



State of New Jersey

Christine Todd Whitman
Governor

Department of Environmental Protection

Robert C. Shinn, Jr.
Commissioner

Debra L Felton
Northern Division
10 Industrial Highway
Mail Stop #82
Lester, PA 19113-2090

OCT 28 1998

Re: Work Plan for Building 21 Mercury Decontamination

Dear Ms. Felton:

The New Jersey Department of Environmental Protection (NJDEP) is in receipt of the Work Plan for Building 21 Mercury Decontamination dated October 8, 1998.

In general, NJDEP does not regulate building interiors. However, since the mercury contamination present inside Building 21 has the potential to impact the environment on the outside, NJDEP can require such action as to prevent this from occurring. Based on this, and the other regulations, the Navy has submitted the Work Plan for Building 21 Mercury Decontamination.

Upon review, NJDEP offers the following comments.

1. Section 2 – Mercury Decontamination, pg. 2

In addition to obtaining real-time readings in the breathing zone during work activities, it is recommended that the Navy perform mercury vapor sampling at the completion of the concrete floor decontamination. This method has already been performed inside several structures at the site, including 21.

The Navy's previous remedial recommendations for building interiors were developed based on comparisons of mercury vapor readings to the NIOSH Recommended Exposure Limit for mercury (i.e., 0.05 mg/m³). The NIOSH Exposure Limit is a 10-hour time-weighted average (TWA) and is considered inappropriate in this case. The NIOSH limits apply to a healthy worker population, take into account economics and assume respiratory protection will be utilized when the 0.05 mg/m³ mercury level is exceeded. NJDEP recommends that EPA's Region III Risk-Based Criterion of 0.0003 mg/m³ of mercury in ambient air be applied instead of the NIOSH limit. The Jerome MVA method is one analytical technique that can detect mercury down to this lower level.

There is also another method which can achieve low detection limits. It is a modification to the enclosed Flow Injection Atomic Absorption Spectrometry

(cold vapor technique). The method is a Wisconsin Occupational Health Laboratory (WOHL) modification to methods OSHA ID 140 and NIOSH 6009. WOHL is located at 979 Jonathon Drive, Madison, WI 53713.

Air sampling is accomplished using an air pump and glass tubes filled with "Hopcalite." Approximately 100 liters of air sample is collected at a flow rate of approximately 250 cc/min. The Hopcalite tubes can be purchased from Supelco, Inc., Bellefonte, PA 16823, (FAX): (814) 359-5459 and (Phone): (814) 359-5426. WOHL can also supply the tubes.

This method was used successfully at the Dupont-Pompton Lakes site to sample air in the basements of residential homes down to a detection limit well below the 0.0003 mg/cubic meter inorganic mercury vapor in ambient air criterion NJDEP recommends for the Navy site.

It is suggested that the Navy contact the WOHL to get obtain more detailed information and sample collection procedures for the modified FIAS method and then contact NJDEP get back to us with a proposal.

NJDEP recommends the affected structures be sampled again following cleanup and the results evaluated against EPA's 0.0003 mg/m³ criterion.

2. Section 2.2 – Concrete Floor Decontamination, pg. 2

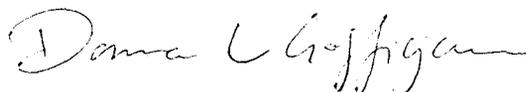
The Work Plan states that the wooden block floor is underlain by a concrete floor. In areas of missing, cracked or broken concrete soil samples shall be collected. The results must be compared to the New Jersey Soil Cleanup Criteria.

3. Section 3 – Waste Characterization Sampling and Analysis, pp. 2-3

Depending on the ultimate disposal of the drummed sludge and rinsate/decontamination water, the proposed analyses may not be required. Please check with the disposal facility for the appropriate requirements.

If you have any questions regarding this letter, please do not hesitate to contact me at (609) 633-1494.

Sincerely,



Donna L. Gaffigan, Case Manager
Bureau of Federal Case Management

Enclosures

cc: Steven Bynes, BEERA
William Lawler, USEPA
Edward Boyle, NorthDiv

Environmental Application Note

Perkin-Elmer Method 245.1A; Determination Of Mercury In Drinking Water And Wastewater By Flow Injection Atomic Absorption Spectrometry (Cold Vapor Technique)

Susan McIntosh, Bernhard Welz
The Perkin-Elmer Corporation

1. Scope and Application

- 1.1 This method is applicable to waters regulated under the National Primary Drinking Water Regulation (NPDWR) and National Pollutant Discharge Elimination System (NPDES) monitoring. These waters include drinking waters, effluents and effluent samples containing high chlorides.
- 1.2 This method is suitable for the determination of total mercury content in the concentration range between 0.2 and 20 $\mu\text{g/L}$ Hg. Using a 500 μL sample, a detection limit of 0.2 $\mu\text{g/L}$ Hg can be achieved (see 13.2); concentrations below this level should be reported as <0.2 $\mu\text{g/L}$ Hg for the hollow cathode lamp and <0.06 $\mu\text{g/L}$ Hg for the electrodeless discharge lamp.

2. Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. This



method determines total mercury, both inorganic and organic, present in the sample. Organic mercury compounds are oxidized and 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 spectrometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

- 2.2 The organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are oxidized and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mer-

cury compounds, if present will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

- 3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. The maximum sample holding time should not exceed 28 days.

4. Interference

- 4.1 Interferences may be seen from volatile organic substances which can absorb in the UV range and be mistaken for mercury. Often, such interference by non-specific absorption can be eliminated using a background correction system. A preliminary run without reagents should determine if this type of interference is present. (see Appendix 13.1)
- 4.2 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.
- 4.3 Copper has also been reported to interfere; however, copper concentrations as high as 50 mg/L had no effect on recovery of mercury from spiked samples.
- 4.4 Industrial effluents high in chlorides require additional permanganate. During the oxidation step, chlorides are converted to free chlorine which will absorb radiation at the 253.7 nm mercury wavelength. Care should 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 hydrochloride reagent (as much as 25 mL). (see Note 1)

Note 1: The analyst is advised to refer to the current EPA Method 245.1. In particular, any revised requirements regarding the amount of potassium permanganate added to samples containing a high salt content.

5. Safety

- 5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. The use of protective clothing and safety goggles is advised.
- 5.2 A reference file of the material safety data sheets, for reagent handling instructions, must be available to all personnel involved in the chemical analysis
- 5.3 Due to the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. The mercury vapor must be vented into an exhaust hood.

6. Apparatus

- 6.1 Atomic absorption spectrometer: Any atomic absorption spectrometer which has an open sample compartment in which to mount the quartz cell. Instrument settings recommended by the manufacturer should be used. A background correction system is desirable but not necessary. (see Section 4.1)
- 6.2 Radiation source for the determination of mercury, such as a hollow cathode lamp or electrodeless discharge lamp (see Section 13.2).
- 6.3 Recording device: Any recorder which is

compatible with the spectrometer is suitable. Any atomic absorption spectrometer which can print spectral peaks is suitable.

6.4 All Apparatus required for sample digestion described in procedures, including a covered water bath capable of maintaining a temperature of 95°C.

6.5 Flow Injection System (Assembled as shown in Figure 1) consisting of:

6.5.1 Autosampler with random access capabilities.

6.5.2 Two Independently Controlled Peristaltic pumps: Pump 1 controls the delivery of sample. Pump 2 controls the delivery of the reductant and acid carrier stream.

6.5.3 Switching Valve: Multiport valve used for injecting discrete sample volumes, determined by sample loop size, into a hydrochloric acid carrier stream. The carrier stream transports the sample

volume to the chemifold. (see Note 2)

6.5.4 Chemifold: Manifold where the sample, reductant and argon are merged and mixed thoroughly. (Figure 2)

6.5.5 Gas/liquid separator.

6.5.6 Flowmeter: Capable of measuring flows of 0-250 mL/min.

6.5.7 Quartz Cell: Absorption cell consisting of a quartz cell 14 cm in length, i.d. = 7mm, with quartz end windows. The cell is positioned in the path of the light beam.

6.5.8 Heating Mantle: The quartz cell is placed in the heating mantle and the temperature along the length of the cell is maintained at about 10°C above ambient. This will prevent condensation within the quartz cell.

Note 2: Recommended sample loop volume is 500 µL.

6.6 The sample and reagent flows, through the

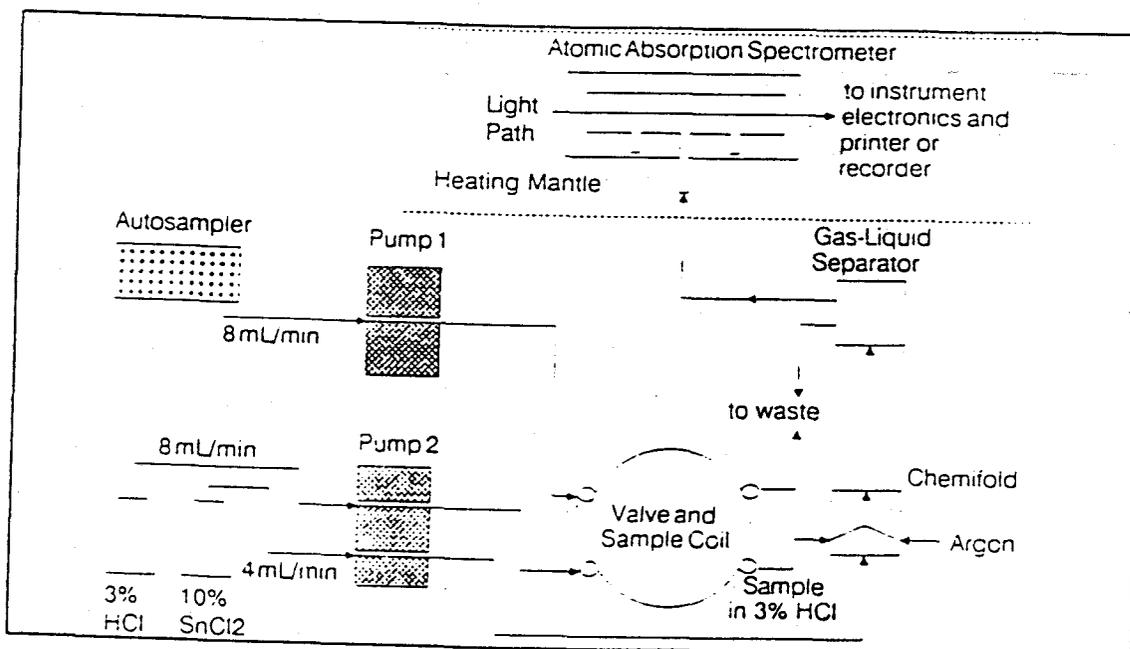


Figure 1. Flow Injection System

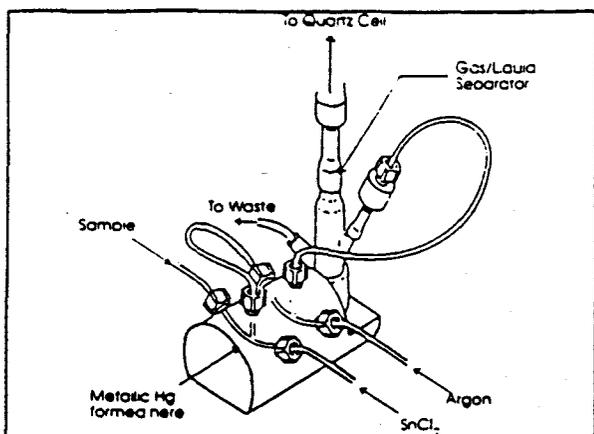


Figure 2. Chemifold and Gas/Liquid Separator

Flow Injection system, are shown in Figure 3 and are as follows:

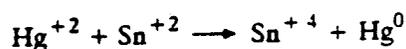
6.6.1 The first channel of Pump 2 transports the 3% HCl acid carrier stream through the Flow Injection valve to the chemifold.

6.6.2 The Flow Injection (FI) valve is electronically switched, moving the sample loop into the Fill or Inject positions. In the Fill position the sample loop

is filled with sample by Pump 1. (see Figure 3)

6.6.3 The FI valve then switches to the Inject position, moving the sample loop into the path of the HCl acid carrier stream. The HCl carrier stream pushes the sample to the chemifold. (see Figure 3)

6.6.4 The second channel of Pump 2 transports the reductant, SnCl₂, to the chemifold. The reductant stream and the sample merge at the chemifold (see Figures 2 and 3) reacting to form metallic mercury as shown below.



6.6.5 An Argon carrier stream is merged with the reaction solution at the chemifold and the gas/liquid mixture is transported to a separator. (see Figure 3)

6.6.6 The gas/liquid mixture is passed through the separator and the liquid is drawn off by Pump 2. The metallic vapor

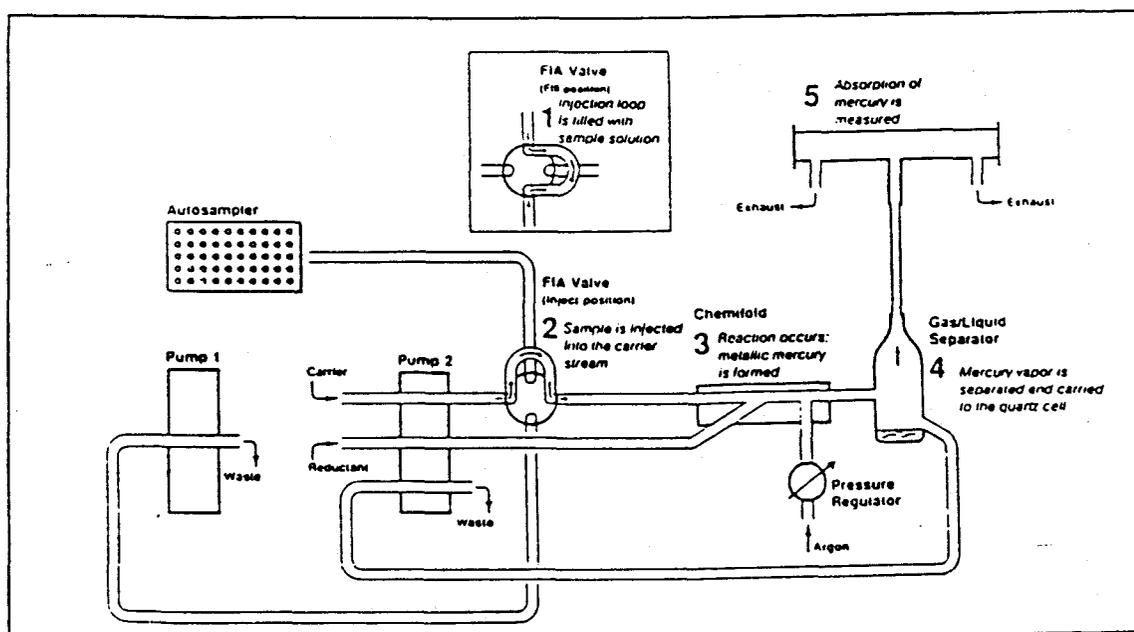


Figure 3. Flow Diagram

is transported to the quartz cell. (see Figure 2)

6.6.7 Absorption of the light source by the mercury vapor collected in the quartz cell is measured. (see Figure 3)

7. Reagents

7.1 Reagents should contain negligible amounts of mercury.

7.2 Sulfuric Acid, Conc.: Reagent grade. (CAS RN 7664-93-9)

7.2.1 Sulfuric acid, 0.5N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

7.3 Nitric Acid, Conc.: Reagent grade containing negligible amounts of mercury. If a high reagent blank is obtained, it may be necessary to distill the nitric acid. (CAS RN 7697-37-2)

7.4 Hydrochloric Acid, Conc.: Reagent grade containing negligible amounts of mercury. (CAS RN 7647-01-0)

7.4.1 Hydrochloric Acid 3% v/v: Dilute 30.0 mL of concentrated hydrochloric acid to 1.0 liter.

7.5 Stannous Chloride: Dissolve 5.5 g of stannous chloride in 15 mL hydrochloric acid (6.3) and dilute to 500 mL with distilled water. (CAS RN 7772-99-8)

7.6 Sodium Chloride - Hydroxylamine Hydrochloride Solution: Dissolve 12 g of Sodium Chloride (CAS RN 7647-14-5) and 24 g of Hydroxylamine Hydrochloride (CAS RN 5470-11-1) in distilled water and dilute to 100 mL.

7.7 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium perman-

ganate in 100 mL distilled water. (CAS RN 7722-64-7)

7.8 Potassium Persulfate: 5% solution, w/v. Add 5 g of potassium persulfate to 100 mL of distilled water and heat at 40°C for 20 minutes until dissolved. (CAS RN 7727-21-1)

7.9 Stock Mercury solution - May be purchased from a reputable commercial source or prepared from high-purity grade chemicals. The stock solution should be stored in Teflon bottles. The following procedure may be used to prepare the stock standard:

7.9.1 Stock Mercury Solution: Dissolve 0.1354 g of Mercuric Chloride (CAS RN 7487-94-7) in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL.
1 mL = 1 mg Hg.

7.9.2 Stock Organic Mercury Solution: Dissolve 0.2018 g of 2-Ethylmercurimercaptobenzoic acid, sodium salt (CAS RN 54-64-8) in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL.
1 mL = 1 mg Hg.

7.10 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 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.

7.11 Blank: A laboratory reagent blank is used to establish the analytical calibration.

curve and correct for any contamination from the sample preparation procedure.

7.11.1 Laboratory reagent blank - Consists of all the reagents in the same volumes as used in processing the samples. The preparation blank must be carried through the entire sample digestion.

7.12 Laboratory Fortified blank - To an aliquot of laboratory reagent blank, add an aliquot of the stock standard (7.9.1) and the organic stock standard (7.9.2) to provide a final concentration which will produce an absorbance of approximately 0.1 for the analyte. The fortified blank must be carried through the entire sample digestion and preparation scheme.

8. Calibration

8.1 Transfer 0, 0.5, 1.0, 5.0, 10.0, and 20.0 mL aliquots of the working mercury solution containing 0 to 2.0 μg of mercury to a series of ~~300~~ mL-BOD bottles containing 40 mL of distilled water.

8.2 Add enough distilled water to make a total volume of 100 mL and mix thoroughly.

8.3 Add 5 mL of Concentrated Sulfuric Acid (7.2) and mix.

8.4 Add 2.5 mL of Concentrated Nitric Acid (7.3) and mix.

8.5 Add 15 mL of Potassium Permanganate (7.7) solution to each bottle and mix.

8.6 Allow mixture to stand for at least 15 minutes.

8.7 After 15 minutes add 8 mL of Potassium Persulfate (7.8) to each bottle and mix thoroughly.

8.8 Heat mixture for 2 hours in a covered water bath maintained at 95°C.

8.9 Cool the solution and Add 6 mL of Sodium Chloride-Hydroxylamine Hydrochloride solution (7.6) to reduce the excess permanganate.

8.10 When the solution becomes decolorized transfer to the autosampler (see Note 3).

8.11 Assemble the Flow Injection System as shown in *Figure 1*. For more detailed information refer to instrument manual provided with the Flow Injection system. Turn on the autosampler and atomic absorption spectrophotometer. All instrument parameters recommended by the manufacturer should be used.

8.12 Align the quartz cell in the optical path.

8.13 Feed all reagents through the system (see *Figures 1 and 2*). Refer to the manual supplied with the Flow Injection for more detailed information.

8.14 Prepare the calibration curve by plotting peak absorbance of the known standards versus concentration.

8.15 The sample concentration is determined by plotting the sample peak absorbance on the standard curve.

8.16 At the completion of the analysis all tubing should be flushed with deionized water and then air.

8.17 Release the pump tension on all tubing.

Note 3: The analyst is advised to follow any future EPA Method 245.1 directions regarding the purging of the air space above the sample in the BOD bottle for 20-30 seconds with air or nitrogen to sweep away any chlorine before transferring the samples to the autosampler.

9. Quality Assurance

9.1 Each laboratory using this method in regulated environmental monitoring is required to operate a formal quality assurance/control program. The minimum initial requirements of this program consist of the demonstration of the laboratory's capability with this method.

9.2 Initial Demonstration of Performance

9.2.1 The initial demonstration of performance is used to characterize instrument performance (method detection limits and linear calibration ranges) for analyses conducted by this method.

9.2.2 Method Detection Limits (MDL):

The method detection limit should be established for the analyte, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. The MDL shall be determined using the procedure as outlined in Appendix B of section 136 of 40 CFR. (13.3) The MDL should be determined every six months.

9.2.3 Linear calibration range:

The upper limit of the linear calibration range should be established by determining the signal response from a minimum of four different concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined every six months.

9.3 On a continuing basis, the laboratory should check its performance (accuracy and precision) by analyzing reagent blanks and check standards, fortified

blanks, and/or fortified samples, preferably at a minimum frequency of 10% of the total samples analyzed by the method.

9.3.1 Laboratory reagent blank:

The laboratory must analyze at least one reagent blank (7.11.1) with each set of samples. Reagent blank data are used to assess contamination from the laboratory environment. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.

9.3.2 Laboratory fortified blank:

The laboratory must analyze at least one fortified blank (7.12) containing a mixture of organic and inorganic mercury with each batch of samples. Calculate accuracy, as a percent recovery, as shown below:

$$R = \frac{C_s (100)}{S}$$

Where:

R: % Recovery

C_s: Determined Fortified Blank Concentration

S: Known Fortified Blank Concentration

If the percent recovery falls outside the limits of 70-130% as promulgated in CFR, 56, (126), pp. 30274-30276, July 1, 1991 (see Note 4), the source of the problem should be identified and resolved before continuing the analysis.

Note 4: The analyst should refer to the Code of Federal Regulations for current information on acceptable percent recovery limits.

9.4 The laboratory should maintain the performance records that define the

quality of the data generated with the method.

10. Procedure

- 10.1 Transfer 100 mL of sample, or an aliquot of the sample diluted to 100 mL, to a 300-mL BOD bottle. This concentration should not exceed 2.0 μg of mercury.
- 10.2 Add 5 mL of Sulfuric Acid (7.1) and mix.
- 10.3 Add 2.5 mL of Nitric Acid (7.2) and mix.
- 10.4 Next add 15 mL of Potassium Permanganate Solution (7.7) to each sample. Sewage samples and samples containing high salts may require additional permanganate see below.
 - 10.4.1 Sewage samples and samples containing a high salt content may require additional portions of Potassium Permanganate Solution (7.7). If necessary, add 15-mL portions of the Potassium Permanganate Solution until the purple color persists for at least 15 minutes. (see Note 5) Be sure to mix sample after each addition.
 - 10.4.2 The same amount of Potassium Permanganate Solution should be added to the standards and blanks as that added to the samples.
- 10.5 Add 8 mL of Potassium Persulfate (7.8) to each bottle and heat for 2 hours in a covered water bath at 95°C.
- 10.6 Cool sample and add 6 mL of Sodium Chloride-Hydroxylamine Hydrochloride (7.6) to reduce the excess permanganate. For samples containing high chlorides,

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continue to add the Sodium Chloride-Hydroxylamine Hydrochloride (up to 25 mLs) in 6-mL increments until the Potassium Permanganate is completely reduced (see Note 6). Be certain to mix the sample after each addition.

Note 6: The analyst is advised to follow any future EPA Method 245.1 directions regarding the purging of the air space above the sample in the BOD bottle for 20-30 seconds with air or nitrogen to sweep away any chlorine before transferring the samples to the autosampler.

- 10.7 Transfer the samples to an autosampler and continue as described in sections 8.11 - 8.17.

11. Calculation

- 11.1 The calibration curve is constructed by plotting the peak absorbance value of the known standards versus their concentration.
- 11.2 The value of the unknown is obtained by plotting the determined peak absorbance on the standard curve.
- 11.3 To determine the concentration of mercury in the sample use the following:
$$\mu\text{g Hg/L} = \frac{(\mu\text{g Hg in Aliquot})(1000)}{(\text{Volume of Aliquot})}$$
- 11.4 If additional dilutions were performed, the appropriate dilution factor must be applied to the sample values.
- 11.5 Report mercury concentrations as follows: Below 0.2 $\mu\text{g/L}$, < 0.2; between 1 and 20 $\mu\text{g/L}$, one decimal; above 20 $\mu\text{g/L}$, whole numbers.

12. Precision and Accuracy

- 12.1 Operating conditions used for the analysis

Table 1
Recommended Operating Conditions for Mercury Determinations

Wavelength	253.7nm
Slit	0.7 nm
Cell Temperature	100 °C
Sample Volume	500 µL

Notes:

Argon carrier gas flow = 60 mL/min
 Electrodeless discharge lamp (EDL System 2) used
 3% HCl carrier flow rate = 8 mL/min
 1.1% SnCl₂ reductant flow rate = 4 mL/min
 MDL: 0.2 µg/L when using a hollow cathode lamp
 MDL: 0.06 µg/L when using EDL System 2

of mercury and the instrumental detection limit are listed in Table 1.

12.2 Data obtained from the analysis of wastewater samples and drinking water are listed in Tables 2 and 3.

13. Appendix

13.1 If an interference has been found to be present (4.1), the sample should be analyzed both by using the normal proce-

dure and again using oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

13.2 Lower detection limits can be achieved by using an electrodeless discharge lamp (EDL System 2).

14. Bibliography

14.1 Hatch, W. R. and Ott, W.L., "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry". *Anal. Chem.* 40, 2085 (1968).

14.2 Standard Methods for the Examination of Water and Wastewater 14th Edition, p. 156 (1975)

14.3 Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

14.4 Methods for Chemical Analysis of Water and Wastes, Mercury Methods 245.1 and 245.2, EMSL - Cincinnati, OH, March 1983.

Table 2
Precision and Recovery for Mercury-Spiked Wastewater Samples

Sample	Hg Spike (µg/L)	Mean (µg/L)	SD	%RSD	%Recovery
Wastewater #1 [*]	1.00	0.96	0.04	4.3	96
Wastewater #2 ^{**}	1.00	1.04	0.06	5.4	104

Notes:

SD: Standard deviation
 %RSD where N = 20

Spiking solutions:

* = 1.00 µg/L Hg (HgCl₂)
 ** = 1.00 µg/L Hg (2-Ethylmercurimercaptobenzoic acid, sodium salt)

Table 3
Precision and Recovery for Mercury-Spiked Drinking Water Samples

Sample	Hg Spike (µg/L)	Mean (µg/L)	SD	%RSD	%Recovery
Drinking Water #1 [*]	1.00	0.99	0.04	4.4	99
Drinking Water #2 ^{**}	1.00	1.08	0.05	4.4	108

Notes:

SD: Standard Deviation
 %RSD where N = 20

Spiking Solutions:

* = 1.00 µg/L Hg (HgCl₂)
 ** = 1.00 µg/L Hg (2-Ethylmercurimercaptobenzoic acid, sodium salt)