METHOD 7471B

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

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is a cold-vapor atomic absorption procedure for measuring the following RCRA analyte in soils, sediments, bottom deposits, and sludge-type materials:

Analyte	CAS Number*
Mercury, total (organic and inorganic)	7439-97-6

* Chemical Abstracts Service Registry Number

1.2 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.

1.3 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.4 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

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 This method uses cold-vapor atomic absorption and 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 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to Method 7000 for a discussion of interferences.

4.2 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.

4.3 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.

4.4 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 254 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. Alternatively, the sample may be allowed to stand for at least an hour under a hood (without active purging) to remove the chlorine.

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

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Atomic absorption spectrophotometer or equivalent -- Any atomic absorption unit equipped 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.

6.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

6.3 Recording device -- Any multirange variable-speed recorder compatible equipped with the UV detection system or any other compatible data collection device.

6.4 Absorption cell -- Standard spectrophotometer cells 10 cm long equipped 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 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.

6.5 Air pump -- Any peristaltic pump capable of delivering air at 1 L/min may be used. A Masterflex pump equipped with electronic speed control has been found to be satisfactory.

6.6 Flowmeter -- Capable of measuring an air flow of 1 L/min.

6.7 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.

6.8 Drying tube -- 6-in x 3/4-in diameter tube containing 20 g of magnesium perchlorate or a small reading lamp, equipped with a 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.

6.9 The cold-vapor generator is assembled as shown in Figure 1 of Ref. 1 or according to the instrument manufacturer's instructions. The apparatus shown in Figure 1 of Ref. 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 was 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. Iodine 0.25% in a 3% KI solution.

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

6.10 Heating source -- Adjustable and capable of maintaining a temperature of 95 ± 3 °C. (e.g., hot plate, block digestor, microwave, etc.)

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- Reagent water should be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Aqua regia -- Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.4 Sulfuric acid, 0.5 N -- Dilute 14.0 mL of concentrated sulfuric acid to 1 L.

7.5 Stannous sulfate -- Add 25 g of 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 (in water) can be substituted for the acidic stannous sulfate solution.

NOTE: If line clogging occurs when using an automated system, use a less concentrated stannous chloride solution.

7.6 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. In this case, dissolve 12 g of hydroxylamine hydrochloride in reagent water and dilute to 100 mL.

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

7.8 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). Alternatively, a mercury stock solution may be purchased from a reputable source with a concentration of 1.0 mg Hg/mL. Verify the quality of the standard by checking it against a second source standard (see second paragraph of Sec. 9.4).

7.9 Mercury working standard -- Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg/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.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 All sample containers must be prewashed with detergents, acids, and reagent water. Glass, plastic, and polytetraflouroethylene (PTFE) containers are suitable in most cases. Polymers are not suitable for samples containing metallic mercury.

8.3 Metallic mercury, some inorganic mercury compounds, and many organic mercury compounds are volatile and unstable. It is advantageous to analyze the samples as soon as possible to determine the total mercury in the sample but in no case exceed the 28-day limit as defined in Chapter Three of this manual. Non-aqueous samples must be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigeration is necessary.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency by following the sample preparation and analytical procedures described in this method and generating data of acceptable accuracy and precision for the target analyte (Mercury) in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.3 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate steps of the analytical process. These steps may include but are not limited to digestion, dilution, filtering, and analysis. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lower level of quantitation or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable then all samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated.

9.4 For each batch of samples processed, at least one laboratory control sample must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value. After the determination of historical data, ± 20% should still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed. Refer to Chapter One for more information.

If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a LCS or mid-range standard or reference standard after every 10 samples. This sample value should be within 20% of the true value, or the previous 10 samples must be reanalyzed.

9.5 Matrix spike/matrix spike duplicates (MS/MSDs) -- MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Based on the analyst's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of sample processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value for precision and $\leq$ 20 relative percent difference (RPD). After the determination of historical data, 20% should still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability.

9.6 The method of standard additions can be used to verify linearity or if matrix interference is suspected. Refer to Method 7000 for standard addition procedures.

9.7 Refer to Method 7000 for additional QA and QC information that may be applicable.

10.0 CALIBRATION AND STANDARDIZATION

10.1 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 µg 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 at 95 ± 3 °C. Allow the sample to cool; add 50 mL of reagent water and 15 mL of $KMnO_4$ solution to each bottle and heat again at 95 ± 3 °C 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 Sec. 11.3.

10.2 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart or other recording device and read the mercury value from the standard curve.

11.0 PROCEDURE

11.1 Sample preparation

Weigh a 0.5 - 0.6 g-aliquot of a well homogenized sample and place in the bottom of a BOD bottle or other appropriate analysis vessel. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min at 95 ± 3 °C. Cool; then add 50 mL of reagent water and 15 mL of potassium permanganate solution to each sample and let stand at least 15 min. Add additional portions of permanganate solution, if needed, until the purple color persists for at least 15 min (see Sec. 4.4). Ensure that equal amounts of permanganate are added to standards and blanks. Mix thoroughly, then heat for 30 min at 95 ± 3 °C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, because Cl_2 could evolve. 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 Sec. 11.3.

See Sec. 10.1 for directions regarding standard preparation.

11.2 Alternate digestion procedure

An alternate digestion procedure employing an autoclave may also be used. In this procedure, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.5 - 0.6 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121 ± 3 °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 Sec. 11.3. Refer to the caution statement in Sec. 11.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

11.3 Analysis

At this point, allow the sample to stand quietly without manual agitation. Allow the circulating pump, which was previously adjusted to a rate of 1 L/min, 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 absorbance reading 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. Because of instrument variation refer to the manufacturer's recommended operating conditions when using this method.

11.4 See Sec. 10.2 for directions regarding calibration curve construction.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

12.2 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 µg/g dry weight).

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.</u>

13.2 Precision and accuracy data are available in Method 245.5 of <u>Methods for Chemical Analysis of Water and Wastes</u>. These data are provided for guidance purposes only.

13.2 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. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. U.S. EPA, "Method 245.5," Methods for Chemical Analysis of Water and Wastes, Pub. EPA-600/4-82-055, December 1982. .

2. A. Gaskill, "Compilation and Evaluation of RCRA Method Performance Data," Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following page contains the table referenced by this method.

TABLE 1

EXAMPLE METHOD PERFORMANCE DATA

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

Data taken from Ref. 2.

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