



- 4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.
- 4.2 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run under oxidizing conditions, without stannous sulfate, would determine if this type of interference is present.
- 4.3 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.
- 4.4 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All the above interferences can be overcome by use of the Manual Mercury method in this manual.

## 5.0 Apparatus

- 5.1 Technicon Auto Analyzer consisting of:
  - 5.1.1 Sampler II with provision for sample mixing.
  - 5.1.2 Manifold.
  - 5.1.3 Proportioning Pump II or III.
  - 5.1.4 High temperature heating bath with two distillation coils (Technicon Part # 116-0163) in series.
- 5.2 Vapor-liquid separator (Figure 1).
- 5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.
- 5.4 Atomic Absorption Spectrophotometer (See Note 2): 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 2: 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.
- 5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.7 Source of cooling water for jacketed mixing coil and connector A-7.
- 5.8 Heat lamp: 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, 2 N: Dilute 56 mL of conc. sulfuric acid to 1 liter with distilled water.
  - 6.1.2 Sulfuric acid, 10%: Dilute 100 mL conc. sulfuric acid to 1 liter with distilled water.

- 6.2 Nitric acid, Conc: Reagent grade of low mercury content.  
 6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 mL of conc. nitric acid to 1 liter with distilled water.
- 6.3 Stannous Sulfate: Add 50 g stannous sulfate to 500 mL of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.  
 NOTE 3: Stannous chloride may be used in place of stannous sulfate.
- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.  
 NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.
- 6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.
- 6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.
- 6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.
- 6.8 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. 1.0 mL = 1.0 mg Hg.
- 6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1  $\mu\text{g}$  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.  
 From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0  $\mu\text{g}$  Hg/L.
- 6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

## 7.0 Procedure

- 7.1 Set up manifold as shown in Figure 2.
- 7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.
- 7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.
- 7.4 Arrange working mercury standards from 0.2 to 20.0  $\mu\text{g}$  Hg/L in sampler and start sampling. Complete loading of sample tray with unknown samples.
- 7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.  
 NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as:  
 a) equal volumes of 0.1 N  $\text{KMnO}_4$  (6.6) and 10%  $\text{H}_2\text{SO}_4$  (6.1.2).  
 b) 0.25% iodine in a 3% KI solution, is recommended.  
 A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus,

Ohio 43219, Cat. #580-13 or #580-22.

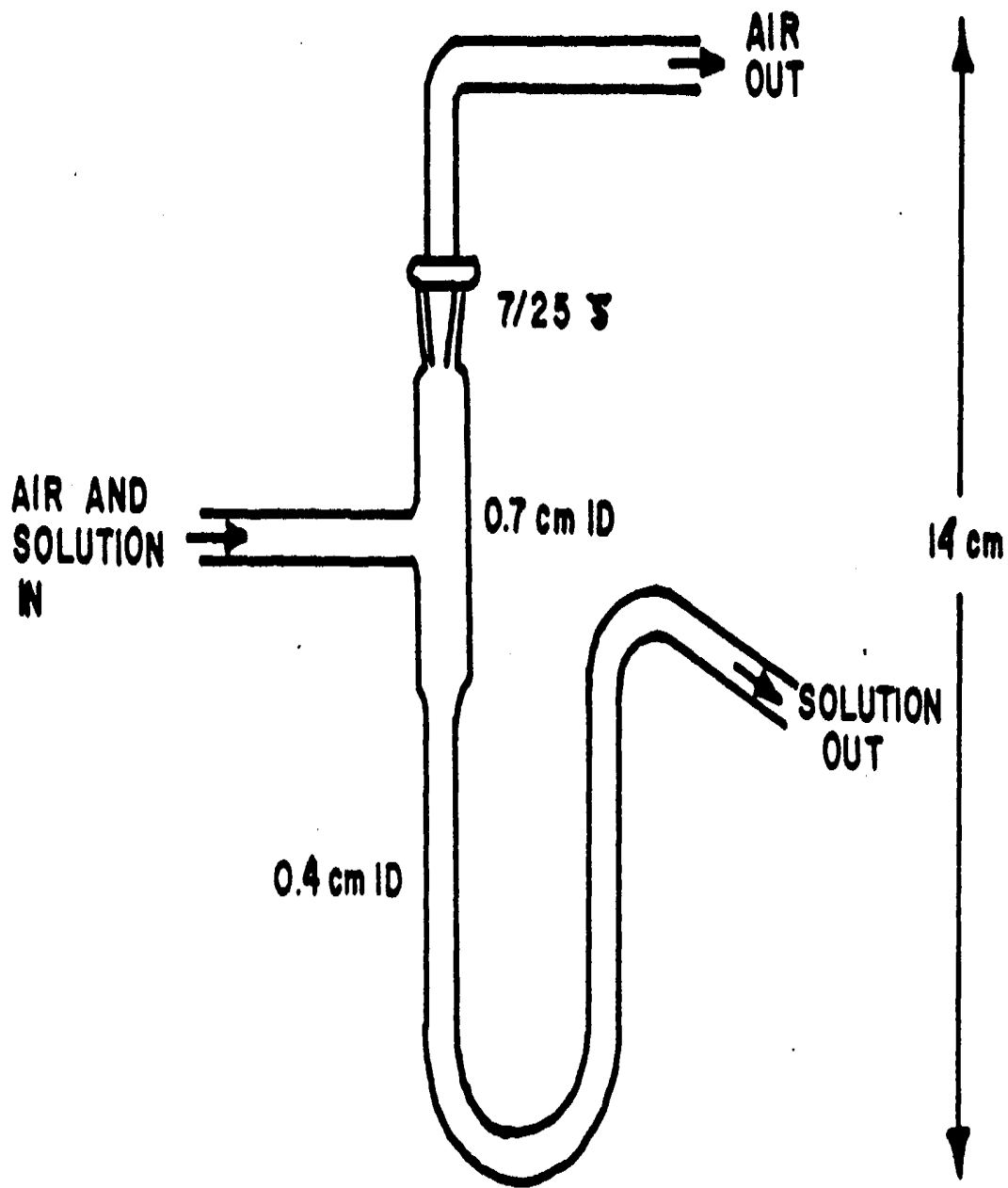
- 7.6 After the analysis is complete put all lines except the  $\text{H}_2\text{SO}_4$  line in distilled water to wash out system. After flushing, wash out the  $\text{H}_2\text{SO}_4$  line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

## 8.0 Precision and Accuracy

- 8.1 In a single laboratory (SEWL), using distilled water standards at concentrations of 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0  $\mu\text{g}$  Hg/L, the standard deviations were  $\pm 0.04$ ,  $\pm 0.07$ ,  $\pm 0.09$ ,  $\pm 0.20$ ,  $\pm 0.40$  and  $\pm 0.84$   $\mu\text{g}$ /L, respectively.
- 8.2 In a single laboratory (SEWL), using surface water samples spiked with ten organic mercurials at the 10  $\mu\text{g}$ /L level, recoveries ranged from 87 to 117%. Recoveries of the same ten organic mercurials in distilled water at the 10  $\mu\text{g}$ /L level, ranged from 92% to 125%

## Bibliography

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**FIGURE 1. VAPOR LIQUID SEPARATOR**

