Mercury, atomic absorption spectrometric, flameless automated-sequential

Parameter and Code:
Mercury, dissolved, I-2462-85 (µg/L as Hg): 71890

1. Application

This method may be used to analyze water and wastewater containing at least 0.1 µg/L mercury. Samples containing mercury concentrations greater than 8.0 µg/L need to be diluted.

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 dichromate and potassium persulfate in acid solution. Mercuric ions are then reduced to the elemental state with stannous chloride, and 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 The method is based on a procedure described by El-Awady and others (1976).

3. Interferences

3.1 Chloride concentrations up to 5,000 mg/L do not interfere; higher concentrations were not tested.

3.2 Hydroxylamine hydrochloride-sodium chloride solution is added to prevent interference from residual chlorine.

3.3 El-Awady and others (1976) reported that copper sulfate (1,000 mg/L) does not interfere and that chemical-oxygen-demand (COD) concentrations of less than 700 mg/L can be tolerated. Ethyl alcohol, methyl alcohol, glycerol, chloroform, and carbon tetrachloride did not interfere when added in concentrations as high as 0.5 percent. Major interferences were observed from benzene and toluene. A maximum tolerance of 500 µg/L was obtained for these compounds.

3.4 Selenate concentrations up to 10,000 µg/L do not interfere; higher concentrations were not tested. Concentrations of selenite greater than 100 µg/L interfere by suppressing the mercury absorption.

4. Apparatus

4.1 *Absorption cell,* 100-mm long, 10-mm diameter, with quartz windows.

4.2 *Atomic absorption spectrometer and recorder* or a commercial mercury analyzer.

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

Grating	Ultraviolet
Wavelength counter	253.7 nm
Source	Mercury-vapor, hollow-cathode, or electrodeless discharge lamp
Carrier	Nitrogen (flow approx. 20 mL/min; adjust for maximum sensitivity with use of a standard)

4.4 *Technicon Autoanalyzer,* consisting of sampler, manifold (fig. 1), proportioning pump, and high-temperature heating bath (NOTE 1). NOTE 1. Nitrogen gas may be used instead of air in manifold (fig. 1).

4.5 *Vapor-liquid separator* (fig. 2).

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride solution:* Dissolve 30 g $NH_2OH \cdot HCl$ and 30 g NaCl in demineralized water and dilute to 1 L.

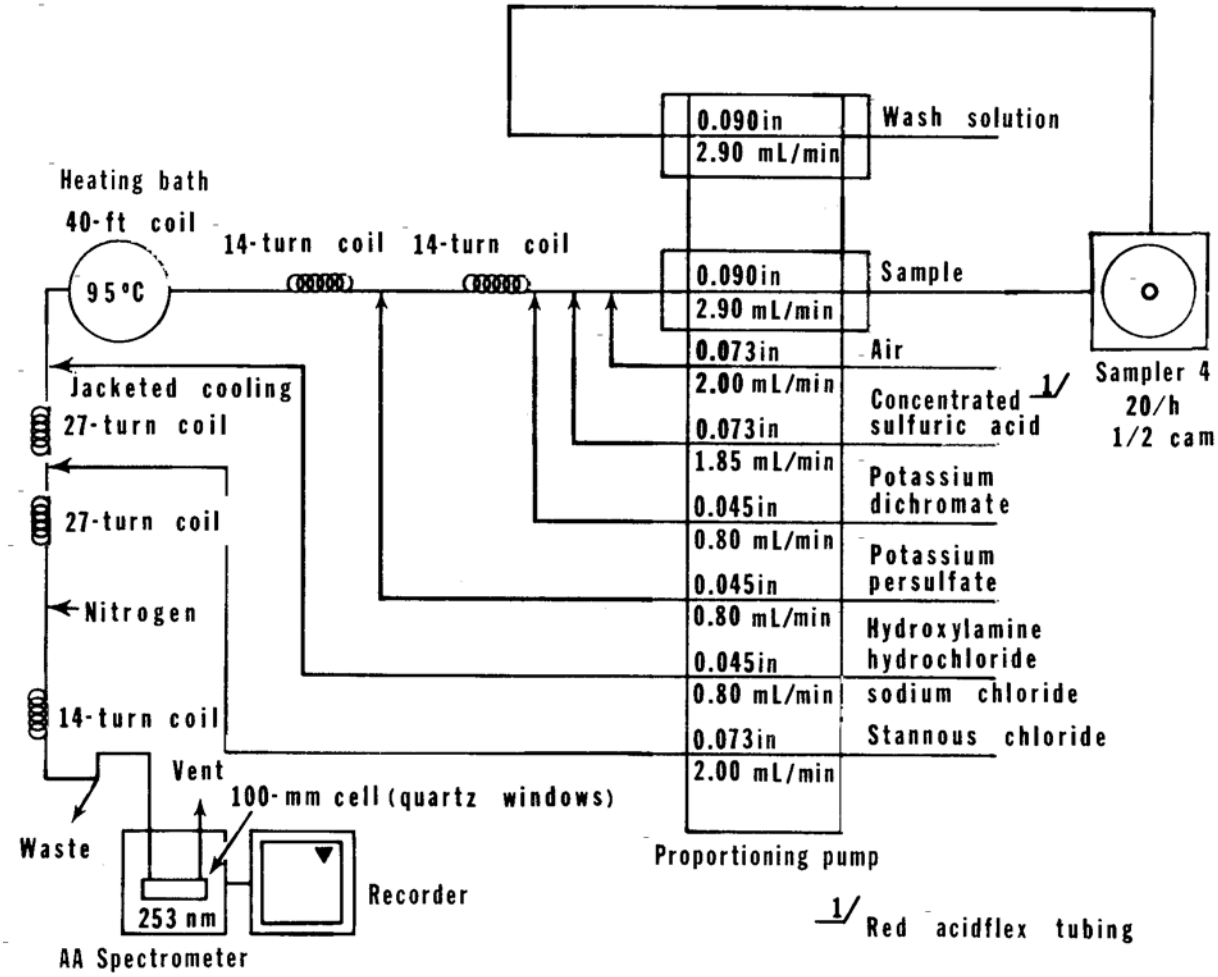

Figure 1.-Mercury manifold

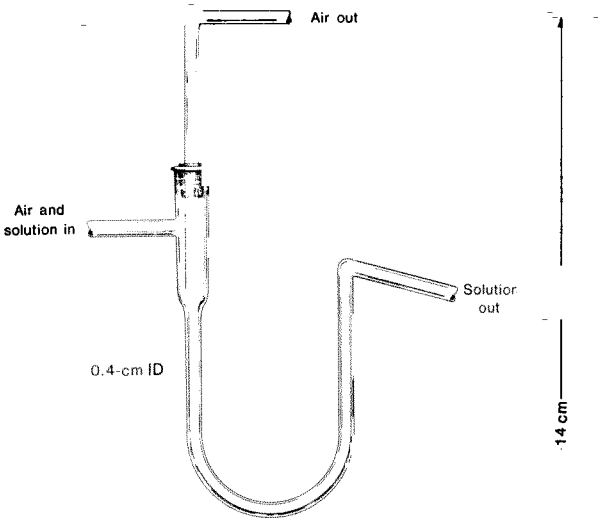

Figure 2.-Vapor-liquid separator

5.2 *Mercury standard solution I,* 1.00 mL = 100 µg Hg: Dissolve 0.1712 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 (sp gr 1.41) and 25 mL $K_2Cr_2O_7$ solution, and dilute to 1,000 mL with demineralized water.

5.3 *Mercury standard solution II*, 1.00 mL = 1.00 µg Hg: Dilute 10.0 mL mercury standard solution I, 5 mL concentrated HNO_3, and 25 mL $K_2Cr_2O_7$ solution to 1,000 mL with demineralized water.

5.4 *Mercury standard solution III,* 1.00 mL = 0.100 µg Hg: Dilute 100.0 mL mercury standard solution II, 5 mL concentrated HNO_3, and 25 mL $K_2Cr_2O_7$ solution to 1,000 mL with demineralized water. Use this solution to prepare working standards. The working standards

should also contain 5 mL/L of concentrated HNO_3 and 25 mL/L of $K_2Cr_2O_7$ solution. The working standards are stable for at least 3 weeks.

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

5.6 *Nitric acid (1+99),* wash solution: Dilute 10 mL of concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

5.7 *Potassium dichromate solution,* 20 g/L: Dissolve 20 g $K_2Cr_2O_7$ in demineralized water and dilute to 1 L.

5.8 *Potassium persulfate solution,* 40 g/L: Dissolve 40 g $K_2S_2O_8$ in demineralized water and dilute to 1 L. Prepare fresh each week.

5.9 *Stannous chloride solution,* 84 g/L: Dissolve 100 g $SnCl{\cdot}2H_2O$ in 100 mL concentrated hydrochloric acid (sp gr 1.19) and dilute to 1 L with demineralized water. This solution is unstable. Prepare fresh daily.

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

6. Procedure

6.1 Set up manifold (fig. 30).

6.2 Prepare a blank of demineralized water and sufficient standards to 8.0 µg/L by appropriate dilutions of mercury standard solution III.

6.3 Initially feed all reagents through the system using the nitric acid wash solution in the sample line. Allow the heating bath to warm to 95°C.

6.4 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with unknown samples.

6.5 Remove the sample line from the nitric acid wash solution when the baseline stabilizes and begin analysis.

7. Calculations

7.1 Prepare an analytical curve by plotting the absorbance of each standard versus its respective mercury concentration.

7.2 Compute the concentration of mercury in each sample by comparing its absorbance to the analytical curve. Any baseline drift that may occur must be taken into account when computing the absorbance of a sample or standard.

8. Report

Report mercury, dissolved (71890), concentrations as follows: less than 10 µg/L, nearest 0.1 µg/L; 10 µg/L and above, two significant figures.

9. Precision

9.1 Precision for dissolved mercury for 11 samples within the range of 0.3 to 16.4 mg/L may be expressed as follows:

$$S_T = 0.134X + 0.106$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of mercury, micrograms per liter.

The correlation coefficient is 0.9722.

9.2 Precision for dissolved mercury for five of the 11 samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (µg/L)	Relative standard deviation (percent)
3	0.33	17
4	0.58	54
3	1.87	32
3	2.80	27
5	16.4	14

Reference

El-Awady, A. A., Miller, R. B., and Carter, M. J., 1976, Automated method for the determination of total and inorganic mercury in water and waste-water samples: Analytical Chemistry, v. 48, p. 110-16.