Mercury, atomic absorption spectrometric, flameless

Parameters and Codes:
Mercury, dissolved, I-1462-85 (μg/L as Hg): 71890
Mercury, total recoverable, I-3462-85 (μg/L as Hg): 71900
Mercury, suspended recoverable, I-7462-85 (μg/L as Hg): 71895
Mercury, recoverable-from-bottom-material, dry wt, I-5462-85 (μg/g as Hg): 71921

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 0.5 μg/L of mercury. Samples containing mercury concentrations greater than 10 μg/L need to be diluted. Industrial and sewage effluent may be analyzed, as well as samples of fresh and saline water.

1.2 Suspended recoverable mercury is calculated by subtracting dissolved mercury from total recoverable mercury.

1.3 This method may be used to analyze bottom material containing at least 0.01 μg/g of mercury. Usually, a 5-g sample of prepared material (method P-0520) is taken for analysis. For samples containing more than 1.0 μg/g, use less sediment.

1.4 Total recoverable mercury in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

2. Summary of method

2.1 The cold-vapor, flameless, atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95°C) digestion with potassium permanganate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride, and the mercury vapor is subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 This method is based on a procedure described by Hatch and Ott (1968) and is similar in substance to the flameless atomic absorption method in "Methods for Chemical Analysis of Water and Wastes," published by the Water Quality Office of the Environmental Protection Agency (1979).

3. Interferences

3.1 Some samples may contain volatile organic compounds that absorb radiation at 253.7 nm and that may be swept from the solution along with the mercury vapor. These constitute a positive interference, and the possibility of their presence must not be overlooked.

3.2 Selenium concentrations, either as selenate or selenite, up to 10,000 μg/L do not interfere; higher concentrations were not tested.

4. Apparatus

4.1 *Absorption cell* (fig. 1). Mount and align an absorption cell (10- to 20-cm path length) in the light path of the spectrometer. Position a 60-watt lamp over the cell (10 to 15 cm) to prevent condensation of water vapor. Attach a sufficient length of tubing to the outlet of the cell and vent to a hood. Connect the inlet of the cell to the aerator with a minimum length of plastic tubing. Attach a water aspirator to the outlet of the stopcock (NOTE 1). Alternately, a forced-air pump may be used.

NOTE 1. The stopcock must remain closed during analysis and be opened only briefly between samples to remove residual mercury vapor from the absorption cell.

4.2 *Aerator* (fig. 1).

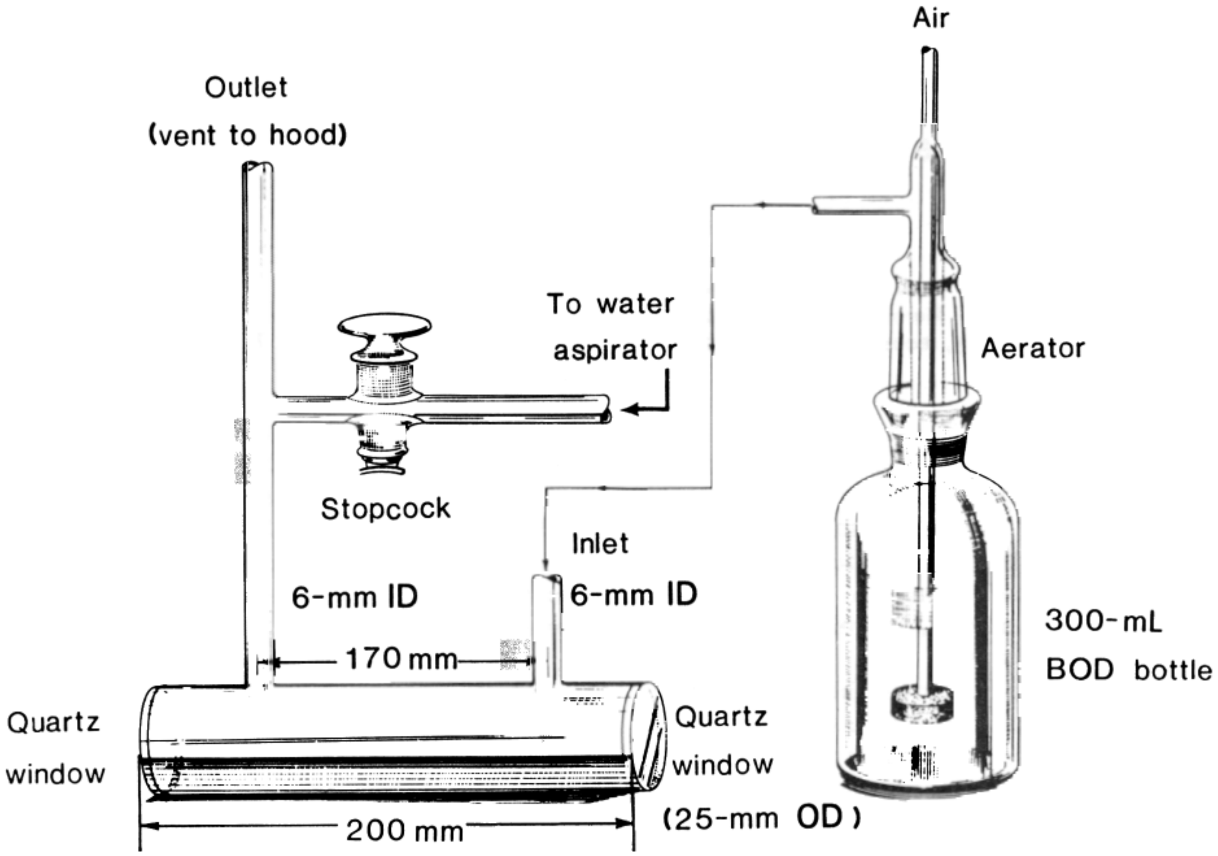

Figure 1. - Absorption cell and aerator

4.3 *Atomic absorption spectrometer and recorder* or a commerical mercury analyzer.

4.4 Refer to the manufacturer's manual to optimize instrument for the following:

Grating……..	Ultraviolet
Wavelength …	253.7 nm
Source…………	Mercury-vapor discharge, hollow-cathode, or electrode-less-discharge lamp

4.5 *BOD bottle,* 300-mL capacity.

4.6 *Water bath* or controlled-temperature oven, 95°C.

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride solution:* Dissolve 10 g $NH_2OH•HCl$ and 12 g NaCl in demineralized water and dilute to 100 mL (NOTE 2). Prepare fresh daily. Alternatively, 12 g hydroxylamine sulfate may be used instead of the hydroxylamine hydrochloride.

NOTE 2. A larger volume of this reagent can be prepared if it is kept refrigerated.

5.2 *Mercury standard solution I,* 1.00 mL = 100 µg Hg: Dissolve 0.1712 g $Hg(NO_3)_2•H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 and dilute to 1,000 mL with demineralized water.

5.3 *Mercury standard solution II,* 1.00 mL = 1.00 µg Hg: Dilute 5.00 mL mercury standard solution I and 1.5 mL concentrated HNO_3 to 500 mL with demineralized water. This and the following mercury standard solutions must be prepared fresh daily.

5.4 *Mercury standard solution III,* 1.00 mL = 0.050 µg Hg: Dilute 10.0 mL mercury standard solution II and 1.5 mL concentrated HNO_3 to 200 mL with demineralized water. Use this solution to prepare working standards at the time of analysis.

5.5 *Nitric acid,* concentrated (sp gr 1.41), with low mercury content: duPont, reagent-grade acid has been found satisfactory.

5.6 *Potassium permanganate solution,* 50 g/L: Dissolve 5 g $KMnO_4$ in demineralized water and dilute to 100 mL. Prepare fresh weekly. Store in brown glass bottle.

5.7 *Potassium persulfate solution,* 50 g/L: Dissolve 5 g $K_2S_2O_8$ in demineralized water and dilute to 100 mL.

5.8 *Stannous chloride solution,* 74 g/L: Add 22 g $SnCl_2 \cdot 2H_2O$ to 250 mL 0.25*M* H_2SO_4. This solution is unstable. Prepare fresh daily.

5.9 *Sulfuric acid,* concentrated (sp gr 1.84).

5.10 *Sulfuric acid,* 0.25*M*: *Cautiously* add 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Immediately before each use, clean all glassware used in this determination by rinsing, first with warm, dilute HNO_3 (1+4), and then with demineralized water.

6.2 Follow instructions in paragraphs 6.2.1 through 6.2.5 for dissolved mercury.

6.2.1 Pipet a volume of sample containing less than 1.0 µg Hg (100 mL max) into a 300-mL capacity BOD bottle and adjust the volume to approx 100 mL.

6.2.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.2.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.2.4 Add 5 mL $KMnO_4$ solution and shake. Add additional small amounts of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.2.5 Add 2 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95°C. Proceed to paragraph 6.5.

6.3 Follow instructions in paragraph 6.3.1 through 6.3.5 for total recoverable mercury.

6.3.1 Pipet a volume of well-mixed sample containing less than 1.0 µg Hg (100 mL max) into a 300-mL capacity BOD bottle and adjust the volume to approx 100 mL.

6.3.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.3.4 Add 15 mL $KMnO_4$ solution and shake. Add additional small amounts of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.3.5 Add 8 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95°C. Proceed to paragraph 6.5.

6.4 Follow instructions in paragraphs 6.4.1 through 6.4.5 for recoverable mercury from bottom material.

6.4.1 Place a weighed portion of sample containing less than 1.0 µg Hg (5 g max) into a 300-mL capacity BOD bottle and add approx 100 mL demineralized water.

6.4.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.4.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.4.4 Add 15 mL $KMnO_4$ solution and shake. Add additional small amounts of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.4.5 Add 8 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an oven at 95°C. Proceed to paragraph 6.5.

6.5 Remove from water bath, cool, and add $NH_2OH \cdot HCl\text{-}NaCl$ solution in 2-mL increments to reduce the excess permanganate, as evidenced by the disappearance of the permanganate color.

6.6 Add 5 mL $SnCl_2$ solution to one sample and immediately attach the bottle to the aerator (NOTE 3). Record the maximum absorbance. After maximum absorbance has been recorded, remove the BOD bottle and open the stopcock to the vacuum. Momentarily pinch off the vent tube in order to remove residual mercury vapor from the absorption cell. Treat each succeeding sample, blank, and standard in a like manner.

NOTE 3. Use the atomic absorption compressed-air supply or a peristaltic pump to aerate the sample. Adjust the rate of air flow to approx 2 L/min.

7. Calculations

7.1 Determine the micrograms of mercury in the sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of dissolved or total recoverable mercury in each sample as follows:

$$\text{Hg } (\mu\text{g/L}) = \mu\text{g Hg} \times \frac{1{,}000}{\text{mL sample aliquot}}$$

7.3 To determine the concentration of suspended recoverable mercury, subtract dissolved-mercury concentration from total-recoverable-mercury concentration.

7.4 Determine the concentration of mercury in air-dried bottom material as follows:

$$\text{Hg } (\mu\text{g/g}) = \frac{\mu\text{g Hg in sample}}{\text{wt of sample (g)}}$$

8. Report

8.1 Report mercury, dissolved (71890), total-recoverable (71900), and suspended-recoverable (71895), concentrations as follows: less than 10 µg/L and greater than or equal to 0.5 µg/L, nearest 0.1 µg/L; 10 µg/L and above, two significant figures.

8.2 Report mercury, recoverable-from-bottom-material (71921), concentrations as follows: less than 1.00 µg/g, nearest 0.01 µg/g; 1.0 µg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved mercury for 23 samples within the range of 0.3 to 15.5 µg/L may be expressed as follows:

$$S_T = 0.152X + 0.164$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of mercury, micrograms per liter.

The correlation coefficient is 0.9229.

9.2 Precision for dissolved mercury for six of the 23 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
22	0.33	50
15	0.60	46
27	1.69	32
7	3.46	30
7	6.54	18
26	15.5	16

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable mercury and for recoverable mercury in bottom material will be greater than that reported for dissolved mercury.

9.4 Precision for total recoverable mercury expressed in terms of percent relative standard deviation for two water-suspended sediment samples is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
19	9.2	32
18	11.4	38

References

Fishman, M.J., and Brown, Eugene, 1976, Selected methods of the U.S. Geological Survey for the analysis of waste waters: U.S. Geological Survey Open-File Report 76-177, p. 51-60.

Hatch, W.R., and Ott, W.L., 1968, Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry: Analytical Chemistry, v. 40, p. 2085-90.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 245.1-1.