

METHOD 7063

ARSENIC 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 free dissolved arsenic in drinking water, natural surface water, seawater, and in domestic and industrial wastewater, and in soil extracts.

1.2 Arsenic concentrations in the linear calibration range of 0.3 to 300 µg/L may be quantified. The upper concentration range may be extended by sample dilution, by decreasing the analyte deposition time, or by increasing the stripping current.

1.3 The method detection limit for free arsenic is about 0.1 µg/L.

1.4 The method is equally sensitive for As(III) and As(V).

2.0 SUMMARY OF METHOD

Standards and samples are made acidic and rendered electrically conductive by adding hydrochloric acid. Free dissolved arsenic is quantified by anodic stripping, at a potential of +145 mV with respect to the saturated calomel electrode (SCE), from a conditioned gold metal film deposited on a glassy carbon electrode (GCE).

3.0 INTERFERENCES

3.1 Dissolved antimony and bismuth are positive interferences. Dissolved copper, at concentrations greater than 1 mg/L, is also a positive interference.

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

3.3 Some wet deposition samples may have insufficient electrical conductivity for proper operation of the ASV instrumentation. This problem is obviated by making the solutions 2 M in HCl.

3.4 When the analysis is performed according to the instructions given below, the following ions, compounds, and sample conditions are known not to interfere with the quantitation of arsenic; seawater salts, water-soluble organic compounds such as sugars and tannic acid, and dissolved copper at concentrations less than 100 times the arsenic concentration.

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 0.45- μm pores.
- 4.4 Adjustable pipetters with polyethylene tips.
- 4.5 pH meter or pH indicator paper.
- 4.6 General laboratory glassware, including beakers, graduated cylinders, volumetric flasks, etc.

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 (2 M), dilute 167 mL of concentrated hydrochloric acid to 1 liter with reagent water.

5.3.2 Hydrochloric acid (0.1 M), dilute 50 mL of the 2M hydrochloric acid solution to 1 liter with reagent water.

5.4 Gold Stock Standard (1000 mg/L Au): Stock solutions are commercially available as spectrophotometric standards.

5.4.1 Gold-plating solution, (50 mg/L Au dissolved in 0.1 M HCl): prepare by diluting 2.5 mL of a 1,000 mg/L Au spectrophotometric standard solution to 50 mL with 0.1 M HCl.

5.5 Arsenic Stock Standard (1000 mg/L of arsenic): Stock solutions are commercially available as spectrophotometric standards.

5.5.1 Arsenic intermediate standard solution, 1,000 $\mu\text{g/L}$ arsenic: Dilute 100 μL of the stock standard to 100 mL with 2% HNO_3 . Prepare weekly.

5.5.2 Arsenic Working Standards: These standards should be prepared from the arsenic intermediate standard to be used as calibration standards at the time of analysis. Prepare at least five working standards over the linear calibration range of 0.3 $\mu\text{g/L}$ to 300 $\mu\text{g/L}$ by diluting appropriate aliquots of the intermediate arsenic stock solution with 2% HNO_3 . The actual concentration of the working standards should cover the anticipated range of sample concentrations.

6.0 SAMPLE HANDLING, 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 arsenic 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 an aqueous sample for free dissolved arsenic by ASV involves three major steps. First, the GCE electrode must be prepared for use by plating on a thin film of gold; the gold working electrode is then conditioned, and finally, the concentration of free arsenic in the samples are determined.

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 entire electrode should be coated with a thin, flat, unbroken water film. If necessary, clean the GCE by wiping it with a wet, soft paper towel, polishing it with polishing powder, and rinsing it thoroughly with water. Keep the cleaned electrode immersed in water or in air saturated with water vapor.

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. 5.4.1) 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 Following deposition of GCE gold film, the electrode must be conditioned prior to actual sample analysis. Unconditioned electrodes may produce irreproducible arsenic peak areas. Condition electrodes by analyzing an arsenic-free 2 M HCl reagent solution (see 5.3.1) or by analyzing a sample adjusted to contain 2 M HCl (to a 25 mL sample, add 5 mL of concentrated HCl, mix well), according to manufacture's recommended procedures.

7.6 When the conditioning procedure is complete, rinse the electrodes with reagent water and store the electrodes in reagent water until ready to analyze the calibration standards or samples.

7.7 Following the instrument manufacturer's recommended calibration procedures, construct a calibration curve by analyzing five working calibration standards (Sec. 5.5.2);

7.7.1 To 25 mL working standard, add 5 mL concentrated HCl, mix.

7.7.2 Immerse the electrodes into the working standard 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 or peak height) versus the standard concentration.

7.8 Analyze the samples by aliquoting 25 mL of sample into a beaker. Allow the temperature of the sample to equilibrate to room temperature (within the range of 20 °C to 30 °C) if necessary. Add 5 mL of concentrated HCl to the sample and mix. Immerse the electrodes into the sample and record instrument response. Determine sample concentration from the calibration curve.

8.0 QUALITY CONTROL

8.1 Initial Calibration Verification standard (ICV): The ICV contains a known arsenic 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 10 or fewer samples has been analyzed, and after the final sample has been analyzed, a CCV containing a known arsenic 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. 7.9) 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.

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 not be more than 0.1 µg/L of arsenic. If more than 0.1 µg/L of arsenic is detected in the blank, 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 arsenic in the sample selected for duplicate analysis is greater than the limit of detection. The spike should increase the concentration of free arsenic 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 should be within the range 75% to 125%. If the recovery of the spike is outside $\pm 25\%$, the problem should be investigated and probable cause determined. 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 $\pm 25\%$, then that sample and any sample of similar make-up should be quantified by the method of standard additions provided that the results are within 10% of the action level of interest. 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) must 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 arsenic concentrations were analyzed according to the instructions given above. The results are listed in Tables 1 and 2.

9.2 In a single-laboratory evaluation, known amounts of arsenic were added to environmental water samples and soil extracts. The results are listed in Table 3.

9.3 In a single-laboratory evaluation, known amounts of arsenic were added to environmental water samples and soil extracts. The resulting solutions were analyzed according to the instruction given above and by graphite furnace atomic absorption spectrophotometry (GFAA). The results are listed in Table 4.

10.0 REFERENCES

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

TABLE 1
ACCURACY AND PRECISION OF ARSENIC (III) DETERMINATIONS

Arsenic (III) Concentration ($\mu\text{g/L}$)	Arsenic (III) Recovery (%)	Relative Standard Deviation (%)
0.700	102	14
7.00	98	2
70.0	100	5

TABLE 2
ACCURACY AND PRECISION OF ARSENIC (V) DETERMINATIONS

Arsenic (V) Concentration ($\mu\text{g/L}$)	Arsenic (V) Recovery (%)	Relative Standard Deviation (%)
0.700	99	10
7.00	100	1
70.0	99	2

TABLE 3
 QUANTIFYING ARSENIC IN ENVIRONMENTAL SAMPLES BY ASV

Sample Identification	Arsenic Added (µg/L)	Arsenic Found (µg/L)	Recovery (%)
Tap Water	20.0	Not Detected	0
Tap Water + 1 g/L Ascorbic Acid	20.0	20.2	101
A12544 (Water)	10.0	9.3	93
A12545 (Water)	5.00	5.11	102
A12582 (Water)	10.0	10.0	100
A12582 (Water)	20.0	19.8	99
A24228 (Water)	10.0	10.6	106
A24228 (Water)	20.0	20.5	103
A22949 (Water)	10.0	9.9	99
A22949 (Water)	20.0	20.2	101
A22949 (Water)	50.0	48.2	96
A23274 (Soil Extract)	10.0	12.3	101
A23274 (Soil Extract)	20.0	22.1	99
A23275 (Soil Extract)	10.0	10.5	105
A23275 (Soil Extract)	30.0	31.6	105

TABLE 4
 COMPARISON OF ASV AND GFAA RESULTS
 FOR ARSENIC IN ENVIRONMENTAL SAMPLES

Sample Identification	Arsenic Added (µg/L)	Arsenic Found, ASV (µg/L)	Arsenic Found, GFAA (µg/L)
A12545 (Water)	5.00	5.11	5.08
A12582 (Water)	10.0	10.0	9.91
A22949 (Water)	50.0	48.2	54.0
A23274 (Soil Extract)	10.0	12.3	12.9
A23275 (Soil Extract)	30.0	31.6	31.5

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