Mercury, total-in-sediment, atomic absorption spectrophotometry, nameless, direct

Parameter and Code:
Mercury, total, I-6463-86 (µg/g as Hg): none assigned

1. Application

1.1 This method is used to analyze samples of suspended sediment and bottom material for the determination of total concentrations of mercury in samples containing at least 0.01 µg/g and not more than 5.0 µg/g. Samples containing mercury concentrations greater than 5.0 µg/g can be analyzed after appropriate dilution; either use less sediment or dilute the sample solution. This method was implemented in April 1986.

1.2 Analyze dried and ground samples that have been digested with a combination of concentrated nitric and hydrochloric acids (Lefort aqua regia) and heat. These solutions then are analyzed by atomic absorption spectrophotometry.

2. Summary of method

A sample is dried, ground, and homogenized and then is digested by a hot Lefort aqua regia solution (3:1 nitric acid to hydrochloric acid). The solution is preserved by the addition of potassium dichromate, and diluted to a known volume with demineralized water. The solution then is made basic and the mercury is reduced to the metal with stannous chloride, purged from the solution with nitrogen, and quantified by flameless-cold vapor atomic absorption spectrophotometry.

3. Interferences

3.1 Volatile organic constituents interfere; however, digestion of samples with hot Lefort aqua regia will decompose organic material if present. In an alkaline media, interferences from gold, platinum, silver, copper, selenium, and tellurium are eliminated.

3.2 Further information can be found in Band and Wilkinson (1972), Koirtyohann and Khalil (1976), Bartha and Ikre'nyi (1981), and Suddendorf (1981).

4. Apparatus

4.1 *Atomic absorption spectrophotometer,* equipped with electronic digital readout, automatic zero and automatic concentration controls, and a deuterium source background corrector. A printer or chart recorder allows automation of the analytical process. A personal computer with a suitable program is used for automatic data reduction and data transfer.

4.2 *Autosample,* Varian PSC 55 or equivalent (optional).

4.3 Refer to manufacturer's manuals to optimize the instruments for the following:

4.3.1 *Atomic absorption spectrophotometer*

Grating	Ultraviolet
Wavelength	253.7 nm
Source	Hollow cathode or electrodeless discharge lamp
Background	On
Slit width	0.5 nm

4.3.2 *Autosampler*

Rinse rate	1
Rinse time	40 seconds
Delay time	70 seconds

4.4 *Vapor generation accessory,* Varian VGA 76 or equivalent. This system consists of a three-channel peristaltic pump, reaction coil, gas-liquid separator, flow-through absorption cell, and bracket for holding the cell in the light path of the spectrophotometer (fig. 1).

4.5 *Erlenmeyer flasks,* pyrex or equivalent, 125-mL capacity.

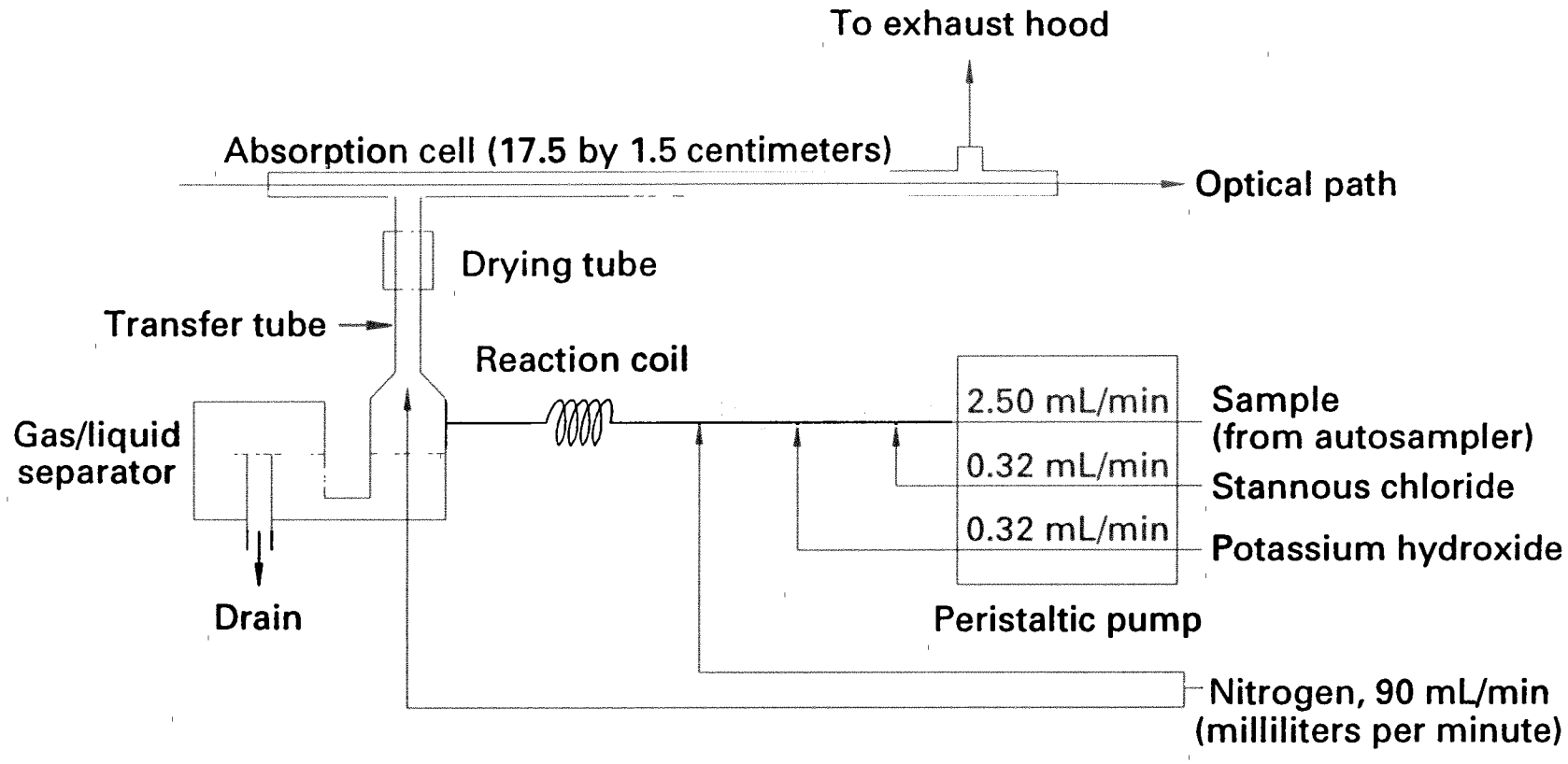
4.6 *Hot plate,* gas or electric, with surface temperature of 150°C.

4.7 *Centrifuge tubes*, with caps, 50-mL capacity

4.8 *Centrifuge (optional).*

4.9 *Drying tube.*

Figure 1.-Mercury vapor generation accessory



5. Reagents

5.1 *Hydrochloric acid,* concentrated (sp gr 1.19).

5.2 *Magnesium perchlorate,* for drying tube (NOTE 1).

NOTE 1. The drying tube is used to prevent moisture carryover into the absorption cell where it can condense and cause erratic readings. The magnesium perchlorate needs to be replaced daily, or sooner if it begins to cake (two-thirds of the drying tube) or if blockage occurs.

5.3 *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 10 mL concentrated HNO_3 (sp gr 1.41), and dilute to 1,000 mL with demineralized water. Alternatively, a commercially prepared stock solution can be diluted and used.

5.4 *Mercury standard solution II*, 1.00 mL = 10.0 µg Hg: Dilute 10.0 mL mercury standard solution I, 10 mL concentrated HNO_3 (sp gr 1.41), and 10 mL $K_2Cr_2O_7$ solution to 100 mL with demineralized water.

5.5 *Mercury working solutions I, II, III*: Pipet 40 µL (working solution I), 500 µL (working solution II), and 1,000 µL (working solution III) of mercury standard solution II into 200-mL volumetric flasks. Add 20 mL concentrated HNO_3 (sp gr 1.41) and 20 mL $K_2Cr_2O_7$ solution to each flask, and dilute each to 200 mL with demineralized water. Prepare fresh daily. Concentrations are as follows: Working solution I (2 µg/L), working solution II (25 µg/L), and working solution III (50 µg/L).

5.6 *Nitric acid,* concentrated (sp gr 1.41).

5.7 *Potassium hydroxide solution,* 45 percent w/v: Dissolve 45 g KOH in 100 mL demineralized water.

5.8 *Potassium dichromate solution,* 50 g/L: Dissolve 50 g $K_2Cr_2O_7$ in demineralized water and dilute to 1,000 mL with demineralized water.

5.9 *Stannous chloride solution,* 125 g/L: Dissolve 125 g $SnCl_2 \cdot H_2O$ in 150 mL concentrated HCl (sp gr 1.19) and dilute to 250 mL with concentrated HCl. Do not heat this solution to dissolve the $SnCl_2 \cdot H_2O$ because heat will cause the solution to rapidly lose its reductive capacity Dilute this solution to L with demineralized water.

5.10 *Rinse solution:* Dilute 100 mL concentrated HNO_3 (sp gr 1.41) to L with demineralized water.

6. Procedure

6.1 Dry the sediment by freeze-drying, oven-drying at either 105°C or 40°C, or air-drying at room temperature (NOTE 2).

NOTE 2. A search of the literature has indicated that sample drying procedures can have a significant effect on mercury quantitation. Various procedures for drying samples prior to digestion and analysis have been used; these include air-drying, freeze-drying, or oven-drying at either 105°C or 40°C. Some investigators recommend that a wet sample be digested and analyzed and that moisture be determined on a separate sample aliquot. Analytical results are corrected for moisture content. Various drying procedures were investigated on several sediment samples from various locations to determine the best procedure for drying the sediments. Data show no significant losses of mercury because of the drying procedures; the variations encountered fall within the variability of the original samples and seem to be caused by inhomogeneity of the samples. Data needs to be compared to determine which procedure is most suitable.

6.2 If the sediment sample is greater than 100 g, split to less than 100 g by the use of a nonmetallic sample splitter (riffle splitter), or by coning and quartering.

6.3 Grind the sample with a mixer mill or an agate mortar and pestle until all material is finer than 100 mesh.

6.4 Weigh and transfer 0.5000 g of finely ground sample to a 125-mL Erlenmeyer flask; weigh appropriate reference standard materials (for example, National Institute of Standards and Technology sediment or U.S. Geological Survey Rock Standards (NOTE 3) and analyze with environmental samples.

NOTE 3. This procedure is used with sample weights between 0.2500 and 1.0000 g. Sample weights greater than 1 g might cause erroneous readings because of unoxidized organic matter.

6.5 Carry several blanks (reagents only) through the digestion steps.

6.6 Add 9 mL concentrated HNO_3 (sp gr 1.41) and 3 mL concentrated HCl (sp gr 1.19) to each flask, and mix. Allow to stand in the hood for 15 to 20 minutes, or until foaming stops.

6.7 Place hotplate in hood and adjust to produce a surface temperature of 150°C.

6.8 Place flasks on hotplate for 15 to 30 minutes, or until reagent blanks become colorless.

6.9 Remove flasks from hotplate and allow to cool for 10 to 15 minutes.

6.10 Add 5 mL $K_2Cr_2O_7$ solution to each flask (NOTE 4).

NOTE 4. If there is an excess of unoxidized material remaining in the sample, it might be necessary to add a 5-mL aliquot of the $K_2Cr_2O_7$ solution if the orange color of dichromate changes to green.

6.11 Quantitatively transfer the solutions from the 125-mL Erlenmeyer flasks to 50-mL centrifuge tubes, dilute to the 50-mL mark with demineralized water, and shake to ensure thorough mixing.

6.12 Centrifuge the samples at 2,000 rpm for 20 minutes to settle the undissolved sediment. Alternatively, allow the samples to stand overnight.

6.13 Set up atomic absorption spectrophotometer, vapor generation accessory, and autosampler according to conditions outlined in Section 4. Allow instruments to warm for 10 minutes or longer using rinse solution in the sample line.

6.14 Analyze the working solution III and the blank alternatively until stable readings are obtained for each.

6.15 Analyze the samples and any standard reference solution for Hg using working solutions I, II, and III. Dilute the sample solutions if they have a concentration greater than working solution III.

7. Calculations

7.1 Determine the concentration of Hg in micrograms per liter from the digital display, printer, or chart recorder, and record the results.

7.2 To convert results from micrograms per liter to micrograms per gram, use the following equation:

$$\text{Hg } (\mu g/g) = \frac{\mu g/L \text{ Hg}}{\text{wt of sample (g)}} \quad X \quad \frac{\text{mL digest}}{1{,}000}$$

8. Report

Report mercury, total concentration, as follows: less than 1.0 µg/g, nearest 0.01 µg/g; between 1.0 and 10.0 µg/g, nearest 0.1 µg/g; 10 µg/g and greater, two significant figures.

9. Precision

Precision for 10 replicates expressed in standard deviation and percentage relative standard deviation is as follows:

Mean (µg/g)	Standard deviation (µg/g)	Relative standard deviation (percent)
0.04	0.006	15.0
.92	.09	9.8
3.3	.06	1.8
4.3	.08	1.9

References

Band, R.B., and Wilkinson, N.M., 1972, Interferences in the determination of mercury in mineralized samples by the wet reduction-flameless atomic absorption method: Journal of Geochemical Exploration, v. 1, p. 195-198.

Bartha, A., and Ikre'nyi, K., 1981, Interfering effects on the determination of low concentrations of mercury in geological materials by cold-vapor atomic absorption spectrometry: Analytica Chimica Acta, v. 139, p. 329-332.

Koirtyohann, S.R., and Khalil, Moheb, 1976, Variables in the determination of mercury by cold vapor atomic absorption: Analytical Chemistry, v. 48, p 136-139.

Suddendorf, R.F., 1981, Interference by selenium or tellurium in the determination of mercury by cold-vapor-generation atomic absorption spectroscopy: Analytical Chemistry, v. 53, p. 22-36.