

METHOD 7470

MERCURY (MANUAL COLD-VAPOR TECHNIC

REVISIONS

1.0 Scope and Application

1.1 Method 7470 is a cold-vapor atomic absorpti for determining the concentration of mercury in mobil aqueous wastes and groundwaters. (Method 7470 can al certain solid and sludge-type wastes; however, Method method of choice for these waste types.) All samples appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis, the samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 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.

3.3 Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure 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 adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

METHOD 7470

MERCURY (MANUAL COLD-VAPOR TECHNIQUE)

1.0 Scope and Application

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility procedure extracts, aqueous wastes and groundwaters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis, the samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 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.

3.3 Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure 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 adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

2 / INORGANIC ANALYTICAL METHODS

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer or equivalent: 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. 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.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter x 1/16 in. 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-in. x 2-in. cards. One-in.-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.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 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.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10° C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.10 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

4 / INORGANIC ANALYTICAL METHODS

4.11 Because mercury vapor is toxic, 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:

1. equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4
2. 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.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities:

5.2 Sulfuric acid, conc.: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

5.4 Nitric acid, conc.: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 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.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 ml of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 ml of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of Type II water. Add 10 ml of conc. HNO_3 and adjust the volume to 100.0 ml (2 ml = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg 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 addition of the aliquot.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid. The suggested maximum holding times for these samples are 38 days in glass containers and 13 in plastic containers.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 μg of mercury, to a 300-ml BOD bottle. Add 5 ml of sulfuric acid and 2.5 ml of conc. nitric acid, mixing after each addition. Add 15 ml of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-ml aliquots of the mercury working standard containing 0 to 1.0 μg of mercury to a series of 300-ml BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid and 2.5 ml of conc. nitric acid to each bottle. Add 15 ml of KMnO_4 solution to each bottle and allow to stand at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 ml of the stannous sulfate solution, and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

6 / INORGANIC ANALYTICAL METHODS

7.3 Analysis: 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/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbance of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.