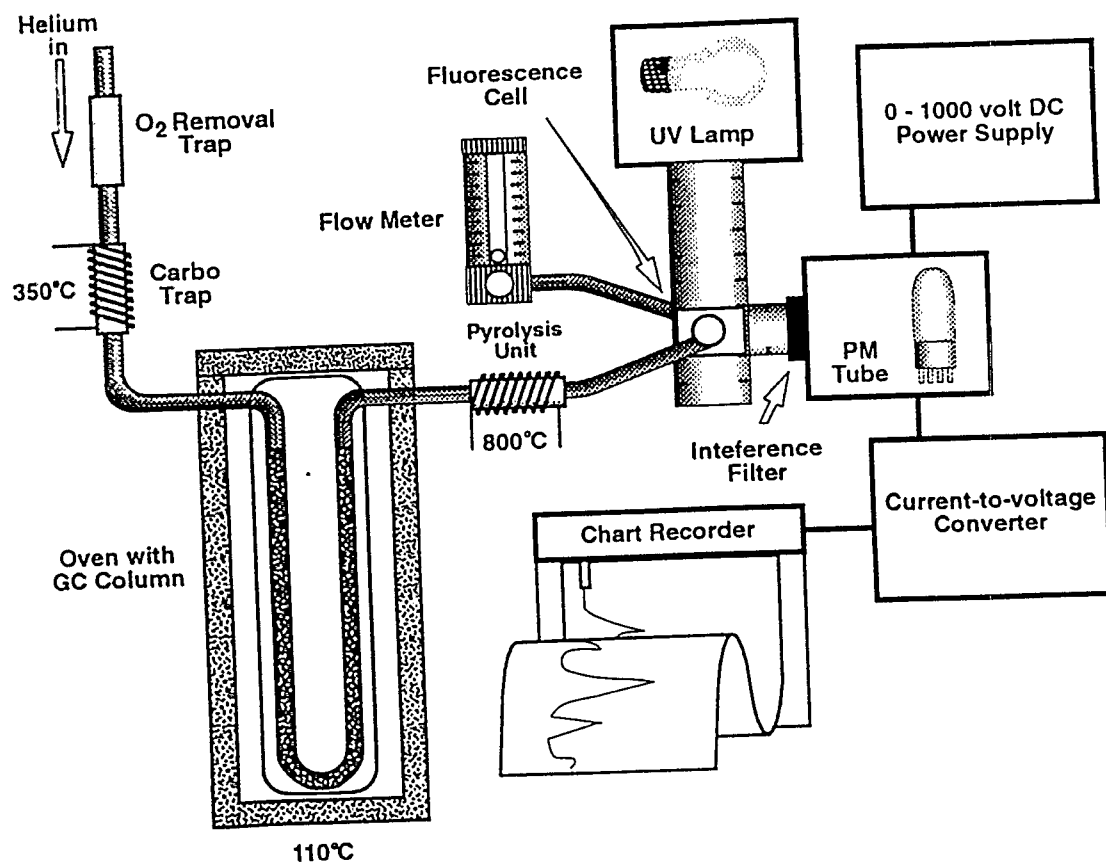


Figure 2. Schematic diagram of bubbler setup (a), and dual-arnalgamation system (b), showing proper orientation of gold traps and soda lime pretraps

