Arsenic, colorimetric, silver diethyldithiocarbamate

Parameters and Codes:

Arsenic, dissolved, I-1060-85 (μg/L as As): 01000
Arsenic, total, I-3060-85 (μg/L as As): 01002
Arsenic, suspended total, I-7060-85 (μg/L as As): 01001
Arsenic, total-in-bottom-material, dry wt, I-5060-85 (μg/g as As): 01003

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 5 to 200 μg/L of arsenic. Samples containing more than 200 μg/L need to be diluted.

1.2 Suspended total arsenic is calculated by subtracting dissolved arsenic from total arsenic.

1.3 This method may be used to analyze bottom material containing from 5 to 200 μg/g of arsenic. Usually, a 100-mg sample of prepared bottom material (method P-0520) is taken for analysis. If the sample contains more than 200 μg/g of arsenic, a smaller sample needs to be used.

1.4 Total arsenic in water-suspended sediment may be determined after each sample has been thoroughly mixed by vigorous shaking and a suitable sample portion has been rapidly withdrawn from the mixture.

1.5 Both inorganic and organic forms of arsenic are determined. To determine only inorganic arsenic, omit the strong-acid digestion, paragraphs 6.4 and 6.5 of the procedure.

2. Summary of method

2.1 Organic compounds are decomposed by adding sulfuric and nitric acids, and by repeatedly evaporating the samples to fumes of sulfur trioxide. The arsenic (V) so liberated, together with inorganic arsenic originally present, is subsequently reduced to arsenic (III) by potassium iodide and stannous chloride, and finally to gaseous arsine by zinc in hydrochloric acid solution. The resultant mixture of gases is passed through a scrubber consisting of borosilicate glass wool impregnated with lead acetate solution, and into a gas absorber containing silver diethyldithiocarbamate (AgDDC) dissolved in pyridine. Arsine reacts with AgDDC to form a soluble red complex having maximum absorbance at about 535 nm. The absorbance of the solution is measured spectrophotometrically, and arsenic determined by reference to an analytical curve prepared from standards.

2.2 Additional information on the determination is given by Liederman and others (1959); by Ballinger and others (1962); by Stratton and Whitehead (1962); and by Fresenius and Schneider (1964).

3. Interferences

3.1 Some samples may contain sulfides; however, small quantities are effectively removed by a lead acetate scrubber. Several metals—cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum—interfere with the evolution of arsine. Antimony salts, under the reducing conditions in the generator, form stibine, which passes into the absorber and causes high results.

3.2 The blank and standards fade slowly on standing, but not enough to influence results significantly during the first 20 min.

4. Apparatus

4.1 *Arsine generator, scrubber, and absorber* (fig. 15).

4.2 *Spectrophotometer*, for use at 535 nm.

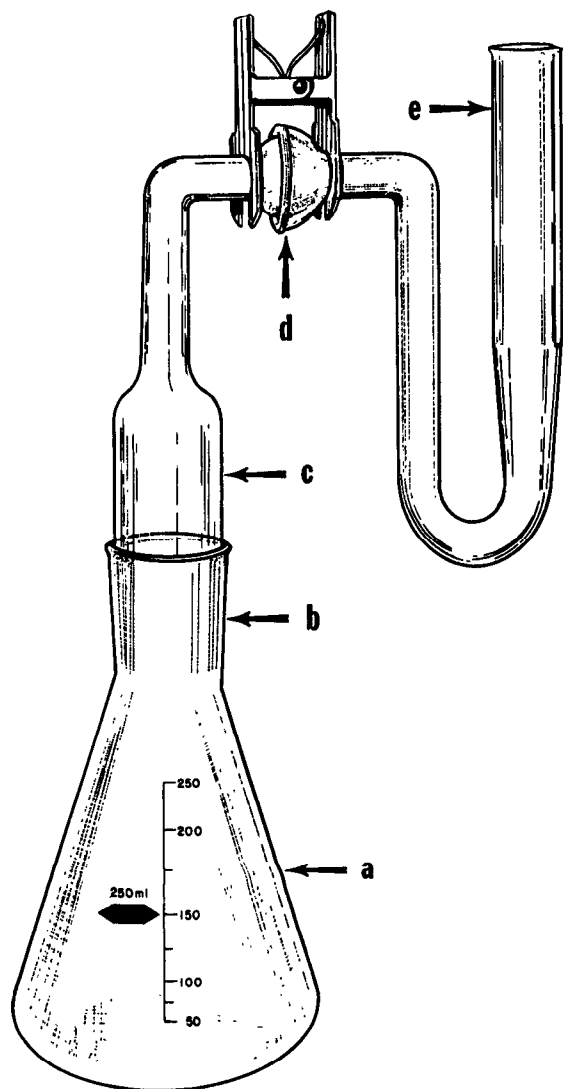4.3 Refer to the manufacturer's manual to optimize instrument.

Figure 15.—Arsine generator, scrubber, and absorber

5. Reagents

5.1 *Arsenic standard solution I*, 1.00 mL= 1.00 mg As: Dissolve 1.320 g As_2O_3, dried for 1 h at 110 °C, in 10 mL 10M NaOH and dilute to 1,000 mL with demineralized water. This solution is stable. However, it should be prepared fresh every 6 months.

5.2 *Arsenic standard solution II*, 1.00 mL= 10.0 μg As: Dilute 5.00 mL arsenic standard solution I and 1 mL concentrated HNO_3 (sp gr 1.41) to 500.0 mL with demineralized water. Discard after 3 months.

5.3 *Arsenic standard solution III*, 1.00 mL= 1.00 μg As: Dilute 10.0 mL arsenic standard solution II and 1 mL concentrated HNO_3 (sp gr 1.41) to 100.0 mL with demineralized water. Prepare fresh weekly.

5.4 *Hydrochloric acid*, concentrated (sp gr 1.19): Use analytical-grade acid with arsenic content not greater than 1×10^{-6} percent.

5.5 *Lead acetate solution*, 8.6 g/100 mL: Dissolve 10 g $(CH_3COO)_2Pb \cdot 3H_2O$ in 100 mL demineralized water. Keep tightly stoppered.

5.6 *Nitric acid*, concentrated (sp gr 1.41): Use analytical-grade acid with arsenic content not greater than 5×10^{-7} percent.

5.7 *Potassium iodide solution*, 15 g/100 mL: Dissolve 15 g KI in 100 mL demineralized water. This solution is stable when stored in an amber bottle.

5.8 *Silver diethyldithiocarbamate (AgDDC) solution*, 0.5 g/100 mL: Dissolve 1 g $(C_2H_5)_2$ NCSSAg in 200 mL pyridine. This solution is stable when stored in an amber bottle.

5.9 *Stannous chloride solution*, 33.6 g/100 mL concentrated HCl: Dissolve 40 g arsenic-free $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. This solution is unstable. Prepare fresh daily.

5.10 *Sulfuric acid, 9M:* Cautiously, and with constant stirring and cooling, add 250 mL concentrated H_2SO_4 (sp gr 1.84) to 250 mL demineralized water.

5.11 *Zinc:* Granular zinc, about 20 mesh, with arsenic content not greater than 1×10^{-6} percent.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+4) and rinse with demineralized water immediately before each use. The absorbers must also be rinsed with acetone and air-dried or briefly oven-dried.

6.2 Follow instructions in paragraph 6.2.1 for water or water-suspended sediment and in paragraph 6.2.2 for bottom material.

6.2.1 Pipet a volume of well-mixed sample containing less than 20 μg As (100 mL max) into the flask of an arsine generator. Rinse the pipet with demineralized water to remove adhering particles and combine with the sample. Dilute the sample to approx 100 mL if less than 100 mL is used.

6.2.2 Weigh a portion (NOTE 1) of prepared bottom-material sample (method P-0520)

containing less than 20 μg As and transfer to the flask of an arsine generator. Add approx 100 mL demineralized water.

NOTE 1. The sample weight must not exceed 100 mg; otherwise severe bumping and loss of arsenic may occur.

6.3 Prepare a blank and sufficient standards (20 μg As max), and adjust the volume of each to approx 100 mL with demineralized water.

6.4 To each flask, add 7 mL $9M$ H_2SO_4 and 5 mL concentrated HNO_3. Add a small boiling chip and carefully evaporate to fumes of SO_3. Cool, add 25 mL demineralized water, and again evaporate to fumes of SO_3 to expel oxides of nitrogen. Maintain excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic.

6.5 Cool, and adjust the volume to approx 100 mL. (NOTE 2).

NOTE 2. If only inorganic arsenic is to be determined, omit steps 6.4 and 6.5.

6.6 To each flask add successively, with thorough mixing after each addition, 10 mL concentrated HCl, 4 mL KI solution, and 1 mL $SnCl_2$ solution. Allow about 15 min for reduction of the arsenic to the tervalent state.

6.7 Place in each scrubber a plug of borosilicate glass wool that has been impregnated with lead acetate solution. Assemble the generator, scrubber, and absorber, making certain that all parts fit and are correctly adjusted. Add 3.00 mL silver diethyldithiocarbamate-pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

6.8 Disconnect each generator, add 6 g granular zinc, and reconnect immediately.

6.9 Allow 30 min for complete evolution of the arsine. Warm the generator flasks for a few minutes to make sure that all the arsine is released, and then pour the solutions from the absorbers directly into the spectrophotometer's cells. Determine the absorbances of the standards and samples against the blank without unnecessary delay, as the color developed is not permanent.

7. Calculations

7.1 Determine the micrograms arsenic in the sample from a plot of absorbances of standards.

7.2 Determine the concentration of dissolved or total arsenic in each sample as follows:

$$\text{As } (\mu g/L) = \frac{1000}{\text{mL sample}} \times \mu g \text{ As in sample}$$

7.3 To determine the concentration of suspended total arsenic, subtract dissolved-arsenic concentration from total-arsenic concentration.

7.4 Determine the concentration of arsenic in bottom-material samples as follows:

$$\text{As } (\mu g/g) = \frac{\mu g \text{ As per sample}}{\text{wt of sample (g)}}$$

8. Report

8.1 Report arsenic, dissolved (01000), total (01002), and suspended-total (01001), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

8.2 Report arsenic, total-in-bottom-material (01003), concentrations as follows: less than 100 μg/g, to the nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved arsenic for 22 samples within the range of 2.7 to 109 μg/L may be expressed as follows:

$$S_T = 0.225X + 2.426$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of arsenic, micrograms per liter.

The correlation coefficient is 0.9430.

9.2 Precision for dissolved arsenic for five of the 22 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
3	2.7	85
12	9.8	42
7	21.0	26
10	40.0	40
16	109	24

9.3   It is estimated that the percent relative standard deviation for total and suspended arsenic and for total arsenic in bottom material will be greater than that reported for dissolved arsenic.

References

Ballinger, D. G., Lishka, R. J., and Gales, M. E., 1962, Application of the silver diethyldithiocarbamate method to the determination of arsenic: American Water Works Association Journal, v. 54, p. 1424–1428.

Fresenius, W., and Schneider, W., 1964, Determination of slight amounts of arsenic with silver diethyldithiocarbamate in water analysis: Journal of Analytical Chemistry, v. 203, p. 417–422.

Liederman, D., Bowen, J. E., and Milner, O. I., 1959, Determination of arsenic in petroleum stocks and catalysts by evolution of arsine: Analytical Chemistry, v. 31, p. 2052–5.

Stratton, G., and Whitehead, H. E., 1962, Colorimetric determination of arsenic in water with silver diethyldithiocarbamate: American Water Works Association Journal, v. 54, p. 861–4.