

METHOD 7472

MERCURY IN AQUEOUS SAMPLES AND EXTRACTS BY ANODIC STRIPPING VOLTAMMETRY (ASV)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for laboratory determinations of dissolved organic and inorganic divalent mercury ions and compounds (Hg(II)) in drinking water, natural surface water, seawater, in domestic and industrial wastewater, and in aqueous soil extracts. Solid matrices must be solubilized by acid digestion prior to quantitation by ASV.

1.2 Dissolved Hg(II) in the form of mercury ions and un-ionized organic and inorganic mercury compounds may be quantified in the concentration range 0.1 to 10,000 µg/L Hg. The upper concentration range may be extended by sample dilution, increasing the stripping current and/or by decreasing the analyte deposition time.

1.3 This method cannot be used for direct determination of water-insoluble mercury compounds. Analytes containing mercury in this form must be chemically processed to liberate Hg(II) before the determination.

1.4 The method detection limit for Hg(II) is 0.1 µg/L using a 10-minute plating time and 3 µg/L using a 1-minute plating time.

2.0 SUMMARY OF METHOD

2.1 Standards and samples are made 0.1 M in Cl⁻ and are rendered electrically conductive by adding concentrated hydrochloric acid (HCL) or solid sodium chloride (NaCl). Hg(II) is quantified by anodic stripping, at a potential of +500 mV with respect to an saturated calomel electrode (SCE), from a gold metal film deposited on a glassy carbon electrode (GCE).

3.0 INTERFERENCES

3.1 ASV cannot distinguish between organic and inorganic divalent mercury compounds.

3.2 Turbid samples should be filtered through a borosilicate glass fiber filter with 0.45-µm pores to preclude physical erosion of the GCE film.

3.3 Highly corrosive and oxidizing samples may corrode the gold film on the GCE and degrade the instrument response. The performance of the GCE electrode must be monitored by analysis of a mid-range calibration standard. Low recovery on the calibration standard may require re-cleaning and re-application of the gold film.

3.4 Samples containing tannic acid in concentrations greater than 100 mg/L cannot be analyzed for mercury by ASV.

3.5 Some wet deposition samples may have insufficient electrical conductivity for proper operation of the ASV instrumentation. This problem is obviated by making the samples 0.1 M in HCL.

4.0. APPARATUS AND MATERIALS

4.1 ASV instrumentation (Radiometer TraceLab, or equivalent), including potentiostat, electrodes, stirrer, sample stand, polyethylene sample cups, and GCE polishing powder.

4.2 Computer, as recommended by ASV instrumentation manufacturer.

4.3 Plastic syringe and a nylon syringe filter with 0.2- μ m pores.

4.4 Polyethylene graduated cylinder, 50-mL, Class B, TC/TD.

4.5 Adjustable pipettors with polyethylene tips.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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.

5.2 Reagent Water. Reagent water is interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Hydrochloric acid, (concentrated 12 M)

5.3.1 Hydrochloric acid (0.1 M), dilute 8.3 mL concentrated HCL to 1 liter with reagent water.

5.4 Sodium Chloride, fine crystals.

5.5 Gold Stock Standard (1000 mg/L), stock solutions are commercially available as spectrophotometric standards.

5.5.1 Gold-plating solution, (50 mg/L Au in 0.1 M HCL), or as recommended by the GCE manufacturer: prepare by diluting 2.5 mL of a 1000 mg/L gold spectrophotometric standard to 50 mL with 0.1 M HCL.

5.6 Mercury Stock Standard (1000 mg/L), stock solutions are commercially available as spectrophotometric standards.

5.6.1 Mercury intermediate standard solution, 1,000 μ g/L mercury: dilute 100 μ L of the stock standard to 100 mL with 2% HNO₃. Prepare weekly.

5.6.2 Mercury Working Standards: These standards should be prepared from the mercury intermediate standard to be used as calibration standards at the time of analysis. Prepare at least five working standards over the expected sample concentration range. Prepare working standards by diluting an appropriate aliquot of the intermediate mercury stock solution with 2% HNO₃.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be 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 At the time of sampling, the sample must be acidified to a pH <2 with nitric acid.

6.4 While samples to be analyzed for free dissolved mercury do not require refrigeration, they should be stored out of direct sunlight in an area no warmer than room temperature.

7.0 PROCEDURE

7.1 Analysis of aqueous samples for free dissolved mercury by ASV involves two major steps. First, the GCE electrode is cleaned and prepared for use by plating on a thin film of gold. The gold-plated electrode is then used to analyze calibration standards and samples.

7.2 Set up ASV instrumentation, electrodes, and computer according to the manufacturer's recommended procedures. Enter the appropriate program and required data parameters into the computer as directed by the instrument software.

7.3 Before applying a gold film to the GCE, the electrode must be thoroughly cleaned. Electrode cleanliness is checked by rinsing the GCE with water. After gently shaking off excess water, the electrode should be coated with a thin, flat, continuous water film. If necessary, clean the GCE by wiping it with a wet, soft paper towel, polish it with polishing powder, and rinse it thoroughly with water. Keep the cleaned electrode immersed in water.

Note: Depending on the composition of the samples, a single application of the gold film may suffice for analysis of up to a dozen or more samples. Highly corrosive and oxidizing samples may corrode the gold film and degrade the instrument response, requiring the re-application of the gold film.

7.4 Place 50 mL of the gold-plating solution (Sec. 5.5.1) or an appropriate volume as recommended by the instrument manufacturer, into a beaker. Immerse the electrodes in the gold-plating solution and initiate the GCE gold-plating program as instructed by the instrument manufacturer.

7.5 Remove the electrodes from the plating solution and rinse well with water. Keep the electrodes immersed in reagent water until ready to analyze samples.

7.6 The instrument response is calibrated by preparing a calibration curve with mercury standards (Sec 5.6.2). The same stripping current and plating time settings that are used for analyzing samples must be used for preparing the calibration curve.

7.7 Prior to instrument calibration, all calibration standards and samples must be made 0.1 M in Cl⁻. Using a graduated cylinder, measure 30 mL of each calibration standard and sample into a sample cup. Add 0.25 mL of 12 M HCL (Sec 5.3) or 0.18 g of solid NaCl (Sec 5.4) to the standard or sample and mix. Samples must be allowed to equilibrate to room temperature (within the range 20°C to 30°C) if necessary.

7.8 Following the instrument manufacturer's recommended calibration procedures, construct a calibration curve by analyzing five working calibration standards. Immerse the electrodes into 30 mL of the prepared working standard (Sec 7.7) and record instrument response. Rinse the electrodes thoroughly with reagent water between each standard. Construct a calibration curve by recording the instrument response (peak area) versus the standard concentration.

7.9 Store the electrodes in reagent water until ready to analyze another sample.

7.10 Analyze the samples for Hg (II) by aliquoting 30 mL of the prepared sample (Sec. 7.7) into a sample cup. Immerse the electrodes into the sample and record instrument response. Determine the sample concentration from the calibration curve.

8.0 QUALITY CONTROL

8.1 Initial Calibration Verification standard (ICV): The ICV contains a known Hg(II) concentration and is obtained from an independent source. The ICV recovery must be within the range 90% to 110%. If it is not, the source of error must be found and corrected. An acceptable ICV must be analyzed prior to analyzing samples. The ICV also serves as a laboratory control sample.

8.2 Continuing Calibration Verification standard (CCV): After a set of not more than 10 samples has been analyzed, and after the final sample has been analyzed, a CCV containing a known mercury concentration must be analyzed. The CCV recovery must be within the range 90% to 110%. If it is not, the source of error must be found and corrected (See the note in Sec. 7.10) All samples analyzed since the last acceptable CCV must be re-analyzed.

8.3 The analyst must monitor performance of the electrode by analyzing a mid-range check standard every ten samples. A low recovery for the check standard indicates that the electrode must be renewed. Follow the procedures in Sec. 7.3 through 7.5 to renew the gold film on the GCE. Following the renewal of the electrode, the instrument calibration must be verified by analyzing a mid-range standard. If the recovery of the standard is within 10% of the true value, a new calibration curve need not be run and analysis may continue.

8.4 Reagent blank: A reagent blank must be analyzed with each analytical batch or 20 samples, whichever is more frequent. A reagent blank is reagent water treated as a sample. The indicated concentration of the reagent blank must be less than the lower detection limit of Hg(II). If it is not, sample carryover or reagent contamination is indicated. The problem must be corrected before analyzing more samples.

8.5 At least one matrix spike (MS) and one matrix spike duplicate (MSD) shall be included in each analytical batch or 20 samples: A matrix duplicate may be substituted for the MSD provided that the concentration of mercury in the sample selected for duplicate analysis is greater than the limit of detection. The spike should increase the concentration of free Hg(II) in the spiked sample by 50% to 200%. The volume of the spike must be no more than 1% of the sample volume.

8.5.1 The spike recovery must be within the range 75% to 125%. If it is not, the source of error must be found and corrected. If a matrix interference is suspected, a second sample aliquot should be spiked to confirm the spike recovery. If the spike recovery is still outside the range of $\pm 25\%$, all samples must be quantified by the method of standard additions. Refer to Method 7000 for information on the method of standard additions.

8.5.2 The duplicate samples (MS/MSD and/or sample/sample duplicate) should give results having a difference not greater than 20% of the mean of the duplicate results. If the difference is greater than 20% of the mean, the source of error must be found and corrected.

9.0 METHOD PERFORMANCE

9.1 In a single-laboratory evaluation, standards with known Hg(II) concentrations were analyzed in quintuplicate according to the instructions given above. The results are listed in Table 1.

9.2 In a single laboratory evaluation, the precision and accuracy of ASV was compared to an EPA-approved spectrophotometric method by analyzing a 1 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$ standard of mercury (II) ten times each. The results of this comparison are listed in Table 2.

10.0 REFERENCES

1. Pyle, Steven; Miller, Eric Leroy; Quantifying Mercury In Aqueous Solutions By Anodic Stripping Voltammetry, EMSL-LV/ORD/USEPA.

TABLE 1
ACCURACY AND PRECISION OF MERCURY ANALYSIS

Mercury Concentration (µg/L)	Mercury Recovery (%)	Relative Standard Deviation (%)
5.00	97	3.8
15.0	101	0.9
50.0	97	1.2

TABLE 2
COMPARISON OF ASV AND SPECTROPHOTOMETRIC METHOD
FOR QUANTIFYING DISSOLVED MERCURY

Analytical Method:	Response in µg/L and (RSD,%) for a 1 µg/L Hg (II) standard	Response in µg/L and (RSD, %) for a 5 µg/L Hg (II) standard
Voltammetry	1.0 (5.2)	5.1 (2.1)
Spectrophotometric	1.1 (6.2)	5.0 (5.7)

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