



collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.

#### 4.0 Interference

- 4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.
- 4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.
- 4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.
- 4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

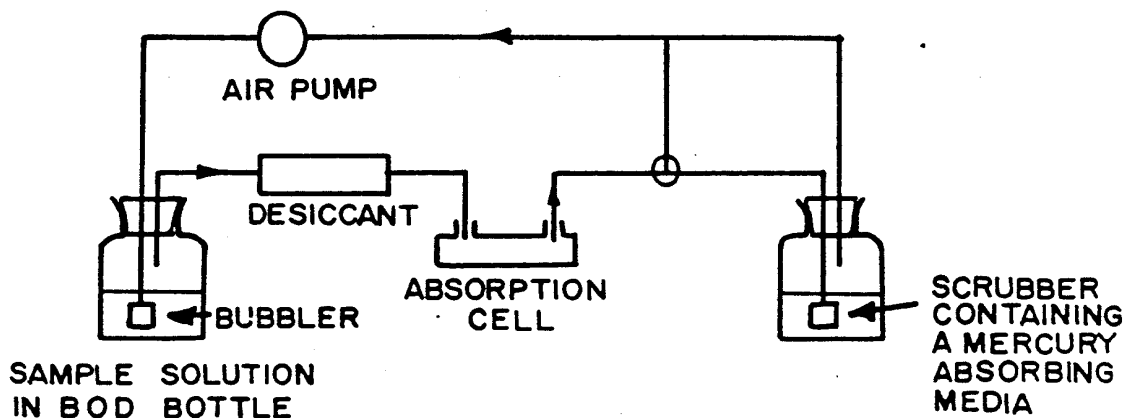
#### 5.0 Apparatus

- 5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.  
NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.
- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.
- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found

- to be satisfactory.
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.  
NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

## 6.0 Reagents

- 6.1 Sulfuric Acid, Conc.: Reagent grade.  
6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.
- 6.2 Nitric Acid, Conc: Reagent grade of low mercury content (See Note 3).  
NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.
- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)
- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)
- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water.
- 6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water.
- 6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1 mL = 1 mg Hg.



**FIGURE 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION**

- 6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

## 7.0 Calibration

- 7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of conc. sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) to each bottle. Add 15 mL of  $\text{KMnO}_4$  (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.
- NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.
- NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:
- a) equal volumes of 0.1 M  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$
  - b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

## 8.0 Procedure

- 8.1 Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) mixing after each addition. Add 15 mL of potassium permanganate solution (6.5) to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple

color persists for at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. After a delay of at least 30 seconds add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

## 9.0 Calculation

- 9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.
- 9.2 Calculate the mercury concentration in the sample by the formula:

$$\mu\text{g Hg/L} = (\mu\text{g Hg in aliquot}) \left( \frac{1,000}{\text{volume of aliquot in mL}} \right)$$

- 9.3 Report mercury concentrations as follows: Below 0.2  $\mu\text{g/L}$ , <0.2; between 1 and 10  $\mu\text{g/L}$ , one decimal; above 10  $\mu\text{g/L}$ , whole numbers.

## 10.0 Precision and Accuracy

- 10.1 In a single laboratory (EMSL), using an Ohio River composite sample with a background mercury concentration of 0.35  $\mu\text{g/L}$ , spiked with concentrations of 1.0, 3.0 and 4.0  $\mu\text{g/L}$ , the standard deviations were  $\pm 0.14$ ,  $\pm 0.10$  and  $\pm 0.08$ , respectively. Standard deviation at the 0.35 level was  $\pm 0.16$ . Percent recoveries at the three levels were 89, 87, and 87%, respectively.
- 10.2 In a joint EPA/ASTM interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study follows:

Number of Labs	Values $\mu\text{g/Liter}$	Standard Mean Value $\mu\text{g/Liter}$	Deviation $\mu\text{g/Liter}$	Accuracy as % Bias
76	0.21	0.349	0.276	66
80	0.27	0.414	0.279	53
82	0.51	0.674	0.541	32
77	0.60	0.709	0.390	18
82	3.4	3.41	1.49	0.34
79	4.1	3.81	1.12	-7.1
79	8.8	8.77	3.69	-0.4
78	9.6	9.10	3.57	-5.2

## 11.0 Appendix

- 11.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.
- 11.2 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025  $\mu\text{g}/\text{L}$  the standard deviations were  $\pm 0.027$ ,  $\pm 0.006$ ,  $\pm 0.01$  and  $\pm 0.004$ . Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.
- 11.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p 349, Method D3223 (1976).

### **Bibliography**

1. Kopp, J. F., Longbottom, M. C. and Lohring, L. B., "Cold Vapor Method for Determining Mercury", AWWA, vol 64, p. 20, Jan., 1972.
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D3223-73, p 343 (1976).
3. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 156 (1975).