



Designation: **D2972—08 D2972 – 15**

Standard Test Methods for Arsenic in Water¹

This standard is issued under the fixed designation D2972; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope-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:

Test Method	Concentration Range	Sections
Test Method A—Silver Diethyldithiocarbamate Colorimetric	5 to 250 $\mu\text{g/L}$	7 to 16
Test Method B—Atomic Absorption, Hydride Generation	1 to 20 $\mu\text{g/L}$	17 to 26
Test Method C—Atomic Absorption, Graphite Furnace	5 to 100 $\mu\text{g/L}$	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. ~~No other units of measurement are included in this~~ 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 [Note 111.1](#) and [Note 620.2](#).

2. Referenced Documents

2.1 ASTM Standards:³

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [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](#)

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.

Current edition approved Oct. 1, 2008; Feb. 1, 2015. Published October 2008; March 2015. Originally approved in 1993. Last previous edition approved in 2003; 2008 as D2972—03; D2972—08. DOI: 10.1520/D2972-08; 10.1520/D2972-15.

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, 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, 1970, p. 46. 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.

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

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 of Terms Specific to This Standard: 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—arsenic, n—an arbitrary analytical a descriptive 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. 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 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 ~~this~~these test ~~method~~methods.

6. Sampling

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

6.2 Preserve the samples with HNO₃ (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 μg/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~~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

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.

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.

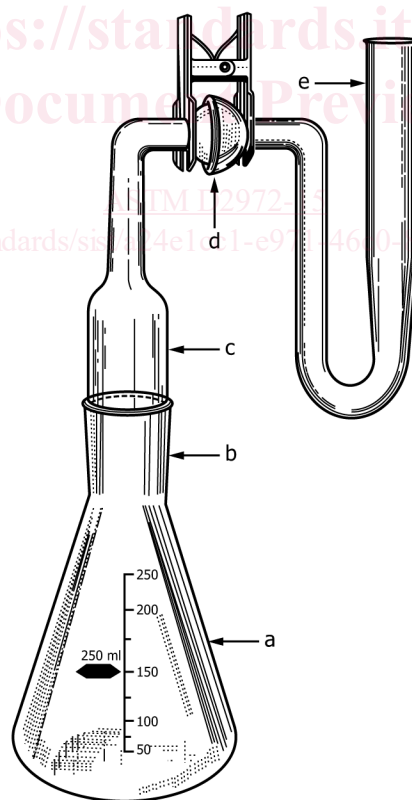
9.3 Antimony interferes by forming stibine, which distills along with the arsine. Stibine reacts with the color-forming reagent to form a somewhat similar red sol having maximum absorbance near 510 nm. The sensitivity for antimony at 540 nm is only about 8 % that of arsenic (1 mg/L of antimony will show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

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 Absorber⁷⁵

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. **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. A purchased arsenic stock solution of appropriate known purity is acceptable.

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 pipette any arsenic solutions by mouth.

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

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 1.191.19)—Concentrated hydrochloric acid (HCl). Use analytical grade acid with an arsenic content not greater than 1×10^{-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 1.421.42)—Concentrated nitric acid (HNO_3). Use analytical grade acid with an arsenic content not greater than 1×10^{-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: (Warning—This is a very exothermic reaction. This is a very exothermic reaction.)**

11.12 *Stannous Chloride Solution*—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 1×10^{-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 ~~Construct~~ 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 H₂SO₄ (1 + 1) (11.13) and 5 mL of concentrated HNO₃ (11.7) (sp gr 1.42). Add a small boiling chip and carefully evaporate to dense fumes of SO₃, maintaining an excess of HNO₃ 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 SO₃. 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 (11.5) (sp gr 1.19), 4 mL of KI solution (11.9), and 1 mL of SnCl₂ solution (11.12). 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 (11.10) 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 (11.14), 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 minutes 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:

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

where:

$$1000 = 1000 \text{ mL} / \text{Litre}$$

$$1000 \equiv 1000 \text{ mL/L}$$

$$V = \text{volume of sample, mL, and}$$

$$W = \text{weight of arsenic in sample, } \mu\text{g}$$

15. Precision and Bias⁶

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.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1049. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Precision and Bias for Arsenic by Test Method A, Diethyldithiocarbamate Colorimetric

Water	Amount Added, µg/L	Amount Found, µg/L	S _i	S _o	Bias, %
Reagent Type II	25.0	23.66	1.76	1.78	-5.4
	100.0	95.28	5.21	5.24	-4.7
	200.0	194.99	8.43	8.79	-2.6
Water of Choice	25.0	24.76	2.07	1.84	-0.96
	100.0	97.00	4.15	3.78	-3.0
	200.0	189.01	9.96	9.70	-5.5

15.4 Three independent laboratories participated in the round robin study. Precision and bias for this test method conform to Practice **D2777 – 77**, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice **D2777 – 06**, – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

16. Quality Control

16.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing arsenic.

16.2 Calibration and Calibration Verification:

16.2.1 Analyze at least ~~three~~ five or more working standards containing concentrations of arsenic that bracket the expected sample concentration, prior to analysis of samples, to calibrate the ~~instrument.~~ instrument (see 12.2). The calibration correlation coefficient shall be equal to or greater than 0.990. ~~In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.~~

16.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within $\pm 15\%$ of the known concentration. Analyze a calibration blank to verify cleanliness.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

16.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or $\pm 15\%$ of the known concentration.

16.3 Initial Demonstration of Laboratory Capability:

16.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

16.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of arsenic. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

16.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in **Table 1**. This study should be repeated until the recoveries are within the limits given in **Table 1**. If a concentration other than the recommended concentration is used, refer to Practice **D5847** for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

16.4 Laboratory Control Sample (LCS):

16.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of arsenic with each batch or 10 samples. (laboratory defined or twenty samples). If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within $\pm 15\%$ of the known concentration.

16.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.5 Method Blank:

16.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The known concentration of arsenic found in the blank should be less than 0.5 times the lowest calibration standard. If the known concentration of arsenic is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.6 Matrix Spike (MS):

16.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of arsenic and taking it through the analytical method.

16.6.2 The spike known concentration plus the background known concentration of arsenic must not exceed the high calibration standard. The spike must produce a known concentration in the spiked sample that is 2 to 5 times the analyte known concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

16.6.3 Calculate the percent recovery of the spike (P) using the following formula: equation:

$$P = 100[A(V_s + V) - B V_s]/C V \quad (2)$$

where:

A = analyte known concentration (mg/L) in spiked sample;