



Standard Test Methods for Arsenic in Water¹

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1. Scope*

1.1 These test methods² cover the photometric and atomic absorption determination of arsenic in most waters and wastewaters. Three test methods are given as follows:

	Concentration Range	Sections
Test Method A—Silver Diethyldithiocarbamate Colorimetric	5 to 250 µg/L	7 to 16
Test Method B—Atomic Absorption, Hydride Generation	1 to 20 µg/L	17 to 26
Test Method C—Atomic Absorption, Graphite Furnace	5 to 100 µg/L	27 to 36

1.2 The analyst should direct attention to the precision and bias statements for each test method. It is the user’s responsibility to ensure the validity of these test methods for waters of untested matrices.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 11.1 and 20.2.

2. Referenced Documents

2.1 *ASTM Standards:*³

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² Similar to that appearing in *Standard Methods for the Examination of Water and Wastewater*, 12th edition, APHA, Inc., New York, NY, 1965; and identical with that in Brown, E., Skougstad, M. W., and Fishman, M. J., “Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases,” *Techniques of Water-Resources Investigations of the U.S. Geological Survey*, Book 5, 1970, p. 46.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard’s Document Summary page on the ASTM website.

- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Closed Conduits
- D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
- D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
- D5810 Guide for Spiking into Aqueous Samples
- D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
- E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in these test methods, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable arsenic, n*—a descriptive term relating to the arsenic forms recovered in the acid-digestion procedure specified in these test methods.

3.2.1.1 *Discussion*—Some organic-arsenic compounds, such as phenylarsonic acid, disodium methane arsonate, and dimethylarsonic acid, are not recovered completely during the digestion step.

4. Significance and Use

4.1 Herbicides, insecticides, and many industrial effluents contain arsenic and are potential sources of water pollution. Arsenic is significant because of its adverse physiological effects on humans.

5. Purity of 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

*A Summary of Changes section appears at the end of this standard

specifications are available.⁴ 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 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D1193**, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round robin testing of these test methods.

6. Sampling

6.1 Collect the sample in accordance with Practices **D3370**.

6.2 Preserve the samples with HNO_3 (sp gr 1.42) to a pH of 2 or less immediately at the time of collection; normally about 2 mL/L is required. If only dissolved arsenic is to be determined, filter the sample through a 0.45- μm membrane filter before acidification. The holding times for the samples may be calculated in accordance with Practice **D4841**.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

TEST METHOD A—SILVER DIETHYLDITHIOCARBAMATE COLORIMETRIC

7. Scope

7.1 This test method covers the determination of dissolved and total recoverable arsenic in most waters and waste waters in the range from 5 to 250 $\mu\text{g/L}$ of arsenic.

7.2 The precision and bias data were obtained on reagent water, river water, and process water. The information on precision and bias may not apply to other waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

8. Summary of Test Method

8.1 Organic arsenic-containing compounds are decomposed by adding sulfuric and nitric acids and repeatedly evaporating the sample to fumes of sulfur trioxide. The arsenic (V) so produced, 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 resulting mixture of gases is passed through a scrubber containing borosilicate wool impregnated with lead acetate solution and then into an absorption tube containing a solution of silver diethyldithiocarbamate in pyridine. Arsine reacts with this reagent to form a red-

colored silver sol having maximum absorbance at about 540 nm. The absorbance of the solution is measured photometrically and the arsenic determined by reference to an analytical curve prepared from standards.

9. Interferences

9.1 Although many samples are relatively free of interferences, several metals, notably cobalt, nickel, mercury, silver, platinum, copper, chromium, and molybdenum, may interfere with the evolution of arsine and with the recovery of arsenic. The presence of any or all of these metals in a sample being analyzed must be considered as a potential source of interference, and the analyst must fully determine the extent of actual interference, if any. This could be accomplished by spiking.

9.2 Hydrogen sulfide and other sulfides interfere, but commonly encountered quantities are effectively removed by the lead acetate scrubber and the digestion.

9.3 Antimony interferes by forming stibine, which distills along with the arsine. Stibine reacts with the color-forming reagent to form a somewhat similar red sol having maximum absorbance near 510 nm. The sensitivity for antimony at 540 nm is only about 8 % that of arsenic (1 mg/L of antimony will show an apparent presence of 0.08 mg/L of arsenic).

9.4 Nitric acid interferes with the test and must be completely eliminated during the digestion.

10. Apparatus

10.1 *Arsine Generator, Scrubber, and Absorber*,⁵ assembled as shown in **Fig. 1**.

10.2 *Spectrophotometer or Filter Photometer*, suitable for use at 540 nm and providing a light path of at least 10 mm. The filter photometer and photometric practice prescribed in this method shall conform to Practice **E60**. The spectrophotometer shall conform to Practice **E275**.

11. Reagents and Materials

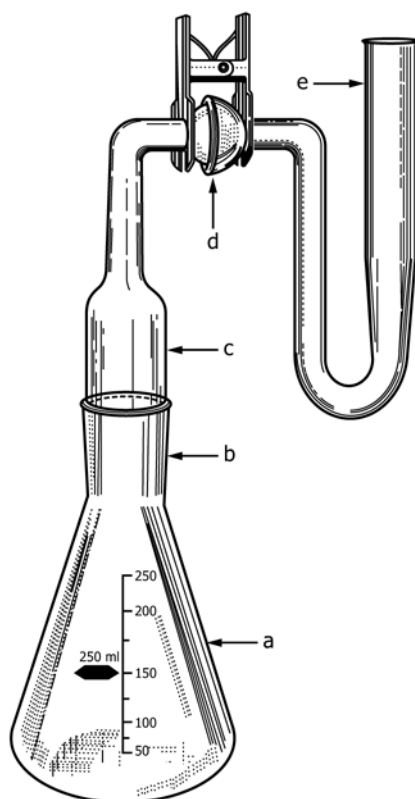
11.1 *Arsenic Solution, Stock* (1.00 mL = 1.00 mg As)—Commercially purchase or dissolve 1.320 g of arsenic trioxide (As_2O_3) (**Warning**—Arsenic trioxide is extremely toxic. Avoid ingestion or inhalation of dry powder during standard preparation. Wash hands thoroughly immediately after handling arsenic trioxide. Under no circumstances pipette any arsenic solutions by mouth.), dried for at least 1 h at 110°C, in 10 mL of NaOH solution (420 g/L) and dilute to 1 L with water. This solution is stable. A purchased arsenic stock solution of appropriate known purity is acceptable.

11.2 *Arsenic Solution, Intermediate* (1.00 mL = 10.0 μg As)—Dilute 5.00 mL of arsenic stock solution to 500 mL with water.

11.3 *Arsenic Solution, Standard* (1.00 mL = 1.00 μg As)—Dilute 10.0 mL of arsenic intermediate solution to 100 mL with water. Prepare fresh before each use.

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁵ Available commercially.



- (a) Generator flask, borosilicate glass, 250-mL capacity.
 (b) Standard-taper neck 24/40.
 (c) Scrubber, borosilicate glass wool impregnated with lead acetate.
 (d) Ground-glass ball-and-socket joint.
 (e) Absorber: add AgDDC solution and pack with glass beads.

FIG. 1 Arsine Generator, Scrubber, and Absorber⁵

11.4 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45- μm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

11.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl). Use analytical grade acid with an arsenic content not greater than $1 \times 10^{-6} \%$.

11.6 *Lead Acetate Solution* (100 g/L)—Dissolve 10 g of lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$) in 100 mL of water. Store reagent in a tightly stoppered container.

11.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3). Use analytical grade acid with an arsenic content not greater than $1 \times 10^{-6} \%$.

11.8 *Nitric Acid* (1 + 1)—Add 250 mL of concentrated nitric acid (sp gr 1.42) to 250 mL of water.

11.9 *Potassium Iodide Solution* (150 g/L)—Dissolve 15 g of potassium iodide (KI) in 100 mL of water. Store in an amber bottle.

11.10 *Silver Diethyldithiocarbamate Solution*—Dissolve 1 g of silver diethyldithiocarbamate (AgDDC) in 200 mL of

pyridine. This solution is stable for at least several months when stored in an amber bottle.

11.11 *Sodium Hydroxide Solution* (420 g/L)—Dissolve 42 g of sodium hydroxide (NaOH) pellets in 100 mL of water. (**Warning**—This is a very exothermic reaction.)

11.12 *Stannous Chloride Solution*—Dissolve 40 g of arsenic-free stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 100 mL of HCl (sp gr 1.19). Add a few small pieces of mossy tin (which is the common name and is commercially available).

11.13 *Sulfuric Acid* (1 + 1)—Cautiously, and with constant stirring and cooling, add 250 mL of concentrated H_2SO_4 (sp gr 1.84) to 250 mL of water.

11.14 *Zinc, Granular*, 20-mesh. Arsenic content must not exceed $1 \times 10^{-6} \%$.

12. Standardization

12.1 Clean all glassware before use by rinsing first with hot HNO_3 (1 + 1) (11.7) and then with water. The absorbers must be additionally rinsed with acetone and then air-dried.

12.2 Prepare, in a 250-mL generator flask, a blank and sufficient standards containing from 0.0 to 25.0 μg of arsenic by diluting 0.0 to 25.0-mL portions of the arsenic standard solution to approximately 100 mL with water. Analyze at least five or more working standards containing concentrations of arsenic to define the nonlinear curve that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. A higher order of the curve may be necessary.

12.3 Proceed as directed in 13.3 – 13.9.

12.4 Read directly the concentration or prepare an analytical curve by plotting the absorbances of standards versus micrograms of arsenic.

NOTE 2—The response is linear up to 15 μg of arsenic; however, because the curve is nonlinear above 15 μg , it is necessary to have sufficient standards above 15 μg to permit constructing an accurate curve.

13. Procedure

13.1 Clean all glassware before use by rinsing first with hot HNO_3 (1 + 1) (11.8) and then with water. The absorbers must be additionally rinsed with acetone and then air-dried.

13.2 Pipette a volume of well-mixed acidified sample containing less than 25 μg of arsenic (100 mL maximum) into a generating flask and dilute to approximately 100 mL.

NOTE 3—If only dissolved arsenic is to be determined use a filtered (11.4) and acidified sample (see 6.2).

13.3 To each flask, add 7 mL of H_2SO_4 (1 + 1) (11.13) and 5 mL of concentrated HNO_3 (11.7) (sp gr 1.42). Add a small boiling chip and carefully evaporate to dense fumes of SO_3 , maintaining an excess of HNO_3 until all organic matter is destroyed. This prevents darkening of the solution and possible reduction and loss of arsenic. Cool, add 25 mL of water, and again evaporate to dense fumes of SO_3 . Maintain heating for 15 min to expel oxides of nitrogen.

13.4 Cool, and adjust the volume in each flask to approximately 100 mL with water.