

METHOD 7471A

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength 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 instrument detection limit (IDL) 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/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, 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.

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 with 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 with quartz end windows may be used. Suitable cells may be constructed from Plexiglas 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 L/min air 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 L/min.

4.7 Aeration tubing: A straight glass frit with 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 of reference 1 or according to the instrument manufacturers instructions. 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. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4 , or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO₃.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 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. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions 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 adding 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 Chapter Nine of this manual.

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

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl₂ could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H₂SO₄ and 2 mL of concentrated HNO₃ are added to the 0.2 g of sample. Add 5 mL of saturated KMnO₄ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10- mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of KMnO₄ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 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 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach 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 fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances 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. Duplicates, spiked samples, and check standards should be routinely analyzed.

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

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

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