

**Method 245.7**

**Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry**

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**Draft**

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## **Acknowledgments**

This method was developed under the direction of William A. Telliard and Maria Gomez-Taylor of the Engineering and Analysis Division (EAD) within the U.S. Environmental Protection Agency's (EPA's) Office of Science and Technology (OST). The Method was developed by EPA's Human Exposure Research and Environmental Services Divisions, in collaboration with Technology Applications, Inc. Additional assistance in preparing the method was provided by DynCorp, Information and Enterprise Technology and Interface, Inc.

## **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. EPA plans further validation of this draft method. The method may be revised following validation to reflect results of the study.

EPA welcomes suggestions for improvement of this method. Questions concerning this Method or its application should be addressed to:

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## Introduction

EPA draft Method 245.7, *Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry* (the "Method"), was developed through a collaboration between EPA's Environmental Monitoring Systems Laboratory, EPA-Region 4, and Technology Applications, Inc. In developing this Method, EPA sought to provide the environmental monitoring community with a rugged analytical protocol capable of determining mercury (Hg) at the concentrations typically regulated under State water quality standards.

EPA developed this Method to specifically address State needs for measuring toxic metals at ambient water quality criteria (WQC) levels, when such measurements are necessary to protect designated uses. 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), and codified at 40 CFR 131.36. Method 245.7 was developed to provide reliable measurements of mercury at EPA WQC levels.

Measurement of mercury by this Method is by cold-vapor atomic fluorescence spectrometry (CVAFS), a brominating digestion which provides minimal interference, and the use of ultra-pure argon as carrier gas. The Method is similar to EPA Method 1631, *Mercury in Water by Oxidation, Purge and Trap, and CVAFS*, which was promulgated for use in CWA programs on June 8, 1999 as a means for providing reliable measurements at the lowest EPA ambient water quality criteria for mercury under the National Toxics Rule and in the Great Lakes and Tribes (40 CFR 132.6). Both methods require use of a CVAFS detector to measure low levels of mercury. However, Method 245.7 uses liquid-gas separation and a dryer tube for analyte isolation, while Method 1631 uses a purge and gold trap isolation procedure.

Method 245.7 has been validated in two EPA laboratories and one university laboratory, and results from these studies indicate that the Method is capable of producing reliable measurements of mercury at toxic criteria levels (40 CFR 136.6). The highest method detection limit (MDL) determined by three laboratories in reagent water was 1.8 ng/L. Following these studies, the Method was revised to conform with recent EPA guidelines.

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. Method 245.7 is designed to preclude contamination in nearly all situations. In recognition of the variety of situations to which this Method may be applied, and in recognition of continuing technological advances, Method 245.7 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	or	EPA Sample Control Center, DynCorp I&ET
11209 Kenwood Road		6101 Stevenson Avenue
Cincinnati, OH 45242		Alexandria, Virginia 22304-3540
513/489-8190		703/461-2100

**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 245.7

### Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry

#### 1.0 Scope and Application

- 1.1 Method 245.7 (the "Method") is for determination of mercury (Hg) in filtered and unfiltered water by cold-vapor atomic fluorescence spectrometry (CVAFS). It is applicable to drinking water, surface and ground waters, marine water, and industrial and municipal wastewater. The 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 method developed through a collaboration between EPA's Environmental Monitoring Systems Laboratory, EPA-Region 4, and Technology Applications, Inc. (Reference 1) and on peer-reviewed, published procedures for the determination of mercury in aqueous samples, ranging from marine water to effluent (References 2–6).
- 1.2 This Method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (Sampling Guidance). The Sampling Guidance is recommended to preclude contamination during the sampling process.
- 1.3 This Method may be used to determine Hg up to 200 ng/L and may be extended by dilution of the sample. The normal calibration range for ambient water monitoring is 5 ng/L to 100 ng/L.
- 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 method detection limit (MDL) and minimum level of quantitation (ML) in this Method usually are dependent on the level of interferences rather than instrumental limitations. The MDL has been determined from single laboratory validation studies as 1.8 ng/L and the ML has been established as 5.0 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 (References 6-8).
- 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, the handling of trace elements and clean laboratory practices and protocols. Each laboratory that uses this Method must demonstrate the ability to generate acceptable results using the procedure in Section 9.1.1.
- 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 9) 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 10).
- 2.2 For dissolved Hg, the sample is filtered through a 0.45- $\mu$ m capsule filter.
- 2.3 The sample is preserved by adding 5 mL/L of pretested 12N HCl.
- 2.4 Inorganic Hg compounds and organomercury species are oxidized by a potassium bromate/potassium bromide reagent.
- 2.5 After oxidation, the sample is sequentially prereduced with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to destroy the excess bromine, then the ionic Hg is reduced with  $\text{SnCl}_2$  to convert Hg(II) to volatile Hg(0).
- 2.6 The Hg(0) is separated from solution by purging with high purity argon gas through a semi-permeable dryer tube (Figure 1).
- 2.7 The Hg passes into an inert gas stream that carries the released Hg(0) into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection. The concentration of Hg is determined by atomic fluorescence spectrometry at 253.7 nm.
- 2.8 Quality is assured through calibration and testing of the oxidation, purging, and detection systems.

## 3.0 Definitions

- 3.1 Total mercury—all  $\text{KBrO}_3/\text{KBr}$ -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 organomercurials (e.g.,  $\text{CH}_3\text{HgCl}$ ,  $(\text{CH}_3)_2\text{Hg}$ , and  $\text{C}_6\text{H}_5\text{HgOOCCH}_3$ ). 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  $\text{KBrO}_3/\text{KBr}$ -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, 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 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 constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals 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 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 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 mercury.
- 4.3.1.1 The integrity of the results produced cannot be compromised by contamination of samples. This Method and the Sampling Guidance 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 Guidance 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. Refer to EPA's Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities for guidance (Reference 8).
- 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, non-talc 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—Apparatus used for determination of mercury at ambient water quality criteria levels must be nonmetallic or free of materials that may contain metals.
- 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, producing 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. Logbooks should be maintained to track samples from containers through the labware to 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 equipment 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 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).
- 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 reagents used during processing and analysis. Reagent blanks must be analyzed for contamination prior to use (see Section 9.2.1). If reagent blanks are contaminated, a new batch of reagents must be prepared (see Section 9.2.1.3).

#### 4.4 Interferences

- 4.4.1 During development of this Method, gold, silver and iodide were known interferences. At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 5 to 100 mg/L, test data have shown that Hg recovery will be reduced from 100 to 0 percent (References 1 and 12). At iodide concentrations greater than 3 mg/L, the sample should be pre-reduced with SnCl<sub>2</sub> (to clarify the brown color). If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4N HCl after the analysis (References 6 and 12).

- 4.4.2 The use of a brominating digestion coupled with atomic fluorescence detection overcomes many of the chloride, sulfide and molecular absorption interferences. No interferences have been noted for sulfide concentrations below 24 mg/L (References 1 and 6).
- 4.4.3 High purity argon (99.998%) must be used as the carrier gas. Using nitrogen may reduce the sensitivity by a factor of eight fold, while the use of air may reduce the sensitivity thirty fold (Reference 1).
- 4.4.3 Water vapor may collect in the fluorescence detector cell, resulting in a degradation of analytical signal or giving a false peak due to scattering of the excitation radiation. The use of a membrane drying tube is required to remove any water vapor from the transfer tubing that can contaminate the detector (References 1 and 6).

## 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 Hg. 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. 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 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. 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 15-18. The references and bibliography at the end of Reference 18 are particularly comprehensive in dealing with the general subject of laboratory safety.
- 5.3 Samples suspected to contain concentrations of Hg at  $\mu\text{g/L}$  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 handling samples known or suspected of containing high concentrations of mercury, all operations (including removal of samples from sample containers,

weighing, transferring, and mixing) should be performed in a glove box demonstrated to be leak-tight 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 work presents no inhalation hazard 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 CVAFS effluent 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. Trash removers and other personnel must be trained in the safe handling of contaminated waste.
- 5.3.8 Decontamination
  - 5.3.8.1 Decontamination of personnel—Use mild soap with plenty of scrubbing action.
  - 5.3.8.1 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  $\mu\text{g}$  per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10  $\mu\text{g}$  constitutes an acute hazard, 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

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*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.*

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### 6.1 Sampling Equipment

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

6.1.1.1 New bottles are cleaned by heating to 65–75 °C in 4N 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, and stored in wooden or plastic boxes until use. See Section 6.2 for equipment needed for bottle and glassware cleaning.

6.1.1.2 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 4N HCl.

6.1.1.3 Bottle blanks should be analyzed as described in Section 9.2.3.1 to verify the effectiveness of the cleaning procedures.

### 6.1.2 Filtration Apparatus

6.1.2.1 Filter—0.45- $\mu$ m, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent).

6.1.2.2 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).

6.1.2.3 Tubing—styrene/ethylene/butylene/silicone (SEBS) resin for use with peristaltic pump, approximately 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 a 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  $\pm 5^\circ\text{C}$  in the 60–70°C temperature range.
- 6.3 Cold Vapor Atomic Fluorescence Spectrometer (CVAFS): The CVAFS system used may be purchased either from a supplier or built in the laboratory from commercially available components.
- 6.3.1 Commercially available CVAFS—Tekran (Toronto, ON) Model 2500 CVAFS, or Brooks-Rand (Seattle, WA) Model III CVAFS, or equivalent.
- 6.3.2 Custom-built CVAFS. 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 or Starna Cell, 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 stabilizing gas flow rate.
- 6.4 Analytical System—Semi-automated mercury atomic fluorescence analytical system (Figure 1). The system consists of the following:
- 6.4.1 Fluoropolymer fittings—connections between components 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.

- 6.4.2 Peristaltic Pump and pump tubing—three-channel peristaltic pump capable of flow rates up to 10 mL/min. Silicone pump tubing for the tin(II), reagent water flush and sample solutions. For the tin(II) solution: Watson-Marlow, Product Code 910, 0005-016, 0.5 mm ID, 1.6 mm wall thickness (w.t.), or equivalent. For the system blank and sample solutions: Watson-Marlow, Product Code 910, 0008-016, 0.8 mm ID, 1.6 mm w.t. or equivalent.
  - 6.4.3 Solenoid switching valve box—Dual, two-way valves activated by timed events.
  - 6.4.4 Argon gas regulator—low pressure regulator with flow controller. Used for maximum stability of gas flow rates through the analytical system.
  - 6.4.5 Gas liquid separator—used to sparge argon gas through the flowing mixture of sample liquid and tin(II) solution to liberate the mercury vapor.
  - 6.4.6 Membrane dryer tube—used for the removal of moisture from the argon gas carrier flow. Perma-Pure, Inc. (Model number MD-070-24F)
  - 6.4.7 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  $10^3$ .
- 6.5 Laboratory equipment
- 6.5.1 Pipettors—all-plastic, pneumatic, fixed-volume and variable pipettors in the range of 5  $\mu$ L to 2500  $\mu$ L.
  - 6.5.2 Analytical balance capable of accurately weighing to the nearest 0.001 g.
  - 6.5.3 Centrifuge vials—polypropylene 50 mL conical vials with screw-cap lids, Falcon, Blue Max, Catalogue #2098 or equivalent.
  - 6.5.4 Mercury wipes—Merconwipes towelettes, EPS Chemical Inc., Fisher Catalogue #17-976-8 or equivalent.
  - 6.5.5 Muffle furnace—Not required if commercially available pre-mixed brominating solution is used. The muffle furnace is used to volatilize Hg contamination from potassium bromate and potassium bromide reagent. It is important that the furnace be Hg free and located in a clean, Hg-free laboratory. The furnace should be vented to a fume hood to avoid laboratory Hg contamination.
  - 6.5.6 Volumetric flasks—clean, glass volumetric flasks at 100, 500, and 1000 mL.

## 7.0 Reagents and Standards

- 7.1 Reagent water—18-M $\Omega$  minimum, ultra-pure 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 laboratory air be low in both particulate and gaseous mercury. Ideally, mercury work should be conducted in a 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 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. 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. Great care should be taken to avoid contaminating the laboratory with gold dust. This could cause analytical interference 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 Argon Gas (Ar)—high-purity grade (99.998%), with two stage regulator or gas from liquid argon. Use of a gas purifier cartridge for removing mercury, oxygen and organic compounds is recommended.
- 7.4 Hydrochloric acid—concentrated, trace-metal purified reagent-grade HCl containing less than 5 pg/mL Hg. The HCl should be preanalyzed for Hg before use.
- 7.5 Nitric acid—concentrated, trace-metal purified reagent-grade HNO<sub>3</sub> containing less than 5 pg/mL Hg. The HNO<sub>3</sub> should be preanalyzed before use.
- 7.6 Reagents
- 7.6.1 Hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl), CASRN 5470-11-1.
- 7.6.2 Mercuric chloride (HgCl<sub>2</sub>) CASRN 7487-94-7, 99.99% pure with assay.
- 7.6.3 Methyl mercury chloride (CH<sub>3</sub>HgCl), CASRN 115-09-3, 95% pure with assay.
- 7.6.4 Potassium bromate (KBrO<sub>3</sub>), CASRN 7758-01-2—volatilize trace mercury impurities by heating in a muffle furnace at 250°C for a minimum of 8 hours. The compound is then placed in a desiccator for cooling.
- 7.6.5 Potassium bromide (KBr) CASRN 7758-02-3—volatilize trace mercury impurities by heating in a muffle furnace at 250°C for a minimum of 8 hours. The compound is then placed in a desiccator for cooling.
- 7.6.6 Stannous chloride (SnCl<sub>2</sub>·2H<sub>2</sub>O), CASRN 10025-69-1—assayed mercury level not exceeding 0.05 ppm.

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

## 7.7 Reagent and Standards

7.7.1 Hydrochloric acid solution—add concentrated HCl (Section 7.4) to reagent water in the ratio of 1:1 (v/v). Prepare 500 mL weekly, or as needed.

7.7.2 Hydroxylamine solution—Dissolve 12.0 g of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 100 mL reagent water. Prepare weekly or as needed. This solution may be purified by the addition of 0.1 mL of  $\text{SnCl}_2$  solution and purging overnight at 500 mL/min with Hg-free Ar.

7.7.3 Stannous chloride solution, 2% (w/v) in 10% (v/v) HCl—add 100 mL concentrated HCl to 400 mL of reagent water to a 1L volumetric flask. To this solution, add 20.0 g stannous chloride (Section 7.6.6) and swirl until dissolved. Bring to 1 L with reagent water. To remove traces of Hg, purge the solution with Ar at a flow rate of approximately 2 L/min for 30 minutes in a fume hood. Store tightly capped.

7.7.4 Bromate/bromide solution—In a fume hood, dissolve 2.78 g  $\text{KBrO}_3$  (Section 7.6.4) and 11.90 g  $\text{KBr}$  (Section 7.6.5) in 500 mL reagent water. It is recommended that 0.1N potassium bromate/bromide solution (Alfa Chemicals, Catalogue #35593, or equivalent) be used. Prepare weekly or as needed.

**WARNING:** *This process generates copious quantities of free halogens, which are released from the bottle. Add the  $\text{KBrO}_3$  slowly in a fume hood!*

7.7.5 Secondary Hg standard—Add approximately 0.5 L of reagent water and 5 mL bromate/bromide solution (Section 7.7.4) to a 1L Class A volumetric flask. Add 0.100 mL stock mercury standard (Section 7.6.7) and dilute to 1.00 L with reagent water. This solution contains 1.00  $\mu\text{g/mL}$  (1.00 ppm) Hg. Transfer the solution to a fluoropolymer bottle and cap tightly. This solution is considered stable until the NIST expiration date.

7.7.6 Working Hg standard—Dilute 1.00 mL of the secondary Hg standard (Section 7.7.5) to 100 mL in a Class A volumetric flask with reagent water containing 0.5% by volume bromate/bromide solution (Section 7.7.4). This solution contains 10.0 ng/mL Hg and should be replaced monthly.

7.7.7 IPR and OPR solutions—Using the working Hg standard solution (Section 7.7.6), prepare IPR and OPR solutions at a concentration of 10 ng/L Hg in reagent water.

## 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 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 sealed caps to avoid diffusion of atmospheric Hg through the threads (Reference 4). Polyethylene sample bottles must not be used (Reference 12).



- 8.3 Collect samples using procedures in the Sampling Guidance (Reference 10). These procedures are based on rigorous protocols for collection of samples for mercury (References 4 and 12).

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**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. 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.

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- 8.4 Sample filtration—For dissolved Hg, samples and field blanks are filtered through a 0.45- $\mu$ m capsule filter (Section 6.1.2.1). The Sampling Guidance gives the filtering procedures.
- 8.5 Preservation—Samples are preserved by adding 5 mL/L of pretested 12 N HCl. Acid-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. Samples for dissolved mercury must be filtered before they are preserved.
- 8.5.2 Samples that are acid-preserved may lose Hg to coagulated organic materials in the water or condensed on the walls (Reference 13). The best approach is to add KBrO<sub>3</sub>/KBr directly to the sample bottle at least 24 hours before analysis. If other Hg species are to be analyzed, aliquots must be removed prior to addition of KBrO<sub>3</sub>/KBr. If KBrO<sub>3</sub>/KBr cannot be added directly to the sample bottle, the bottle must be shaken vigorously prior to sub-sampling.
- 8.5.3 Handling 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 hood.

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**Note:** Due to the potential for contamination, sample filtration and preservation should be performed in a clean room in the laboratory. However, if circumstances 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 the Sampling Guidance (Reference 10).

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- 8.6 Storage—Sample bottles should be stored in clean (new) polyethylene bags until sample analysis. If properly preserved, samples can be held up to 28 days before 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 14). 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 bias (as recovery) and precision. Laboratory performance is compared to performance criteria to determine that the results of analyses meet the performance characteristics of the Method.

- 9.1.1 Initial Demonstration of Performance—The laboratory shall make an initial demonstration of the ability to generate acceptable recovery and precision with this Method.
- 9.1.1.1 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 used in this Method. This MDL shall be used for determination of laboratory capability, and should be determined when a new operator begins work or whenever there is a change in instrument hardware or operating conditions.
- 9.1.1.2 Initial demonstration of freedom from contamination—The analysis of ultra-trace Hg concentrations require extreme care in minimizing the contamination during sample preparation prior to and including the analysis. Given the inherent skill and unique laboratory facilities required to control contamination at these concentrations, it is required that the laboratory initially demonstrate that the analytical system is free from contamination. This demonstration consists of analysis of a blank along with the precision and recovery samples (Section 9.1.1.3). The level of mercury in the blank shall be less than the MDL specified in Section 1.5 of this Method or, if the mercury measurements will be used for compliance monitoring, less than one-third the regulatory compliance limit, whichever is greater. If mercury is found in a blank above these levels, the source of contamination must be identified and corrected prior to the analysis of samples.
- 9.1.1.3 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the laboratory shall perform the following operations:
- 9.1.1.3.1 Analyze four replicates of the IPR solution (10 ng/L, Section 7.7.7) according to the procedure beginning in Section 11.
- 9.1.1.3.2 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 Hg.
- 9.1.1.3.3 Compare  $s$  and  $\bar{X}$  with the corresponding limits for initial precision and recovery in Table 2. 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 9.1.1.3).
- 9.1.2 Method modifications—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 direct electronic data acquisition, calibration using gas-phase elemental Hg standards, changes in the gas-liquid separator or dryer tube design, 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 a 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 9.1.1 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 9.1.1.3)
- (c) Analysis of blanks (Section 9.2)
- (d) Matrix spike/matrix spike duplicate (Section 9.5)
- (e) Ongoing precision and recovery (Section 9.4)
- (f) Quality control sample (Section 9.3)
- (g) Method detection limit (Section 9.1.1.1)

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
- (g) Calculations linking raw data to the results reported

9.2 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.

9.2.1 Reagent blanks—The Hg concentration in reagent blanks must be determined on solutions of reagents by adding these reagents to reagent water in the same amounts at which they are added to a sample(s).

- 9.2.1.1 Reagent blanks are required when the batch of reagents are prepared, with verification in triplicate each month until a new batch of reagents is needed. Reagent blank analysis also is required with each set of 20 samples.
  - 9.2.1.2 Add aliquots of  $\text{KBrO}_3/\text{KBr}$ ,  $\text{NH}_2\text{OH}$  and  $\text{SnCl}_2$  to reagent water and analyze as though analyzing a sample. 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). Samples high in organic materials may require additional  $\text{KBrO}_3/\text{KBr}$ .
  - 9.2.1.3 The presence of Hg at a level greater than the MDL indicates a problem with the reagent solution. The purging of reagent solutions, such as  $\text{SnCl}_2$  or  $\text{NH}_2\text{OH}$ , with mercury-free argon can reduce Hg to acceptable levels. Because the  $\text{KBrO}_3/\text{KBr}$  solution 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  $\text{KBrO}_3/\text{KBr}$  solution is too high.
- 9.2.2 Field blanks
- 9.2.2.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time). Analyze the blank immediately before analyzing the samples in the batch.
  - 9.2.2.2 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 samples, 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.
  - 9.2.2.3 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 limit or less than one-half the level in the associated sample, whichever is greater. If this criteria is not met, the results for the associated samples may not be reported or otherwise used for regulatory compliance purposes.
  - 9.2.2.4 If contamination of the field blank(s) 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.
- 9.2.3 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.
- 9.2.3.1 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 a bottle shows contamination at or above the level specified for the field blank (Section 9.2.2.2) the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles recleaned.

9.2.3.2 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 Guidance). 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.

9.2.3.2.1 Sampler check blanks are generated by filling a 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 Guidance, Reference 10). Manual grab sample 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.

9.2.3.2.2 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 9.2.2.2), 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.

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

9.3 Quality Control Sample (QCS)—The laboratory must obtain a QCS from a source different from the Hg source used to produce the standards used routinely in this Method (Section 7.7). The QCS should be analyzed as an independent check of system performance.

9.4 Ongoing precision and recovery (OPR)—To demonstrate that acceptable precision and recovery is being maintained within each analytical batch, the laboratory shall perform the following operations:

9.4.1 Analyze the OPR solution (10 ng/L, Section 7.7.7) 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 each analytical batch or at the end of each 12-hour shift, whichever occurs first. Calculate the percent recovery for the OPR.

9.4.2 Compare the 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.

- 9.4.3 The laboratory should add results that pass the specification in Section 9.4.2 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%.
- 9.5 Matrix spike (MS) and matrix spike duplicate (MSD)—To assess the performance of the Method on a given matrix, the laboratory must spike, in duplicate, a minimum of 10% of the samples collected from a given sampling site or, if for compliance monitoring, from a given discharge. Analysis of 20 samples would require two pairs of MS/MSD samples (four spiked samples total).
- 9.5.1 The concentration of the spike in the sample shall be determined as follows:
- 9.5.1.1 If, as in compliance monitoring, the concentration of Hg in the sample is being checked against a regulatory compliance limit, the spike level shall be at that limit or at 1–5 times the background concentration of the sample, whichever is greater.
- 9.5.1.2 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 the concentration in the IPR/OPR solution (Section 7.7.7).
- 9.5.2 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*.
- 9.5.2.1 If necessary, prepare a standard solution to produce an appropriate level in the sample (Section 9.5.1).
- 9.5.2.2 Spike two additional sample aliquots with the spiking solution and analyze as described in Section 11 to determine the concentration after spiking (A).
- 9.5.3 Calculate the percent recovery (R) in each aliquot using the following equation:

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**Equation 1**

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

where:

A = Measured concentration of analyte after spiking

B = Measured concentration (background) of analyte before spiking

T = True concentration of the spike

R = Recovery (%)

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- 9.5.4 Compare percent recovery (R) with the QC acceptance criteria in Table 2.
- 9.5.4.1 If results of the MS/MSD are similar and fail the acceptance criteria, and recovery for the OPR standard (Section 9.4) 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 9.1.1, and repeat analysis of the sample and MS/MSD. However, during the development of Method 245.7, very few interferences have been noted in the determination of Hg using this Method. (See Section 4 for information on interferences.)
- 9.5.4.2 If the results of both the MS/MSD and the OPR test fall outside the acceptance criteria, the analytical system is judged to be out of control. Analyses must be halted and the laboratory must identify and correct the problem and reanalyze all samples in the sample batch.
- 9.5.5 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 9.5.3 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

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**Equation 2**

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

Where:

*D1* = concentration of Hg in the MS sample

*D2* = concentration of Hg in the MSD sample

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- 9.5.6 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.
- 9.5.7 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 performance criteria in Table 2 have been met, 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).
- 9.6 The laboratory shall, on an ongoing basis, demonstrate through analysis of the quality control sample (QCS) and the ongoing precision and recovery (OPR) sample that the system is in control. Sections 9.3 and 9.4 describe these procedures, respectively.
- 9.7 The laboratory shall maintain records to define the quality of the data that are generated. Sections 9.4.3 and 9.5.7 describe the development of accuracy statements.

- 9.8 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 one reagent blank (Section 9.2.1), an OPR sample, and a QCS. In addition, there must be at least one MS and one MSD sample for every 10 samples (a frequency of 10%).
- 9.9 Depending on specific program requirements, the laboratory may be required to analyze field duplicates 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 gas-liquid separator and dryer tube and produce a clear detection peak. Further details for operating the analytical system are given in Section 11. 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 standards. The lowest calibration standard must be at the minimum level (ML) of 5 ng/L.
- 10.1.1.2 Calibration standards are prepared by the addition of aliquots of the Hg working standard solution (Section 7.7.6) to 50 mL conical vials containing 25-30 mL reagent water. To each vial, add 20-30 mL reagent water. Except for the calibration blanks, dispense into each of 5 vials the following volumes of working standard solution (Section 7.7.6): 25.0  $\mu$ L, 50.0  $\mu$ L, 125.0  $\mu$ L, 250.0  $\mu$ L, 500.0  $\mu$ L. Dilute each calibration standard and calibration blank to the 50 mL vial mark with reagent water, cap vials and invert to mix. The concentrations in these vials will be 5.0 ng/L, 10.0 ng/L, 25.0 ng/L, 50.0 ng/L and 100.0 ng/L respectively.
- 10.1.1.3 Remove caps and add 50  $\mu$ L of the hydroxylamine solution (Section 7.7.2). Recap and invert once to mix and allow to stand until the yellow color disappears. Remove all caps and place vials into the analysis rack.
- 10.1.1.4 For each calibration standard, determine the peak height or area. Calculate the calibration factor ( $CF_x$ ) for Hg in each of the five standards using the following equation:



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**Equation 3**

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

Where:

$A_x$  = peak height or area for Hg in standard

$C_x$  = concentration of standard analyzed (ng/L)

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- 10.1.1.5 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  $RSD = 100 \times SD/CF_m$ .
- 10.1.1.6 If  $RSD \leq 15\%$ , calculate the recovery for the lowest standard (5.0 ng/L) using  $CF_m$ . If the  $RSD \leq 15\%$  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.
- 10.1.1.7 Determine the concentration in at least two calibration blanks using the equation 4 in Section 12.2. If either calibration blank has a concentration of Hg > MDL, the analytical system and reagents should be checked for contamination, the problem remediated, and the system recalibrated.
- 10.2 Ongoing precision and recovery (OPR)
- 10.2.1 Perform the ongoing precision and recovery test (Section 9.4) to verify calibration prior to and after analysis of samples in each analytical batch.
- 10.2.2 The CF for the OPR must fall within  $\pm 15\%$  of  $CF_m$ .
- 10.2.3 If the CF is not within this range, calibration has not been verified. In this event prepare and analyze a new IPR/OPR solution (Section 7.7.7) and repeat the test (Section 10.2.1). If calibration is not verified (Section 10.2.2), recalibrate the system (Section 10.1). All analyses must be run on a system that has met the calibration criteria (Section 10.1.1.6) or on which calibration has been verified (Section 10.2).

## 11.0 Procedure

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**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 gas flow rates, for the laboratory's specific instrumental set-up.

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### 11.1 Sample Preparation

- 11.1.1 The following procedure should be conducted within a class 100-clean hood, glove box/dry-box or glove bag to prevent contamination of reagents, samples, and equipment. Reagents should be stored within the clean hood, glove box or glove bag until use.
- 11.1.2 Transfer samples to a class-100 clean fume hood or a disposable glove bag filled with argon. Care should be taken to isolate samples from reagents and other solutions. Label sample vials and corresponding lids to assure that vials and caps are not interchanged.
- 11.1.3 For determination of dissolved mercury using samples not filtered or preserved during sampling or upon receipt by the laboratory, use a disposable syringe with an attached 0.45  $\mu\text{m}$  filter. Remove the syringe plunger and pour the sample into the syringe to overflowing. Replace the plunger and press the sample through the filter into the corresponding sample vial, filling to the 50 mL mark.
- 11.1.4 Prepare the conical vials for sample digestion by adding 5 mL (1:1) HCl solution (Section 7.7.1) and 1.0 mL  $\text{KBrO}_3/\text{KBr}$  solution (Section 7.7.4). For clear water and filtered samples, add 1.0 mL of  $\text{KBrO}_3/\text{KBr}$  solution; for brown or turbid samples, add 2.0 mL of  $\text{KBrO}_3/\text{KBr}$  solution.
- 11.1.5 Transfer samples to corresponding vials and fill to the 50 mL mark. Immediately cap the vials and check each for a complete seal. Discard any leaking vials, and reprocess that sample. Allow samples to digest for at least 30 minutes. If the yellow color disappears because of consumption by organic matter or sulfides, more  $\text{KBrO}_3/\text{KBr}$  solution should be added until a permanent yellow color is obtained.
- 11.1.6 Some highly organic matrices, such as sewage effluent, will require high levels of  $\text{KBrO}_3/\text{KBr}$  solution (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 hours). The amount of reagent added to a sample must be the same as the amount added to the reagent blank to detect contamination in the reagents (see Section 9.2.1.2). The oxidation must be continued until it is complete. Complete oxidation can be determined either by observation of a permanent yellow color remaining in the sample or the use of starch iodide indicating paper to test for residual free oxidizer.
- 11.1.7 After oxidation is complete, remove each vial cap and add 50  $\mu\text{L}$  of hydroxylamine solution (Section 7.7.2) to eliminate excess bromine. Recap and invert once to mix. Allow to stand for a few seconds. The yellow color will disappear, indicating the destruction of the  $\text{KBrO}_3/\text{KBr}$ . Allow the sample to react for 5 minutes with periodic swirling to be sure that no traces of halogens remain. Remove all caps and place vials into the analysis rack.

- 11.2 Instrument set up and operation—The automated mercury analytical system is usually configured as shown in Figure 1.

- 11.2.1 Initiate operation of the atomic fluorescence instrument and data collection system. Follow the instrument manufacturer's recommendations for settings as the setting may vary between manufacturers and upgrades. Typical instrument settings for the PSA Automated Mercury Analyzer are listed in Table 3.
- 11.2.2 Adjust the gain on the detector to produce a peak height of 35% full scale for 50 ng/L Hg.
- 11.2.3 Allow sufficient time for the system to equilibrate before initiating sample analysis. It is recommended that this time be coordinated with the completion of sample oxidation and the addition of hydroxylamine hydrochloride solution (Section 11.1.7).
- 11.3 Sample analysis
- 11.3.1 After instrument calibration and before sample analysis, at least two reagent blanks must be analyzed (Section 10.1.1.7). If the reagent blank contains Hg at greater than MDL given in Section 1.5 of this Method, blank control has not been demonstrated, and the source of contamination must be identified and corrected.
- 11.3.2 If an autosampler is used, set up a reagent water wash solution, or place a vial containing reagent water between each vial to be analyzed. The purpose of this solution is to wash mercury from the sample probe and the sample tubing.
- 11.3.3 If the analytical system is operated manually, the sample line should be inserted into a reagent water wash solution between analysis of samples. Insert the sample tubing or sample probe at the time the "delay" cycle starts, and withdraw when the "analysis" cycle ends. During the "memory" cycle, return the sample tubing or probe to the wash solution. Repeat this operation until all samples have been analyzed.
- 11.3.4 Any sample indicating a Hg concentration greater than 100 µg/L must be diluted and re-analyzed. *Do not dilute the digested sample.* Instead, dilute the original sample with reagent water to bring the concentration within the calibration range.

## 12.0 Data Analysis and Calculations

- 12.1 Measure the peak height or area for each sample.
- 12.2 Calculate the concentration of Hg in ng/L (parts-per-trillion; ppt) in each sample according to the following equation:

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### Equation 4

$$[\text{Hg}] \text{ (ng/L)} = \frac{A_s}{CF_m} \times \frac{V_{std}}{V_{sample}}$$

where:

$A_s$  = peak height (or area) for Hg in sample

$CF_m$  = mean calibration factor (Section 10.1.1.6)

$V_{std}$  = 50 mL - mL reagent used in standards

$V_{sample}$  = 50 mL - mL reagent used in sample

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- 12.3 To determine the concentration of Hg in the reagent blank, use the equation in Section 12.2 and substitute the peak height or area resulting from the reagent blank for  $A_s$ . To determine the amount of Hg in the reagent blank that may have been introduced into a sample ( $C_{RB}$ ), correct the concentration of Hg in the reagent blank by the volume of  $KBrO_3/KBr$  solution used for the particular sample (Section 11.1) using the following equation:

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**Equation 5**

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

where:

$V_{BS}$  = volume of  $KBrO_3/KBr$  solution used in sample (Section 11.1.3)

$V_{BRB}$  = volume of  $KBrO_3/KBr$  solution used in reagent blank (Section 9.2.1.2)

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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 <5.0 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 as < 1.8 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, unless otherwise requested or required by a regulatory authority or in a permit. If blank correction is requested or required, subtract the concentration of Hg in either the reagent blank or the field blank from the concentration of Hg in the sample to obtain the net sample Hg concentration.
- 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 do not relieve a discharger or permittee of timely reporting.

## 13.0 Method Performance

- 13.1 This method was tested in 3 laboratories using reagent water, freshwater, marine water, marsh water and effluent. The quality control acceptance criteria listed in Table 2 and the MDL given in Section 1.5 and Table 1 were determined by data gathered in these studies.
- 13.2 Precision and recovery data for reagent water, freshwater, marine water, marsh water and effluent are given in Table 4.

## 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 wastes cannot be reduced feasibly 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 reagent 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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- 6 Method 1631: Mercury in Water by Oxidation, Purge and Trap, and CVAFS, U.S. EPA Office of Water, Office of Science and Technology, Engineering and Analysis Division, March 1998.
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- 10 Method 1669, "Method for Sampling Ambient Water for Determination of Metals at EPA Ambient Criteria Levels," U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460, April 1995 with January 1996 revisions.
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- 13 Bloom, N.S. "Influence of Analytical Conditions on the Observed 'Reactive Mercury,' Concentrations in Natural Fresh Waters." In *Mercury as a Global Pollutant*; Huckabee, J. and Watras, C.J., Eds.; Lewis Publishers, Ann Arbor, MI: 1994.

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- 15 "Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service. Centers for Disease Control. NIOSH Publication 77-206, Aug. 1977, NTIS PB-277256.
- 16 "OSHA Safety and Health Standards, General Industry," OSHA 2206, 29 CFR 1910.
- 17 "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety, 1979.
- 18 "Standard Methods for the Examination of Water and Wastewater," 18th ed. and later revisions, American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 1-35: Section 1090 (Safety), 1992.

## 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 one reagent blank, 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 **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.
- 17.4 **May**—This action, activity, or procedural step is allowed but not required.
- 17.5 **May not**—This action, activity, or procedural step is prohibited.
- 17.6 **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  $(1, 2, \text{ or } 5) \times 10^n$ , where n is an integer.
- 17.7 **Must**—This action, activity, or procedural step is required.
- 17.8 **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.

- 17.9 **Reagent Water**—Water demonstrated to be free of mercury at the MDL of this Method. It is prepared from 18 MΩ ultra-pure 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.
- 17.10 **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.
- 17.11 **Shall**—This action, activity, or procedure is required.
- 17.12 **Should**—This action, activity, or procedure is suggested, but not required.
- 17.13 **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.
- 17.14 **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 245.7**

Metal	Lowest Nationwide Water Quality Criterion <sup>(1)</sup>	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL <sup>(2)</sup>	ML <sup>(3)</sup>
Mercury (Hg)	12 ng/L	1.8 ng/L	5.0 ng/L

- 1. 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 245.7**

Metal	IPR % Recovery		OPR % Recovery	MS/MSD	
	RSD	X		%R	RPD
Mercury (Hg)	16	78-108	76-111	76-111	18

**Table 3****Instrument Control and Gas Flow Settings**

Fluorescence Instrument Parameters	PSA Merlin Series AFS Range of Settings
Delay Time	5 to 15 seconds
Rise Time	20 to 30 seconds
Analysis Time	30 seconds
Memory Time	60 seconds
Argon Gas Control	Range of Settings
Gas Regulator	20 to 30 psi.
Carrier Flow	150 to 450 mL/minute
Drier Tube Flow	2.5 to 3.5 L/minute
Sheath Flow	150 to 250 mL/minute

**Table 4**

**Precision and Recovery for Reagent Water, Fresh Water, Marine Water, and Effluent Water  
Using Method 245.1**

<b>Matrix</b>	<b>*Mean Recovery (%)</b>	<b>*Precision (% RSD)</b>
Drinking Water	96	1.7
Drinking / groundwater	93	2.8
Artificial Marine Water	94	1.5
Freshwater	91	2.2
Municipal Effluent	88	7.4
Marsh Water	97	1.2

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

**Figure 1:** Automated Mercury Fluorescence System

