# Methods of Analysis by The U.S. Geological Survey National Water Quality Laboratory—Determination of Organic Plus Inorganic Mercury in Filtered and Unfiltered Natural Water with Cold Vapor–Atomic Fluorescence Spectrometry

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Water-Resources Investigations Report 01-4132

U.S. Department of the Interior
U.S. Geological Survey

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By John R. Garbarino and Donna L. Damrau

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**Gale A. Norton, Secretary**

**U.S. Geological Survey**
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## FIGURES

1-3. Box plots showing:

## TABLES

## CONVERSION FACTORS

| Multiply | By | To obtain |
|---|---|---|
| | **Length** | |
| micrometer (µm) | $3.94 \times 10^{-5}$ | inch |
| millimeter (mm) | $3.94 \times 10^{-2}$ | inch |
| nanometer (nm) | $3.94 \times 10^{-8}$ | inch |
| | **Mass** | |
| gram (g) | $3.53 \times 10^{-2}$ | ounce, avoirdupois |
| milligram (mg) | $3.53 \times 10^{-5}$ | ounce, avoirdupois |
| nanogram (ng) | $3.53 \times 10^{-11}$ | ounce, avoirdupois |
| | **Volume** | |
| liter (L) | $2.64 \times 10^{-1}$ | gallon |
| microliter (µL) | $2.64 \times 10^{-7}$ | gallon |
| milliliter (mL) | $2.64 \times 10^{-4}$ | gallon |
| | **Pressure** | |
| kilopascal (kPa) | $1.45 \times 10^{-1}$ | pounds per square inch |

Degrees Celsius ($^{o}$C) may be converted to degrees Fahrenheit ($^{o}$F) by using the following equation:

$$^{o}F = 9/5\,(^{o}C) + 32.$$

## ABBREVIATED WATER-QUALITY UNITS

| | |
|---|---|
| mg/L | milligrams per liter |
| µg/L | micrograms per liter |
| µg/mL | microgram per milliliter |
| ng/L | nanograms per liter |
| mL/min | milliliters per minute |
| L/min | liters per minute |

## ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| ASTM | American Society for Testing and Materials |
| CASRN | Chemical Abstract Service Registry Number |
| CV–AAS | cold vapor–atomic absorption spectrometry |
| CV–AFS | cold vapor–atomic fluorescence spectrometry |
| HCl | hydrochloric acid |
| M | Molar (moles per liter) |
| LT–MDL | long-term method detection level |
| MDL(s) | method detection limit(s) |
| MRL | method reporting level |
| $HNO_3$ | nitric acid |
| N | Normal (acid equivalents per liter) |
| NIST | National Institute of Standards and Technology |
| NWQL | National Water Quality Laboratory |
| s | second |
| sp. gr. | Specific gravity |
| SRM | standard reference material |
| SRWS(s) | U.S. Geological Survey standard reference water sample(s) |
| USEPA | U.S. Environmental Protection Agency |
| USGS | U.S. Geological Survey |
| < | less than |
| ± | plus or minus |

## GLOSSARY

**MDL** — The method detection limit (MDL) is defined as the minimum concentration of an element that can be measured and reported with 99-percent confidence that the element concentration is greater than zero and is determined from analysis of a sample in a given matrix that contains the element of interest (U.S. Environmental Protection Agency, 2000).

# Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organic Plus Inorganic Mercury in Filtered and Unfiltered Natural Water with Cold Vapor – Atomic Fluorescence Spectrometry

*By* John R. Garbarino and Donna L. Damrau

## Abstract

An analytical method using cold vapor–atomic fluorescence spectrometry was developed by the U.S. Geological Survey in 2001 for the determination of organic plus inorganic mercury in filtered and unfiltered natural water. This method was developed to eliminate the use of acid dichromate preservative and to provide capability to measure ambient mercury concentrations in natural water. Dissolved mercury includes all oxidizable mercury species present in natural water that has been filtered through a 0.45-micrometer pore size capsule filter. Whole-water recoverable mercury includes dissolved mercury species and mercury species adsorbed to particulate matter in unfiltered natural water. Mercury species can include elemental mercury, mercury (II), mercury (II) complexes, various alkyl- and phenyl-mercury compounds, and other forms of mercury. In this method, samples are collected and processed according to standard U.S. Geological Survey protocols. Samples are preserved onsite with 6N hydrochloric acid in a ratio of 1 to 100 in a borosilicate-glass bottle with fluoropolymer-lined cap. Mercury species are oxidized to mercury (II) by using bromine monochloride; excess oxidation reagent is neutralized with hydroxylamine hydrochloride. Elemental mercury produced after adding stannous chloride is purged from the solution with ultrapure argon gas into a cell in which the mercury concentration is measured by atomic fluorescence emission at 253.7 nanometers. The analytical response is linear up to 125 nanograms per liter (ng/L) of mercury, and the short-term method detection limit is about 5 ng/L. The analytical variability at 50 ng/L is about 10 percent.

This report describes the method and compares the use of hydrochloric acid to acid dichromate as a field preservative. Ambient mercury concentrations in hydrochloric acid-preserved samples stored in borosilicate-glass bottles with fluoropolymer-lined caps are shown to be stable for at least 30 days. Mercury concentrations are stable for at least 5 months after bromine monochloride is added to the sample bottles in the laboratory. The long-term average percent recoveries at 20, 45, and 75 ng/L in reagent water, filtered and unfiltered ground water, and filtered and unfiltered surface water range from 89 to 108, 96 to 103, and 94 to 98 percent, respectively.

## INTRODUCTION

The ambient concentration for dissolved and whole-water recoverable mercury is generally at the parts-per-trillion level (nanograms-per-liter, ng/L) for natural-water samples. Measurement at this concentration level is important because mercury bioaccumulates in living organisms. The previous method (Fishman and Friedman, 1989, p. 289–291) that used cold vapor–atomic absorption spectrometry (CV–AAS) was not capable of measuring such low concentrations. Cold vapor–atomic fluorescence spectrometry (CV–AFS) is capable of measuring 5 ng/L mercury directly, without sample preconcentration. By eliminating sample preconcentration, analysis throughput is increased while maintaining the capability to determine mercury concentrations at levels typically regulated by water-quality standards. The mercury concentration, organic plus inorganic species, is determined in filtered and unfiltered natural-water samples by using a brominating digestion procedure that minimizes interferences. Samples are preserved with hydrochloric acid instead of acid dichromate solution, which has previously been used. This change was necessary because shipment of samples preserved with dichromate solution is restricted, and the cost of disposing of chromium waste is expensive. In addition, hydrochloric acid sample preservation has been shown as effective as sample preservation with acid dichromate solution.

This report describes a method for determining mercury in natural-water samples. It was developed by the U.S. Geological Survey (USGS) for use in the National Water Quality Laboratory (NWQL). It is rapid, more efficient, and can detect lower concentration levels compared to previous USGS methods (Fishman and Friedman, 1989, p. 289–291). This method supplements other methods of the USGS for the determination of mercury that are described by Fishman and Friedman (1989) and by Fishman (1993). The new method was implemented at NWQL in April 2001.

This report provides a detailed description of all aspects of the method, including the instrumentation, the reagents, the analytical procedure, and the quality-control procedures. Mercury concentration is reported by NWQL in micrograms per liter instead of nanograms per liter, the concentration unit used throughout this report, because of current (2001) limitations in the data base.

## ANALYTICAL METHOD

### Inorganic Constituents and Method, Lab, and Parameter Codes

| Constituent | Method | Lab code | Parameter and method code |
|---|---|---|---|
| Mercury, water filtered, organic + inorganic, μg/L | I-2464-01 | 2707 | 71890C |
| Mercury, water unfiltered, organic + inorganic, μg/L | I-4464-01 | 2708 | 71900D |

### 1. Application

This method is used to determine concentrations of organic plus inorganic mercury in filtered and unfiltered natural-water samples. Bromine monochloride is used to oxidize elemental mercury, mercury complexes, various alkyl- and phenyl-mercury compounds, and other forms of mercury. The upper limit of the linear concentration range is 125 ng/L mercury. The short-term method detection limit (MDL, see Glossary) is 5 ng/L mercury (table 1).

### 2. Summary of Method

Concentrations of organic plus inorganic mercury in filtered and unfiltered natural-water samples are determined by using CV–AFS. The method is based on U.S. Environmental

Protection Agency (1999) Method 1631 but does not use gold amalgamation for mercury preconcentration. By eliminating the preconcentration procedure, the MDL is at least a factor of 10 greater, yet the method provides the determination of mercury at ambient concentrations. Mercury species in a natural-water sample are oxidized to mercury (II) inside the borosilicate-glass sample bottle by using bromine monochloride; excess oxidant is neutralized with hydroxylamine hydrochloride. Mercury (II) is reduced to elemental mercury by using stannous chloride, and is purged from the solution with ultrapure argon gas into a cell in which the mercury concentration is measured by atomic fluorescence emission at 253.7 nanometers (nm).

**Table 1.** Method detection limit and analytical precision for the determination of mercury by cold vapor–atomic fluorescence spectrometry

[ng/L, nanograms per liter; MDL, method detection limit]

| Element | Mean, ng/L | Standard deviation, ng/L | *t*-statistic | Degrees of freedom | MDL, ng/L |
|---|---|---|---|---|---|
| Mercury | 11 | 2 | 2.492 | 24 | 5 |

## 3. Sample Collection and Storage

Sample-collection protocol must follow either the procedure outlined for trace elements in Horowitz and others (1994) or for mercury in Olson and DeWild (1999). The level of contamination related to field collection and processing for either protocol, however, must be established by using an equipment blank. Filtered and unfiltered natural-water samples are preserved with hydrochloric acid to a pH less than 2. Samples are stored in clean borosilicate-glass sample bottles with fluoropolymer-lined caps. Bottles are prepared by rinsing once with 10 percent (by volume) mercury-free nitric acid and three times with deionized water before air-drying on a laminar-flow clean bench. The sample bottle must be rinsed with a portion of the filtered or unfiltered natural water prior to filling the bottle with about 200 mL of sample. Every sample must be preserved with 2 mL of 6N hydrochloric acid (HCl); more acid might be required to lower the pH to 2 in some matrices. It is important that field personnel use 6N HCl prepackaged in polypropylene vials that can be obtained from the USGS Ocala Water Quality and Research Laboratory in Florida (part number 06910) because the quality control is continually monitored. Ambient mercury concentrations are stable for 1 month in preserved samples. Nevertheless, samples should be shipped to the laboratory for analysis as quickly as possible.

## 4. Quality-Control Samples, Sampling Methods, Sample-Collection Equipment, and Cleaning Procedures

4.1 *Quality-control samples.* Collection of quality-control (QC) samples is a required component of sample collection for water-quality studies. QC samples are collected, usually onsite, to identify, quantify, and document bias and variability in data that result from collecting, processing, shipping, and handling of samples by field and laboratory personnel. The type, number, and distribution of QC samples are determined by the design and data-quality requirements of the study. Detailed discussion of the types and purposes of quality-control samples is provided in Wilde and others (1999).

The primary purpose of a blank sample is to identify potential sources of sample contamination and to assess the magnitude of mercury contamination. Field blanks are collected and processed onsite in the same manner and by using the same equipment as for the environmental samples. The field blank is an aliquot of blank water that is processed sequentially through each component of the sampling system. The source water needed for blank samples must be produced and certified by a laboratory to have mercury concentrations that do not exceed a specified method detection limit. Inorganic-free blank water must be used for all equipment field blanks (Horowitz and others, 1994, p. 22).

Replicate samples also may be collected. The primary purpose of replicate samples is to quantify the variability in all or part of the sampling and analysis process. Replicates, environmental samples collected in duplicate, triplicate, or higher multiples, are considered identical in composition and are analyzed for the same chemical constituents.

4.2 *Sampling methods*. Use methods that allow collection of water samples that accurately represent the water-quality characteristics of the surface water or ground water at a given time or location. Detailed descriptions of sampling methods used by the USGS for obtaining surface-water samples, ground-water samples, and sample-processing procedures (splitting, filtration, and shipping) are provided by Wilde and others (1999).

4.3 *Sample-collection equipment.* Use sample-collection equipment and automatic samplers that are free of tubing, gaskets, and other components made of metal or that might sorb mercury from the water. The best material for sample-collection and processing equipment is any type of fluorocarbon polymer.

4.4 *Cleaning procedures.* Follow the procedures outlined in either Horowitz and others (1994) or Olsen and DeWild (1999).

## 5. Contamination and Interferences

Contamination must be avoided because of the inherently low mercury concentration found in natural water. The analyst and field personnel need to be attentive to potential sources of contamination. Sampling equipment must be cleaned, and samples need to be collected as described by Horowitz and others (1994) or by Olson and DeWild (1999). Every sample must be preserved with 2 mL of 6N HCl that can be obtained from the USGS Ocala Water Quality and Research Laboratory in Florida. Samples might become contaminated during analysis by carryover from a previous sample that had unusually high mercury concentration. Contamination from airborne sources can be minimized by placing the autosampler inside a plastic enclosure pressurized with mercury-free nitrogen.

Gold, silver, and iodide interfere with the determination of mercury by this method. Elemental mercury is amalgamated by gold or silver. The recovery of 2.5 ng/L of mercury in the presence of 5 to 100 mg/L iodide ranges from 100 to 0 percent (U.S. Environmental Protection Agency, 1996; Bloom, 1995). After analyzing a sample that contains greater than 30 mg/L iodide, it may be necessary to clean the analytical system with 4N HCl (U.S. Environmental Protection Agency, 1999; Bloom, 1995). Most forms of mercury are oxidized by the bromine monochloride solution; however, the recovery of mercury bound within microbial cells might require additional ultraviolet photooxidation (U.S. Environmental Protection Agency, 1999). Buildup of condensation in the vapor generator or fluorescence cell will degrade the analytical signal. Condensation can be eliminated by wrapping heating tape around the vapor generator and by using a drying tube in front of the fluorescence cell. The drying tube should be replaced after about 1 year of operation. Ultrapure argon (99.998 percent) must be used for the purge gas to minimize the possibility of fluorescent quenching by impurities.

## 6. Apparatus and Instrumentation

6.1 *Labware.* Use clean Type A glass volumetric flasks to prepare all solutions. Store mercury stock solutions in borosilicate-glass bottles with fluoropolymer-lined caps. The accuracy of all pipets and volumetric flasks should be regularly verified gravimetrically or by using an automatic volume-calibrating spectrophotometer system before preparing standard solutions.

6.2 *Instrumentation*. Several commercial automated CV–AFS systems are available. These systems are composed of a spectrometer, mercury-vapor generator, autosampler, and computer. The major components of the spectrometer are a mercury line source, a quartz flow-through fluorescence cell, and a photometer. The mercury-vapor generator is composed of several peristaltic pumps and a series of computer controlled, time-actuated solenoid valves that introduce sample and reagents, a gas-liquid separator, and a membrane dryer tube that removes moisture. The autosampler and computer automate sample introduction, data acquisition, and quantitation.

## 7. Reagents and Calibration Standards

All solutions used in this method must be verified to have mercury-contaminant concentration, after the prescribed dilution, that is less than the MDL. ASTM Type I reagent water (American Society for Testing and Materials, 2000) must always be used to prepare solutions. Heating each compound used in this method, with the exception of the hydrated stannous chloride, in a muffle furnace at 250 °C for 8 hours will volatilize mercury impurities. All solutions must be stored in designated borosilicate-glass bottles with fluoropolymer-lined caps. All calibration standards are stable for 1 month.

7.1 *Argon gas* is used as the purge (carrier) gas. Its purity must be at least 99.998 percent.

7.2 *Nitrogen gas* is used as the sheath gas. Its purity must be at least 99.998 percent.

7.3 *Hydroxylamine hydrochloride* ($NH_2OH{\cdot}HCl$) Chemical Abstract Service Registry Number (CASRN) 5470-11-1.

7.4 *Potassium bromate* ($KBrO_3$) CASRN 7758-01-2.

7.5 *Potassium bromide* (KBr) CASRN 7758-02-3.

7.6 *Stannous chloride* ($SnCl_2{\cdot}2H_2O$) CASRN 10025-69-1.

7.7 *Nitric acid solution*, 0.4 percent (by volume). Add 4 mL of concentrated nitric acid [$HNO_3$, 16 M, specific gravity (sp. gr.) 1.41] to 500 mL of water in a 1-L volumetric flask. Bring to volume with water. This solution is used to rinse between sample analyses.

7.8 *Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) solution*, 15 percent (by weight). Dissolve 30 g of $NH_2OH{\cdot}HCl$ in a 200-mL volumetric flask that contains about 10 mL of water. Bring to volume with water. Solution must be prepared weekly.

7.9 *Bromine monochloride (BrCl) solution.* This solution is used to oxidize mercury species in a sample to mercury (II). Dissolve 10.8 g of KBr in 1 L of concentrated hydrochloric acid (HCl, 12 M, sp. gr. 1.19) in a borosilicate-glass bottle. Place a clean magnetic stir bar in the bottle and stir for (NOTE: This process produces copious quantities of free halogens, such as $Cl_2$, $Br_2$, BrCl.) When all of the $KBrO_3$ has been added, the color of the solution should change from yellow to red to orange. Loosely cap the bottle, and stir another hour before tightening.

7.10 *Stannous chloride ($SnCl_2$) solution*, 2 percent (weight-to-volume ratio). This solution is used to reduce mercury (II) to elemental mercury. Dissolve 20 g of $SnCl_2 \cdot 2H_2O$ into a 1-L volumetric flask that contains 200 mL of water. Slowly add 30 mL concentrated HCl, mix, and bring to volume with water. Allow solution to equilibrate 1 hour before use. Solution must be prepared daily.

7.11 *Primary mercury stock solution*, 10,000 mg/L. National Institute of Standards and Technology (NIST) standard reference material (SRM) 3133. This reference material is stable until the NIST expiration date.

7.12 *Secondary mercury stock solution*, 1.00 mg/L. Pipet 100 µL of primary standard solution into a 1-L volumetric flask, and 5 mL of BrCl solution, and bring to volume with water. Solution is stable for 1 year.

7.13 *Tertiary mercury stock solution*, 2.0 µg/L. Pipet 2.0 mL of secondary stock solution into a 1-L volumetric flask, and 5 mL of BrCl solution, and bring to volume with water. Solution is stable for 1 month.

7.14 *Calibration standard 1*, 0 ng/L. Add 1 mL of BrCl solution to a 200-mL volumetric flask and bring to volume with water.

7.15 *Calibration standard 2*, 5.0 ng/L. Add 0.5 mL of the tertiary mercury stock solution and 1 mL of BrCl solution to a 200-mL volumetric flask and bring to volume with water.

7.16 *Calibration standard 3*, 10.0 ng/L. Add 1.0 mL of the tertiary mercury stock solution and 1 mL of BrCl solution to a 200-mL volumetric flask and bring to volume with water.

7.17 *Calibration standard 4*, 25.0 ng/L. Add 2.5 mL of the tertiary mercury stock solution and 1 mL of BrCl solution to a 200-mL volumetric flask and bring to volume with water.

7.18 *Calibration standard 5*, 50.0 ng/L. Add 5.0 mL of the tertiary mercury stock solution and 1 mL of BrCl solution to a 200-mL volumetric flask and bring to volume with water.

7.19 *Calibration standard 6*, 100.0 ng/L. Add 10.0 mL of the tertiary mercury stock solution and 1 mL of BrCl solution to a 200-mL volumetric flask and bring to volume with water.

## 8. Sample Preparation

Samples and calibration solutions are processed identically. Mercury species are oxidized to mercury (II) by adding 1 mL of BrCl solution (see section 7.9) to 200 mL of field-acidified, filtered or unfiltered, natural-water sample. The sample is digested for at least 12 hours at room temperature prior to analysis. If the yellow color disappears, add more BrCl solution to fully digest the sample. The sample is completely digested when the yellow color persists for at least 12 hours. Record the total volume of BrCl solution added so that the final mercury concentration can be adjusted for dilution. Mercury bound within microbial cells also might require ultraviolet photooxidation (U.S. Environmental Protection Agency, 1999). Some highly organic matrices might require longer oxidation times at an elevated temperature. The sample bottles can be placed in an oven set at 50 °C for 6 hours when elevated temperature is required. Nevertheless, samples should be analyzed as quickly as possible after the oxidation procedure.

Just prior to analysis, 10 mL of BrCl-oxidized sample is pipetd into an autosampler borosilicate-glass test tube. Adding 40 µL of hydroxylamine hydrochloride solution (see section 7.8) neutralizes excess BrCl. Allow about 5 minutes for the reaction to reach completion. The disappearance of the yellow color indicates that all the BrCl has been destroyed and no traces of halogens remain.

## 9. Analytical Procedure

The analytical procedure for the method is fully automated. After calibration standards and unknown samples have been processed by using the procedure outlined in section 8, they are loaded into the autosampler. The system introduces a given volume of sample and $SnCl_2$ solution (see section 7.10) with a series of peristaltic pumps and solenoid valves. The mercury (II) present is reduced to elemental mercury that is purged from the reactor into the fluorescence cell with argon gas. The mercury concentration is determined by relating the signal peak area for the samples to the peak area for the calibration standards. Refer to the NWQL Standard Operating Procedure IM0348.0 (D.L. Damrau, U.S. Geological Survey, written commun., 2001), Zellweger Analytics Inc. (1996; 1997), and Wendt (1997) for details of the operation and maintenance of the instrumentation used in this method. Typical operating conditions are listed in table 2.

**Table 2.** Typical instrument operating conditions

[kPa, kilopascal; lbs/in$^2$, pounds per square inch; mL/min, milliliters per minute; L/min, liters per minute; s, second]

| Parameter | Setting |
|---|---|
| **Mercury-vapor generator flow rates** | |
| Argon at 276 kPa (40 lbs/in$^2$) | |
| Purge (carrier) gas - - - - - - - - - - - - - | 300 mL/min |
| Nitrogen at 276 kPa (40 lbs/in$^2$) | |
| Dryer gas - - - - - - - - - - - - - - - - - - - | 2.75 L/min |
| Sheath gas - - - - - - - - - - - - - - - - - - | 250 mL/min |
| **Mercury-vapor generator timing** | |
| Sample delay - - - - - - - - - - - - - - - - - - | 18 s |
| Wash period - - - - - - - - - - - - - - - - - - | 170 s |
| Load period - - - - - - - - - - - - - - - - - - - | 45 s |
| **Spectrometer** | |
| Calibration range- - - - - - - - - - - - - - - - | 1,000 |
| Fine gain - - - - - - - - - - - - - - - - - - - - | 6.50 |
| Mode switch - - - - - - - - - - - - - - - - - - | Ratio |
| Integration time - - - - - - - - - - - - - - - - | 0.25 s |

## 10. Calculations

No calculations are required except when samples are diluted and dilution factors are applied.

## 11. Reporting Results

Mercury concentration is reported by NWQL in micrograms per liter (µg/L) instead of nanograms per liter (ng/L) because of the current (2001) limitations of the data base. The number of significant figures reported are listed as follows:

- If the mercury concentration is less than the long-term method detection level (LT–MDL), then the result is reported as less than (<) the method reporting level (MRL), in micrograms per liter. Samples between the LT–MDL and MRL will be "E" coded to indicate an estimated concentration.

- If the mercury concentration is greater than or equal to the MDL, but less than 0.100 µg/L, then the result is reported to the nearest 0.001 µg/L.

- If the mercury concentration is greater than 0.100 µg/L, then the result is reported to the nearest 0.01 µg/L.

## DISCUSSION OF RESULTS

The CV–AFS mercury method was developed to eliminate the use of the acid dichromate preservative and to provide a method that is capable of measuring ambient mercury concentrations in natural water. A U.S. Department of Transportation regulation on the shipment of natural-water samples preserved with acid dichromate requires packaging and shipment protocols that are expensive. In addition, it is expensive to dispose of samples that contain high concentrations of chromium because it is a priority pollutant. Several U.S. Environmental Protection Agency (USEPA) methods [for example, Method 1631 (U.S. Environmental Protection Agency, 1999], use hydrochloric acid (HCl) as a preservative. A water sample preserved with HCl passes all required corrosion tests and can be shipped without expensive packaging.

A filtered or unfiltered natural-water sample is stored in a 250-mL borosilicate-glass bottle with a fluoropolymer-lined cap after adding 2 mL of 6N HCl to about 200 mL water (water level at the shoulder of the bottle). More acid must be added to samples that have high alkalinity to ensure that the pH is less than 2. If more than 2 mL of HCl is used, the total volume of acid should be listed on the Analytical Services Request form so that adjustments for dilution can be applied. It is important that samples are preserved with HCl specifically packaged and tested for such use. Polypropylene vials that contain HCl preservative can be obtained from the USGS Ocala Water Quality and Research Laboratory (part number 06910). The HCl preserves the mercury concentration in water samples for at least 30 days; the relative standard deviation of the results was less than 10 percent for a solution that had 10 ng/L mercury and that was analyzed two to three times a week for 1 month. No significant difference was found between the HCl and the previously used (prior to April 2001) acid dichromate preservatives. The average concentration for a sample that had 10 ng/L mercury preserved with HCl and that was analyzed repetitively for 90 days was not significantly different at the 95-percent confidence level (p=0.20) than the average concentration for a similar solution preserved with acid dichromate. Results obtained for solutions that had 5, 10, 25, 50, and 100 ng/L mercury (fig. 1) showed that the variation, as a function of mercury concentration, was similar for both preservation agents.

Mercury species in natural water can take various forms, including elemental mercury, mercury complexes, plus various alkyl- and phenyl-mercury compounds. Oxidation of such species to mercury (II) by using BrCl makes it possible to determine concentrations of organic plus inorganic mercury and also serves as a preservative to increase sample-holding times. Experiments have indicated that samples are stable for up to 3 months after the addition of BrCl. The percent-relative standard deviation for a sample that had 10 ng/L mercury that was analyzed more than 24 times for 3 months

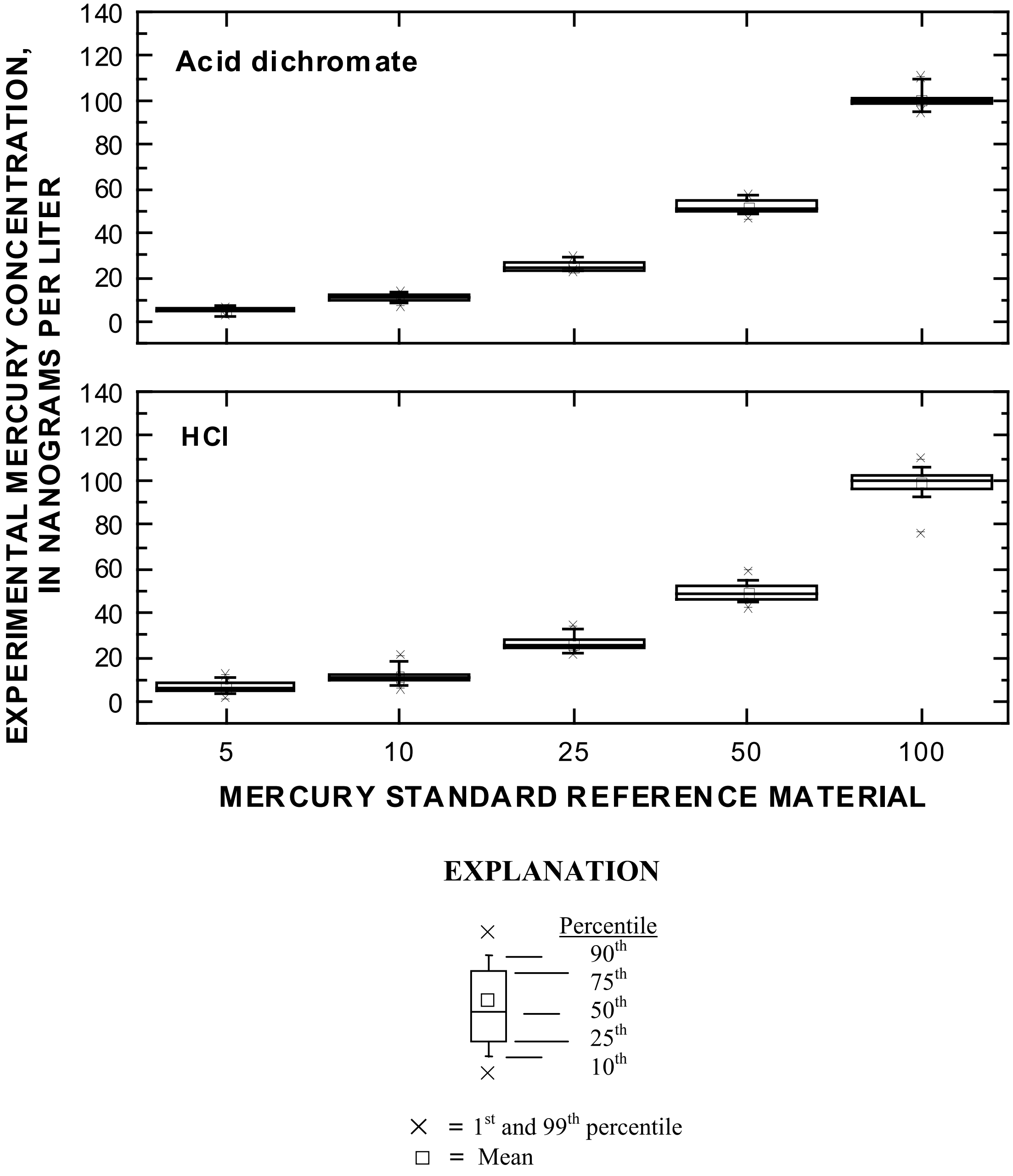

**Figure 1.** Results for a series of solutions based on a National Institute of Standards and Technology standard reference material preserved with acid dichromate or hydrochloric acid (HCl). Standard reference material concentration is in nanograms per liter.

was about 15 percent, an acceptable level of variability considering the concentration level and daily deviations in instrument performance and calibration standards.

The bias and variability of the method was tested by using standard reference materials from several different sources. The method performance is validated through the repetitive analysis of reagent-water, ground-water, and surface-water matrices spiked at three different mercury concentrations. Comparison of the analytical performance between the new CV–AFS method and the previously used CV–AAS (prior to April 2001) is not feasible because the method reporting level for the CV–AAS is only about 100 ng/L. This reporting level is about 20 times greater than the MDL for the new CV–AFS method, and 100 ng/L corresponds to the upper calibration limit. Onsite samples collected before April 2001 were preserved with acid dichromate, thus making direct comparisons problematic. Furthermore, during a typical year, more than 90 percent of the results for samples analyzed by CV–AAS for dissolved and whole-water recoverable mercury were less than or equal to 100 ng/L.

The accuracy of CV–AFS was tested by using two USGS standard reference water samples (SRWS). Calibration standards were prepared from NIST SRM-3133 in acid dichromate because all available reference water samples were preserved in the same preservative. The SRWSs were diluted by a factor of 10 because the most probable mean mercury concentration for all available SRWSs exceeded the calibration range. Additional mercury solutions preserved in acid dichromate were prepared at 10 and 50 ng/L from Baker Instra-Analyzed 1,000-µg/mL standard solution to provide another reference check. These four reference solutions were analyzed repetitively for 2 months after calibrating the instrument with NIST standards preserved with acid dichromate. Results for the diluted SRWSs compared favorably with expected concentrations (fig. 2). The experimental results of 38±2 (n=21) and 71±3 ng/L (n=19) correspond to the theoretical means of 420 and 700 ng/L, respectively, after being adjusted for dilution. The results for the 10- and 50-ng/L solutions prepared from the Baker Instra-Analyzed standard were acceptable at 10±2 and 55±3 ng/L, respectively.

Either nitrogen or argon gas has been used in analytical methods for mercury to purge elemental mercury from the reactor cell. Experimental results (fig. 3) show that there is little difference between the two gases when mercury concentrations exceed 10 ng/L. The use of argon gas significantly increases the precision at 10 ng/L, because the sensitivity of the measurement is increased by about a factor of 2 over nitrogen gas. Thus, the use of argon gas is necessary for measuring ambient mercury concentrations. The accuracy and variability of using argon was established by analyzing reference standards prepared from two different sources repetitively for 1 month. Mercury solutions preserved in HCl were prepared from Baker Instra-Analyzed 1,000-µg/mL (25 and 75 ng/L) and Spex CertiPrep 10-µg/mL (10 and 50 ng/L) standard solutions. Experimental concentrations were determined for these solutions relative to NIST calibration standards. Linear regression analysis (fig. 4) of results shows a significant correlation between the experimental (Baker and Spex) solutions and the theoretical concentrations (slope=0.925, correlation coefficient=0.9992). The variability ranged from 5 to 15 percent and was a function of concentration. In addition, the stability of the preservation and instrumentation is supported by the data that were accumulated for a month.

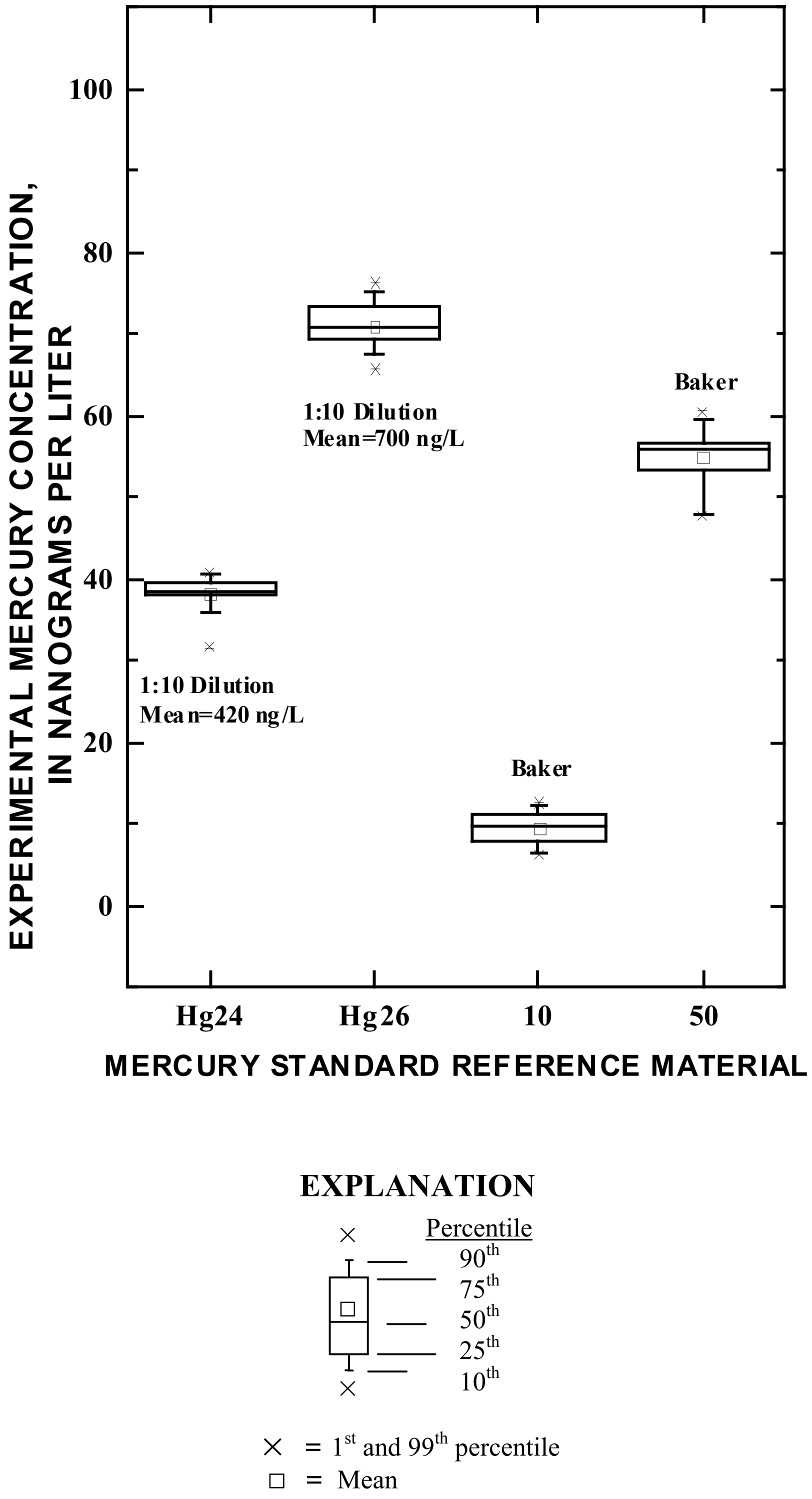

**Figure 2.** Results for U.S. Geological Survey standard reference water samples Hg24 and Hg26 and two dilutions of a Baker Instra-Analyzed standard preserved in acid dichromate. Mercury concentrations for standard reference materials are in nanograms per liter (ng/L).

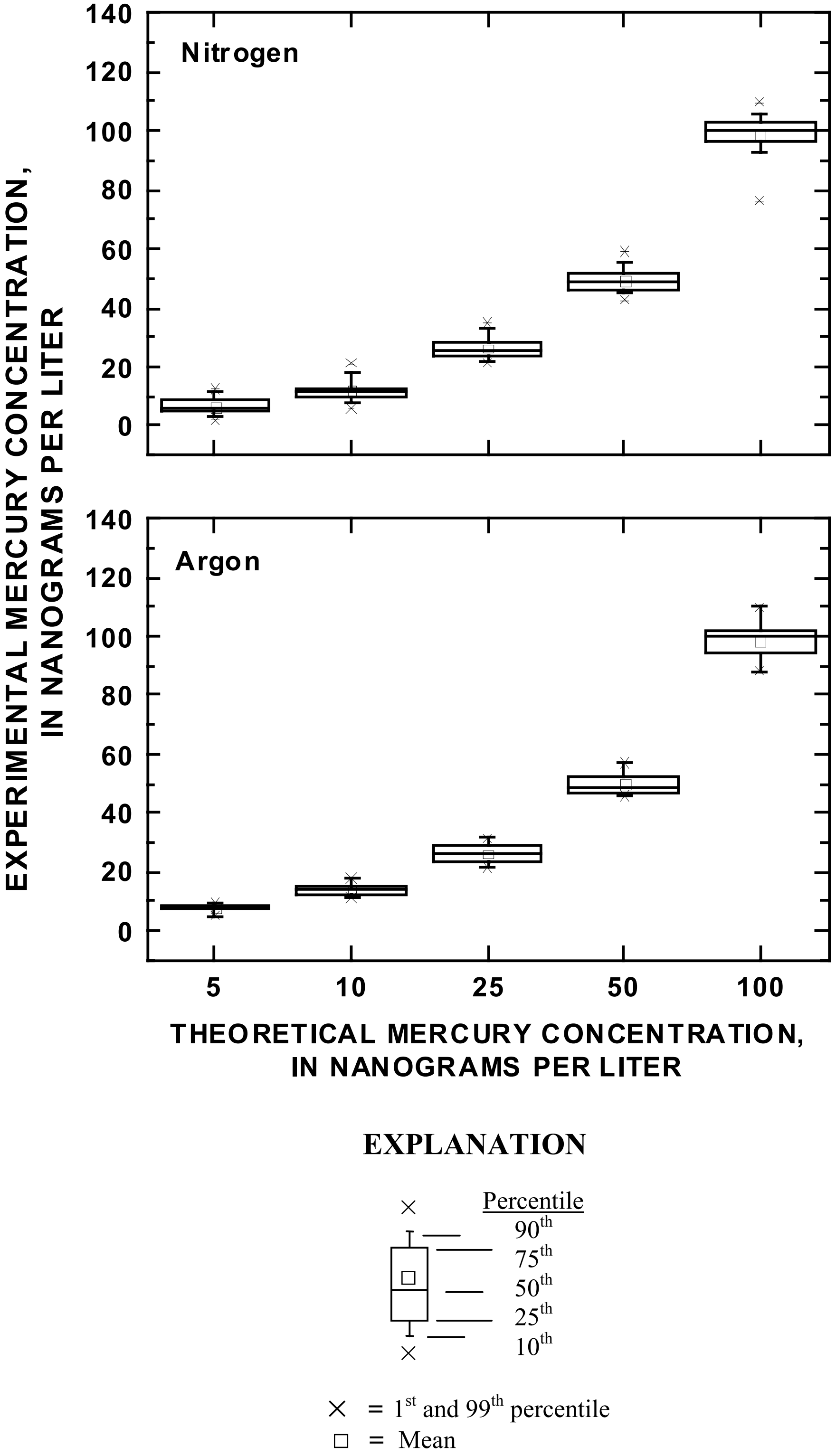

**Figure 3.** The effects of using argon instead of nitrogen as the purge gas in cold vapor–atomic fluorescence spectrometry.

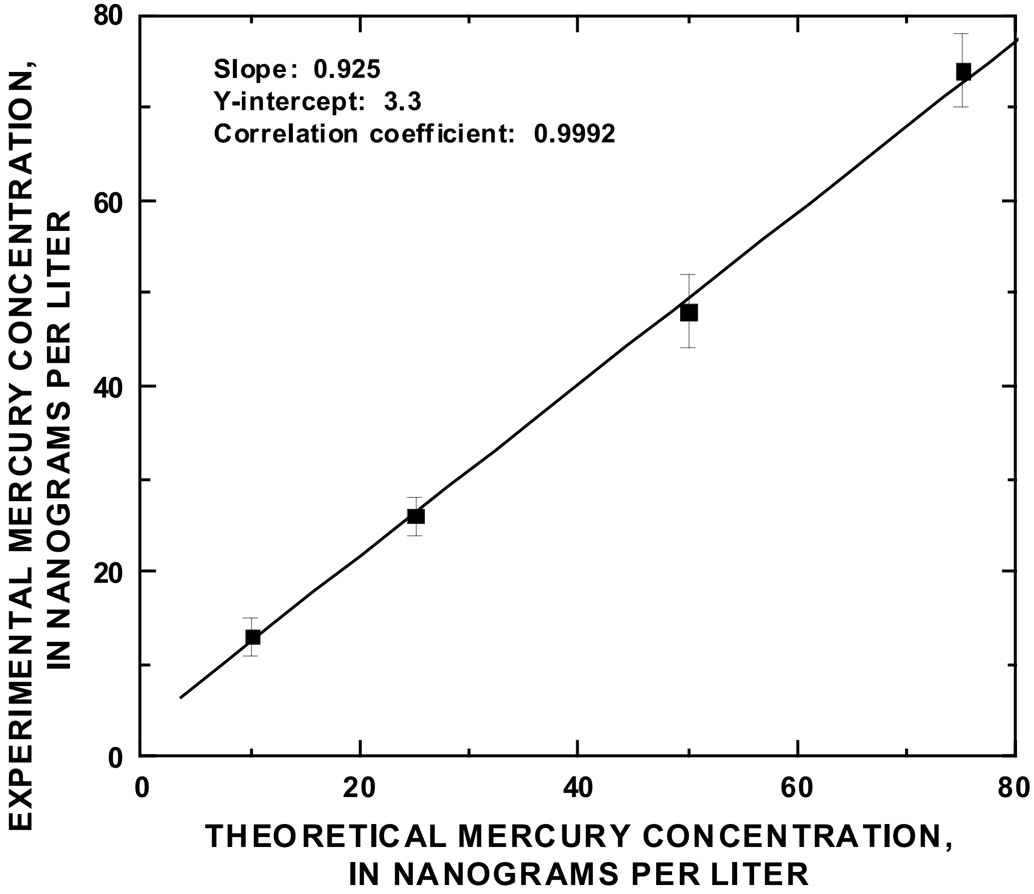

**Figure 4.** Linear regression analysis of results for sample solutions based on two reference standards (experimental) and National Institute of Standards and Technology standard reference material (theoretical). Error bars correspond to the standard deviation.

The percentage recovery of results for various concentrations of mercury spiked into reagent water, filtered and unfiltered surface water, and filtered and unfiltered ground water was used to validate the method. Data were acquired during 7 nonconsecutive days. No more than two sets of data were acquired in 1 day. The range of average percent recovery for all filtered and unfiltered matrices at 20, 45, and 75 ng/L was 89 to108, 96 to 103, and 94 to 98 percent, respectively (table 3). The variability in the recovery of 20 ng/L, a concentration about four times the short-term MDL, was about twice that of higher spike concentrations. In addition, the variability in recoveries at 20 ng/L for the unfiltered matrices was about twice those for corresponding filtered matrices. There was little difference, however, in variability for filtered and unfiltered matrices for spike concentrations of 45 and 75 ng/L. Sorption to particulate matter might contribute to the increase in variability for the 20-ng/L-mercury spike in unfiltered matrices.

**Table 3.** Average percent spike recoveries for mercury in reagent-water, filtered and unfiltered surface-water, and filtered and unfiltered ground-water matrices

[Average is based on 9 to 11 replicates acquired on 7 nonconsecutive days; ng/L, nanograms per liter; %, percent; ±, plus or minus; filtered, surface or ground water processed through a 0.45-micrometer membrane]

| Matrix | Mercury spike concentration, ng/L | | |
|---|---|---|---|
| | 20 | 45 | 75 |
| | Average recovery, % | Average recovery, % | Average recovery, % |
| Reagent water - - - - - - - - - - - - - - - - | 94±11 | 100±6 | 98±8 |
| Surface water, filtered - - - - - - - - - - - | 89±8 | 100±9 | 96±6 |
| Surface water, unfiltered - - - - - - - - - | 108±20 | 101±10 | 95±8 |
| Ground water, filtered - - - - - - - - - - - | 91±13 | 96±6 | 95±9 |
| Ground water, unfiltered - - - - - - - - - | 102±20 | 103±10 | 94±7 |

## CONCLUSIONS

The new cold vapor–atomic fluorescence spectrometric (CV–AFS) method for the determination of inorganic plus organic mercury species in filtered and unfiltered natural water has several advantages when compared to the previously used (prior to April 2001) cold vapor–atomic absorption spectrometric method. Primary advantages are improved method detection limit and elimination of a corrosive preservative. The CV–AFS method has a short-term method detection limit of 5 ng/L without using gold amalgamation for mercury preconcentration. Without mercury preconcentration, analysis throughput is increased while maintaining the capability of determining mercury at concentrations typically regulated by water-quality standards. Mercury samples are preserved with hydrochloric acid (HCl) instead of acid dichromate. Although acid dichromate has been used extensively to preserve mercury samples, shipping and disposal regulations have made continued use too expensive. Experiments suggest that there is no significant difference, however, between the average mercury concentration in a water sample preserved with HCl and one preserved with acid dichromate. Ambient mercury concentrations in samples preserved with HCl in borosilicate-glass bottles with fluoropolymer-lined caps have been shown to be stable for at least 30 days. Oxidation of inorganic and organic mercury species with bromine monochloride makes it possible to determine total recoverable mercury and extends the sample-holding time to 3 months.

The bias and variability of the method were established using standard reference materials and spike recovery results. Comparison of the analytical performance between CV–AFS and the previously used method were not feasible because of the sizable disparity in method detection limits. The concentration of the upper calibration standard used by the new method corresponds to the detection limit of the old method. Results for USGS standard reference water samples were acceptable with respect to the most probable concentration. Other solutions that have varying mercury concentrations were prepared from certified standards from two different sources. Linear regression of the results for these solutions were significantly correlated (correlation coefficient=0.9992) with standard solutions traceable to National Institute of Standards and Technology materials. The analytical variability is expected to extend from 15 to 5 percent with increasing concentration bounded by the calibration range. The average percent recovery of 20, 45, and 75 ng/L of mercury in reagent-water, surface-water, and ground-water matrices was determined during 7 nonconsecutive days. The average percent recoveries for all filtered and unfiltered matrices ranged from 89 to108 (20 ng/L), 96 to 103 (45 ng/L), and 94 to 98 percent (75 ng/L). The variability for the recovery of the 20-ng/L spike, a concentration about four times the method detection limit, was about twice that of higher spike concentrations. In addition, the variability in percentage recoveries for unfiltered matrices was twice that for matching filtered matrices, possibly because of sorption to particulate matter.

Analytical results from the new CV–AFS method will most likely impact interpretation of long-term trends observed in water-quality studies involving mercury. The method detection limit of 5 ng/L is about a factor of 20 times lower than the previously used method. More than 90 percent of the mercury concentrations reported with the previous analytical method during a typical year were less than or equal to 100 ng/L prior to April 2001. Implementation of the CV–AFS method will likely provide more definitive results because its analytical range extends well below 100 ng/L.

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