



## Standard Test Methods for Arsenic in Water<sup>1</sup>

This standard is issued under the fixed designation D 2972; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 These test methods<sup>2</sup> 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 $\mu\text{g/L}$	7 to 15
Test Method B—Atomic Absorption, Hydride Generation	1 to 20 $\mu\text{g/L}$	16 to 24
Test Method C—Atomic Absorption, Graphite Furnace	5 to 100 $\mu\text{g/L}$	25 to 33

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 *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 Note 1 and Note 5.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1129 Terminology Relating to Water<sup>3</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>3</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>3</sup>
- D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry<sup>3</sup>
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>3</sup>
- E 60 Practice for Photometric and Spectrophotometric

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D 19.05 on Inorganic Constituents in Water.

Current edition approved Dec. 10, 1997. Published February 1998. Originally published as D 2972-93 T. Last previous edition D 2972-93.

<sup>2</sup> 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, Eugene, 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, Chapter , 1970 p. 46.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

#### Methods for Chemical Analysis of Metals<sup>4</sup>

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers<sup>5</sup>

### 3. Terminology

#### 3.1 Definitions of Term Specific to This Standard:

3.1.1 For definitions of terms used in these test methods refer to Terminology D 1129.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *total recoverable arsenic*—an arbitrary analytical term relating to the forms of arsenic that are determinable by the digestion method which is included in the procedure. 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 specifications are available.<sup>6</sup> 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 D 1193 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.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 03.06.

<sup>6</sup> *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

Type II water was specified at the time of round robin testing of this test method.

## 6. Sampling

6.1 Collect the sample in accordance with Practices D 3370.

6.2 Preserve the samples with  $\text{HNO}_3$  (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- $\mu\text{m}$  membrane filter before acidification. The holding times for the samples may be calculated in accordance with Practice D 4841.

## 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*<sup>7</sup>, 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 E 60. The spectrophotometer shall conform to Practice E 275.

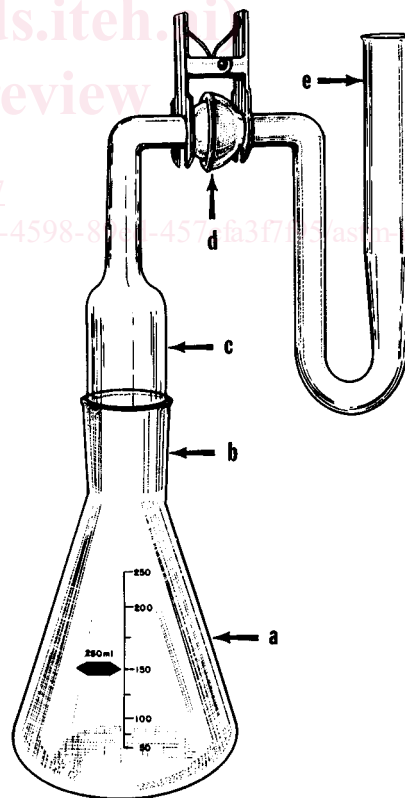
## 11. Reagents

11.1 *Arsenic Solution, Stock* (1.00 mL = 1.00 mg As)—Dissolve 1.320 g of arsenic trioxide ( $\text{As}_2\text{O}_3$ ) (**Warning**, see Note 1), 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.

NOTE 1—**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 pipet any arsenic solutions by mouth.

11.2 *Arsenic Solution, Intermediate* (1.00 mL = 10.0  $\mu\text{g}$  As)—Dilute 5.00 mL of arsenic stock solution to 500 mL with water.

<sup>7</sup> 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 Absorber<sup>7</sup>

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.

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

11.5 *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.

11.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ). Use analytical grade acid with an arsenic content not greater than  $1 \times 10^{-6}$  %.

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

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

11.9 *Silver Diethyldithiocarbamate Solution*—Dissolve 1 g of silver diethyldithiocarbamate ( $\text{AgDDC}$ ) in 200 mL of pyridine. This solution is stable for at least several months when stored in an amber bottle.

11.10 *Sodium Hydroxide Solution* (420 g/L)—Dissolve 42 g of sodium hydroxide (NaOH) pellets in 100 mL of water.

11.11 *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.

11.12 *Sulfuric Acid* (1 + 1)—Cautiously, and with constant stirring and cooling, add 250 mL of concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84) to 250 mL of water.

11.13 *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  $\text{HNO}_3$ (1 + 1) 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.

12.3 Proceed as directed in 13.3-13.9.

12.4 Construct 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  $\text{HNO}_3$ (1 + 1) and then with water. The absorbers must be additionally rinsed with acetone and then air-dried.

13.2 Pipet 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 and acidified sample (see 6.2).

13.3 To each flask, add 7 mL of  $\text{H}_2\text{SO}_4$ (1 + 1) and 5 mL of concentrated  $\text{HNO}_3$ . Add a small boiling chip and carefully

evaporate to dense fumes of  $\text{SO}_3$ , maintaining an excess of  $\text{HNO}_3$  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  $\text{SO}_3$ . 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.

13.5 To each flask add successively, with thorough mixing after each addition, 8 mL of concentrated HCl, 4 mL of KI solution, and 1 mL of  $\text{SnCl}_2$  solution. Allow about 15 min for complete reduction of the arsenic to the trivalent state.

13.6 Place in each scrubber a plug of borosilicate 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 of silver diethyldithiocarbamate-pyridine solution to each absorber. Add glass beads to the absorbers until the liquid just covers them.

NOTE 4—Four millilitres of silver diethyldithiocarbamate-pyridine solution may be used with some loss of sensitivity.

13.7 Disconnect each generator, add 6 g of zinc, and reconnect immediately.

13.8 Allow 30 min for complete evolution of arsine. Warm the generator flasks for a few minutes to make sure that all arsine is released.

13.9 Pour the solutions from the absorbers directly into clean spectrophotometer cells and within 30 min measure the absorbance of each at 540 nm.

## 14. Calculation

14.1 Determine the weight of arsenic in each sample by referring to the analytical curve. Calculate the concentration of arsenic in the sample in micrograms per litre, using Eq 1:

$$\text{Arsenic, } \mu\text{g/L} = 1000 \text{ W/V} \quad (1)$$

where:

V = volume of sample, mL, and

W = weight of arsenic in sample, µg.

## 15. Precision and Bias <sup>8</sup>

15.1 The single-operator and overall precision of this method for three laboratories, which included a total of six operators analyzing each sample on three different days, within its designated range varies with the quantity being tested in accordance with Table 1.

15.2 Recoveries of known amounts of arsenic (arsenic trioxide) in a series of prepared standards are given in Table 1.

15.3 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.

15.4 Three independent laboratories participated in the roundrobin study. Precision and bias for this test method

<sup>8</sup> Supporting data are available from ASTM Headquarters. Request RR:D 19 – 1049.