



## **Chapter N**

# **Mercury in water by flow injection-cold vapor-atomic fluorescence spectrometry**

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**U.S. Geological Survey Open File Report 02-223-N**

**Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey**

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Code: T13

Accepted: 3/07/02

## Principle

To determine dissolved mercury in water, samples must be filtered and preserved at the time of collection with a 1 percent sodium dichromate/nitric acid solution. In the analytical laboratory, all samples are mixed with stannous chloride ( $\text{SnCl}_2$ ). Mercury (II) is reduced to  $\text{Hg}^\circ$  in a flow injection manifold. The mercury vapor is purged from the aqueous phase with argon, passed through a drying tube, separated, and measured using flow injection cold vapor-atomic fluorescence spectrometry (CV-AFS). Further details of the determination of mercury in environmental samples are given in Crock (1996), Crock and others (1999), Kennedy and Crock (1986), and chapter M of this report.

## Interferences

There are no spectral interferences when using atomic fluorescence because only the element corresponding to the excitation source will fluoresce. Water vapor is a non-spectral interference, but is removed by drying the analytical vapor stream by the use of a drying tube incorporated in the instrument, and the installation of an in-line desiccator for the argon supply. Special precautions must be taken due to the ubiquitous nature of mercury. Contamination from ambient mercury needs to be minimized, and the analyst must eliminate all possible sources of mercury contamination to the sample and the laboratory environment if reliable low - level mercury analyses are to be achieved. Mercury contamination can be derived from any source including sample collection procedures, and sample preparation, handling, and storage. In the laboratory, mercury contamination can be derived from the ambient air, argon, glassware, lab ware, and reagents. In order to minimize these sources of contamination, all glassware should be rinsed with nitric acid (10%  $\text{HNO}_3$ ) and triple rinsed with DI prior to use. Clean glassware should be kept in a heated (95° C.) oven to keep it mercury free. Potential contamination from reagents can be minimized by use of mercury-free, research grade products. Finally, the analyst should never use polymer containers as storage vessels because mercury has the ability to diffuse across these materials and contaminate adjoining containers or the laboratory environment.

## Scope

For water samples, the method offers a lower reporting limit of 5 ng/L. Samples exceeding the upper calibration limit of 735 ng/L mercury must be diluted, or reanalyzed using CV-AAS (Mercury in water, geologic, and plant materials by continuous flow-cold vapor-atomic absorption spectrometry, chapter M of this report). Approximately 14 samples can be analyzed per hour.

## Apparatus

- Lachat QuikChem® Mercury Analyzer with fluorescence detector
- Ultra Pure Argon with in-line dehumidifier (drying canister filled with Drierite® (anhydrous calcium sulfate))
- Mercury-free laboratory air supply (pressurized, from bench) for use as air supply for the in-line drying tube.
- Standard incandescent heating lamp (position above the phase separator).

## Reagents

Unless otherwise noted, chemicals are research grade and water is deionized (DI) and mercury-free. The DI water should have a resistance of greater than 17 mega-ohms.

*10% nitric acid for rinsing bottles:* dilute 100 mL research grade HNO<sub>3</sub> (16M) to 1 L DI water.

*1 percent (w/v) sodium dichromate-nitric acid solution:* Dissolve 10 g Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O (mercury-free) in 1 L concentrated J.T. Baker ® 'INSTRANA-ANALYZED' grade HNO<sub>3</sub>.

*25 percent (w/v) sodium dichromate solution:* Dissolve 500 g reagent grade Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>·2H<sub>2</sub>O (mercury-free) in sufficient DI water to bring the volume to 2 L.

*Nitric acid wash:* Dilute 40 mL research grade HNO<sub>3</sub> (16 M) to 4 L with DI water.

*Stannous chloride solution:* Dissolve 20 g SnCl<sub>2</sub>·2H<sub>2</sub>O (J.T. Baker ® Suitable for Mercury Determination Grade) in 80 mL concentrated (12 M) J.T. Baker ® 'INSTRANA-ANALYZED' grade HCl. Let the solution stand for 20 to 30 min until the SnCl<sub>2</sub>·2H<sub>2</sub>O totally dissolves. Dilute to 1 L with DI water. Purge the SnCl<sub>2</sub>·2H<sub>2</sub>O reducing solution by bubbling with argon for 15 minutes in order to remove any mercury contamination that may have been present in the reagents. This reagent must be made fresh daily.

*Stock solution:* Certified Standard Reference Material SRM 1641c (1.47 ppm mercury in water), (National Institute of Standards and Technology).

*Mercury calibration standards:* First, prepare a 1.47 ppb stock solution by adding 1.0 mL of SRM 1641c to a 1 L volumetric flask containing 200 mL concentrated HNO<sub>3</sub> and 20 mL 25 percent sodium dichromate solution. Bring to volume with DI water. Prepare 735 ng/L, 147 ng/L, and 14.7 ng/L Hg calibration standards by adding 50 mL, 10 mL, and 1 mL of 1.47 ppb Hg stock solution to three separate 100 mL volumetric flasks containing 20 mL concentrated HNO<sub>3</sub> and 2 mL 25 percent sodium dichromate solution. Bring to volume with DI water and thoroughly mix contents. These calibration solutions are stable for at least one week.

## Safety precautions

Normal laboratory safety procedures should be observed, including the use of protective eyewear, laboratory coat, and gloves. All chemical and reagent handling activities should be performed in a chemical hood. See the *CHP and MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method. The atomic fluorescence spectrophotometer should be located under an exhaust hood in order to vent the acid gases and mercury vapors that may be generated by the flow injection-cold vapor system.

## Procedure for water samples

Water samples must arrive at the laboratory filtered (0.45- $\mu\text{m}$ ) and acidified/preserved (at time of collection) with a 1 percent sodium dichromate/concentrated  $\text{HNO}_3$  solution in a ratio of 1:19 (one part sodium dichromate/ $\text{HNO}_3$  solution to 19 parts water sample). Water samples must be collected in nitric acid-washed, flint glass bottles with Teflon® lined lids.

1. Upon arrival at the laboratory, water samples are shaken and aliquots are transferred into 16 x 100 mm disposable borosilicate glass test tubes that have been stored in a heated (95° C.) oven to prevent mercury contamination. The samples are then placed in the auto sampler of the flow injection AFS system.
2. Aqueous mercury calibration standards of 14.7, 147, and 735 ng/L Hg are used for water analysis. They are obtained by dilution of the NIST certified calibration standard (SRM 1641c), using the dilution technique previously described.
3. Preserved water samples along with aqueous calibration standards are analyzed using the Lachat QuikChem® mercury system. Modifications to the standard Lachat system include the use of an air supply instead of argon to the drying tube. This change was found to have no negative impact on the analysis while reducing the amount of high-grade argon used during instrument operation. A standard incandescent heat lamp was placed above the phase separator to keep the separator and connecting tubing warm in order to reduce the formation of water condensation. Finally, an in-line desiccator (Drierite®), was installed for the argon purge supply. Samples with mercury concentration greater than the highest calibration standard (735 ng/L) must be diluted and reanalyzed or reanalyzed using CV-AAS. Any sample following a sample that exceeds the concentration of the upper standard should be reanalyzed due to potential mercury carry over from the previous sample. If a solution containing elevated Hg is analyzed, allow the fluorescence signal to regain the baseline before continuing with the analytical run.
4. The calibration curve is checked at the beginning and end of every analytical run and the instrument is respoped every 20 samples throughout the run.

## Calculation

The instrument software calculates sample concentration. To do this, the data system program prepares a calibration curve based on the analysis of the calibration standards and determines sample concentration by use of a second-degree polynomial regression equation.

## Assignment of Uncertainty

Table 1 shows the analytical results of selected reference materials, and method blanks obtained by this method.

**Table 1.—Analytical performance summary for mercury by CV-FAAS (water reference standards in ng/L)**

[a= USGS OPF 97-20; b= USGS OPF 98-391; c= USGS OPF 00-227; d= USGS OPF 01-137]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

<i>Reference</i>	<i>Description</i>	<i>n</i>	<i>Mean</i>	<i>s</i>	<i>pv</i>		<i>% RSD</i>	<i>% R</i>
HG 23	water	9	282	6.1	340	a	2.17	83
HG 29	water	9	429	10	463	c	2.34	93
HG 31	water	9	409	21.1	496	d	4.92	87
HG 26	water	9	552	21.9	700	b	3.97	79

**Table 1.—Continued—Duplicate samples results not yet available**

**Table 1.—Continued--Method blank results** 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

<i>Method blank</i>	<i>n</i>	<i>Mean</i>	<i>s</i>	<i>3s</i>	<i>5s</i>
procedure blank	9	1	0.87	2.6	4.35

Each daily run of samples is preceded by 3 aqueous calibration standards, at least one reference sample taken through the preservation procedure, and a reagent blank. The aqueous standards establish the sensitivity; the reference sample is a check of preservation and the blank establishes if there is any contamination. Low values for the aqueous standards and/or high values for the reference sample suggest a problem with preservation of samples or need of maintenance or optimization of the instrumentation.

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