Designation: D2972 – 15

# Standard Test Methods for Arsenic in Water[1]

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*

1.1 These test methods[2] 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

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

[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.

***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 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 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

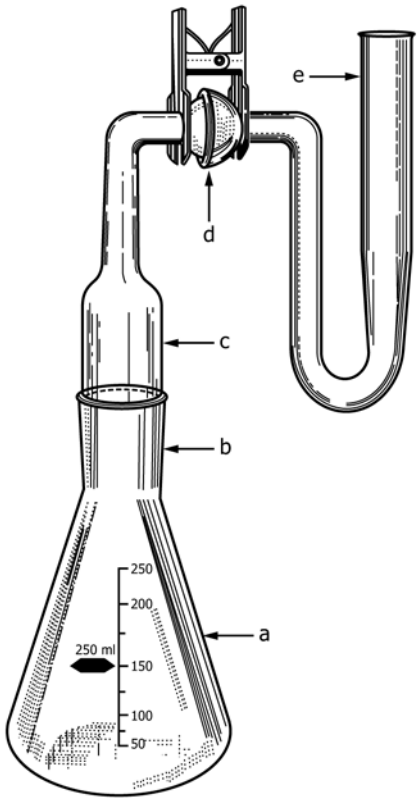
11.1 *Arsenic Solution, Stock* (1.00 mL = 1.00 mg As)—Commercially purchase or dissolve 1.320 g of arsenic trioxide ($As_2O_3$) (**Warning—**Arsenic trioxide is extremely toxic. Avoid ingestion or inhalation of dry powder during standard preparation. Wash hands thoroughly immediately after handling arsenic 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 Absorber[5]**

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 ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$) 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 ($SnCl_2 \cdot 2H_2O$) 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.

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 $SnCl_2$ 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:

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

where:

*1000* = 1000 mL/L,
*V* = volume of sample, mL, and
*W* = weight of arsenic in sample, µg.

## 15. Precision and Bias[6]

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.

[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 | $S_t$ | $S_o$ | 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 |

15.3 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 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 – 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 five or more working standards containing concentrations of arsenic that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 12.2). The calibration correlation coefficient shall be equal to or greater than 0.990.

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 ±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 ±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 (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 ±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 equation:

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

where:

$A$ = analyte known concentration (µg/L) in spiked sample,
$B$ = analyte known concentration (µg/L) in unspiked sample,
$C$ = known concentration (µg/L) of analyte in spiking solution,
$V_s$ = volume (mL) of sample used, and
$V$ = volume (mL) of spiking solution added.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte known concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 5—Acceptable spike recoveries are dependent on the known concentration of the component of interest. See Guide D5810 for additional information.

16.7 *Duplicate:*

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the known concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

16.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

16.7.3 If the result exceeds the precision limit, 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.

16.8 *Independent Reference Material (IRM):*

16.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The known concentration of the IRM should be in the known concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

## TEST METHOD B—ATOMIC ABSORPTION, HYDRIDE GENERATION

### 17. Scope

17.1 This test method covers the determination of dissolved and total recoverable arsenic in most waters and wastewaters in the range from 1 to 20 µg/L of arsenic. The range may be extended by dilution of the sample.

17.2 The precision and bias data were obtained on reagent water, tap water, salt water, river water, and untreated wastewater. 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.

### 18. Summary of Test Method

18.1 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. Alternatively, the arsenic is converted to arsine by sodium borohydride in hydrochloric acid solution. The arsine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen flame where it is determined by atomic absorption at 193.7 nm.

### 19. Interferences

19.1 See 9.1.

## 20. Apparatus

20.1 *Arsine Vapor Analyzer,* assembled as shown in Fig. 2.[7]

20.2 *Atomic Absorption Spectrophotometer* (**Warning—** Because of the toxicity of arsenic, a well-ventilated hood must be used with the atomic absorption spectrometer.) for use at 193.7 nm.

NOTE 6—Follow the manufacturer's instructions for all instrumental parameters.

20.2.1 *Arsenic Light Source*—Arsenic electrodeless discharge lamp or hollow-cathode lamp.

## 21. Reagents and Materials

21.1 *Arsenic Solution, Stock* (1.00 mL = 1.00 mg As)—See 11.1.

21.2 *Arsenic Solution, Intermediate* (1.00 mL = 10.0 µg As)—See 11.2.

21.3 *Arsenic Solution, Standard* (1.00 mL = 0.10 µg As)—Dilute 10.0 mL of arsenic intermediate solution to 1000 mL with water. Prepare fresh before each use.

21.4 *Filter Paper*—See 11.4.

21.5 *Hydrochloric Acid* (sp gr 1.19)—See 11.5.

21.6 *Nitric Acid* (sp gr 1.42)—See 11.7.

21.7 *Nitric Acid* (1 + 1)—See 11.8.

21.8 *Nitric Acid* (1 + 4)—Add 20 mL of nitric acid (sp gr 1.42) to 80 mL of water.

21.9 *Potassium Iodide Solution* (150 g/L)—See 11.9.

21.10 *Sodium Borohydride Solution* (4 g/100 mL)—Dissolve 4 g of sodium borohydride ($NaBH_4$) in 100 mL of water. Prepare fresh before each use.

21.11 *Stannous Chloride Solution* (400 g/L)—See 11.12.

21.12 *Sulfuric Acid* (1 + 1)—See 11.13.

21.13 *Zinc Metal (Dust) Suspension*—Add 10 g of zinc dust to 20 mL of water.

21.14 *Hydrogen*—Set burner control box to a gauge pressure of 55 kPa (8 psi) and adjust the flowmeter to approximately 6 L/min.

21.15 *Nitrogen or Argon*—Set burner control box to a gauge pressure of 207 kPa (30 psi) and adjust the flowmeter for maximum sensitivity by volatilizing standards. A flow of approximately 8 L/min has been found satisfactory for this purpose. This will depend on the burner used.

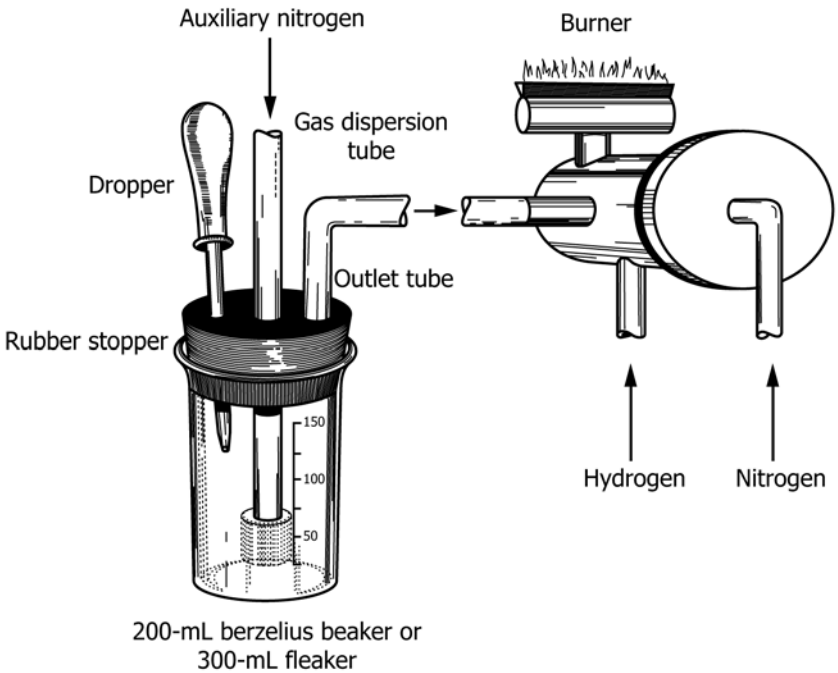
## 22. Standardization

22.1 Clean all glassware before use by rinsing first with hot $HNO_3$ (1 + 1) and then with water.

22.2 Prepare, in 200-mL Berzelius beakers or similar apparatus, a blank and sufficient standards containing from 0.0 to 1.0 µg of arsenic by diluting 0.0 to 10.0-mL portions of the arsenic standard solution to approximately 50 mL. Analyze at least three working standards containing known concentrations of arsenic that bracket the expected sample known concentration, prior to analysis of samples, to calibrate the instrument.

22.3 Proceed as directed in 23.1.3 – 23.1.8 or 23.2.3 – 23.2.7.

[7] A static system, such as one using a balloon, has been found satisfactory for this purpose. See McFarren, E. F., "New Simplified Methods for Metal Analysis," *Journal of American Water Works Association*, Vol 64, 1972, p. 28.




NOTE 1—Fleaker, trademarked product of Corning Glass Works, and Berzelius beaker are available from most laboratory apparatus dealers.

**FIG. 2 Arsine Vapor Analyzer**

22.4 Read directly in concentration if a concentration readout is provided with the instrument or prepare an analytical curve by plotting recorder scale readings versus micrograms of arsenic on linear graph paper or use a computer.

## 23. Procedure

23.1 *Determination of Arsenic with Zinc:*

23.1.1 Clean all glassware before use by rinsing first with hot $HNO_3$ (1 + 1) (21.7) and then with water.

23.1.2 Pipette a volume of well-mixed acidified sample containing less than 1.0 µg of arsenic (50-mL maximum) into a 200-mL Berzelius beaker (or similar apparatus) and dilute to approximately 50 mL.

NOTE 7—If only dissolved arsenic is to be determined use a filtered (21.4) and acidified sample (see 6.2).

23.1.3 To each beaker, add 7 mL of $H_2SO_4$ (1 + 1) (21.13) and 5 mL of concentrated $HNO_3$ (21.6) (sp gr 1.42). Add a small boiling chip and carefully evaporate to 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 fumes of $SO_3$ to expel oxides of nitrogen.

23.1.4 Cool, and adjust the volume in each beaker to approximately 50 mL with water.

23.1.5 To each beaker, add successively, with thorough mixing after each addition, 8 mL of HCl (21.5) (sp gr 1.19), 5 mL of KI solution (21.9), and 1 mL of $SnCl_2$ solution (21.11). Allow about 15 min for reduction of the arsenic to the trivalent state.

23.1.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube.

23.1.7 Fill the dropper or syringe with 2 mL of zinc dust suspension (21.13) and insert into the hole in the rubber stopper.

NOTE 8—The zinc dust is kept in suspension by continuous stirring. A magnetic stirrer is satisfactory.

23.1.8 Add the zinc suspension to the sample solution. After the absorbance has reached a maximum and has returned to the baseline remove the beaker. Rinse the gas dispersion tube first in $HNO_3$ (1 + 4) (21.8), and then in water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

23.2 *Determination of Arsenic with Sodium Borohydride:*

23.2.1 Clean all glassware before use by rinsing first with hot $HNO_3$ (1 + 1) (21.7) and then with water.

23.2.2 Pipette a volume of well-mixed acidified sample containing less than 1.0 µg of arsenic (50 mL maximum) into a 200-mL Berzelius beaker (or similar apparatus) and dilute to approximately 50 mL (see Note 7).

23.2.3 To each beaker, add 7 mL of $H_2SO_4$ (1 + 1) (21.12) and 5 mL of concentrated $HNO_3$ (21.6) (sp gr 1.42). Add a small boiling chip and carefully evaporate to 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 fumes of $SO_3$ to expel oxides of nitrogen.

23.2.4 Cool, and adjust the volume in each beaker to approximately 50 mL with water.

23.2.5 Add 8 mL of concentrated HCl (21.5) (sp gr 1.19) and mix.

23.2.6 Attach one beaker at a time to the rubber stopper containing the gas dispersion tube.

23.2.7 Fill the dropper or syringe with 0.5 mL of sodium borohydride solution (21.10) and insert into the hole in the rubber stopper.

23.2.8 Add the sodium borohydride solution (21.10) to the sample solution. After the absorbance has reached a maximum and has returned to the baseline remove the beaker. Rinse the gas dispersion tube with water before proceeding to the next sample. Treat each succeeding sample, blank, and standard in a like manner.

## 24. Calculation

24.1 Determine the weight or concentration of arsenic in each sample by referring to 22.4. If the weight is determined from the analytical curve, calculate the concentration of arsenic in the sample in micrograms per litre, using Eq 3:

$$\text{Arsenic } \mu g/L = 1000\ W/V \tag{3}$$

where:

*1000* = 1000 mL/L,
*V* = volume of sample, mL, and
*W* = weight of arsenic in sample, µg.

## 25. Precision and Bias[8]

25.1 The single-operator and overall precision of this test method for six laboratories, which included a total of ten operators analyzing each sample on three different days, within its designated range varies with the quantity being tested in accordance with Table 2.

25.2 See Table 2 for recoveries of known amounts of arsenic (arsenic trioxide) in a series of prepared standards.

25.3 The precision and bias data were obtained on reagent water, tap water, salt water, river water, and untreated wastewater. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1050. Contact ASTM Customer Service at service@astm.org.

**TABLE 2 Precision and Bias for Arsenic by Test Method B, Atomic Absorption-Hydride Generation**

| Water | Amount Added, µg/L | Amount Found, µg/L | $S_t$ | $S_o$ | Bias, % |
|---|---|---|---|---|---|
| Reagent Type II | 3 | 3.16 | 0.76 | 0.74 | +5 |
| | 10 | 9.74 | 0.93 | 0.97 | −3 |
| | 18 | 17.67 | 1.81 | 1.93 | −2 |
| Water of Choice | 3 | 2.70 | 0.70 | 0.48 | −10 |
| | 10 | 8.76 | 1.93 | 0.94 | −12 |
| | 18 | 18.07 | 2.93 | 2.22 | + 0.4 |

25.4 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

## 26. Quality Control

26.1 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.

26.2 *Calibration and Calibration Verification:*

26.2.1 Analyze at least three working standards containing known concentrations of arsenic that bracket the expected sample known concentration, prior to analysis of samples, to calibrate the instrument (see 22.2). 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.

26.2.2 Verify instrument calibration after standardization by analyzing a standard at the known concentration of one of the calibration standards. The known concentration of a mid-range standard should fall within ±15 % of the known concentration.

26.2.3 If calibration cannot be verified, recalibrate the instrument.

26.2.4 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 ±15 % of the known concentration.

26.3 *Initial Demonstration of Laboratory Capability:*

26.3.1 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.

26.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range known 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.

26.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 2. This study should be repeated until the recoveries are within the limits given in Table 2. If a known concentration other than the recommended known 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.

26.4 *Laboratory Control Sample (LCS):*

26.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of arsenic with each batch (laboratory defined or twenty 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 ±15 % of the known concentration.

26.4.2 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.

26.5 *Method Blank:*

26.5.1 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.

26.6 *Matrix Spike (MS):*

26.6.1 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.

26.6.2 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.

26.6.3 Calculate the percent recovery of the spike ($P$) using the following equation:

$$P = 100[A(V_s + V) - B\,V_s]/C\,V \quad (4)$$

where:

$A$ = analyte known concentration (µg/L) in spiked sample,
$B$ = analyte known concentration (µg/L) in unspiked sample,
$C$ = known concentration (µg/L) of analyte in spiking solution,
$V_s$ = volume (mL) of sample used, and
$V$ = volume (mL) of spiking solution added.

26.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte known concentration, listed in Guide D5810, Table 2. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 9—Acceptable spike recoveries are dependent on the known concentration of the component of interest. See Guide D5810 for additional information.

26.7 *Duplicate:*

26.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the known concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

26.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

26.7.3 If the result exceeds the precision limit, 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.

26.8 *Independent Reference Material (IRM):*

26.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The known concentration of the IRM should be in the known concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

## TEST METHOD C—ATOMIC ABSORPTION, GRAPHITE FURNACE

### 27. Scope

27.1 This test method covers the determination of dissolved and total recoverable arsenic in most waters and wastewaters.

27.2 This test method is applicable in the range from 5 to 100 µg/L of arsenic using a 20-µL injection. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by the atomic absorption-hydride method. ICP-MS may also be appropriate but at a higher instrument cost. See Test Method D5673.

27.3 This test method has been used successfully with reagent water, lake water, river water, well water, filtered well water, and condensate from a medium Btu coal gasification process. It is the user's responsibility to ensure the validity of the test method to other matrices.

27.4 The analyst is encouraged to consult Practice D3919 for a general discussion of interferences and sample analysis procedures for graphite furnace atomic absorption spectrophotometry.

### 28. Summary of Test Method

28.1 Arsenic is determined by an atomic-absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed), and atomized. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations of elements in small sample volumes is possible. Finally, the absorption signal generated during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D3919.

28.2 Dissolved arsenic is determined on a filtered and acidified sample with no pretreatment.

28.3 Total recoverable arsenic is determined following acid digestion and centrifugation. Because chlorides interfere with furnace procedures for some metals, the use of hydrochloric acid in the digestion or solubilization step is to be avoided.

### 29. Interferences

29.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D3919.

### 30. Apparatus

30.1 *Atomic-Absorption Spectrophotometer,* for use at 193.7 nm with background correction.

NOTE 10—A wavelength other than 193.7 nm may be used if it has been determined to be suitable. Greater linearity may be obtained at high concentrations by using a less sensitive wavelength.

NOTE 11—The manufacturer's instructions should be followed for all instrumental parameters.

30.2 *Centrifuge,* capable of holding centrifuge tubes of 15-mL volume.

30.3 *Centrifuge Tubes,* graduated centrifuge tubes of 15-mL capacity with stoppers.

30.4 *Graphite Furnace,* capable of reaching temperatures sufficient to atomize arsenic.

30.5 *Graphite Tubes,* compatible with the furnace device. Standard graphite tubes are recommended for the determination of arsenic.

30.6 *Light Source*—Arsenic electrodeless discharge lamps are recommended, but hollow-cathode lamps may be used.

30.7 *Pipettes*—Microlitre with disposable tips. Sizes may range from 1 to 100 µL, as required.

30.8 *Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders* should be utilized for data collection, storage, reduction, and problem recognition (drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full-scale deflection time of 0.2 s or less to ensure accuracy.

30.9 *Automatic Sampling,* is recommended if available.

### 31. Reagents and Materials

31.1 *Arsenic Solution, Intermediate* (1.00 mL = 10.0 µg As)—See 11.2.

31.2 *Arsenic Solution, Standard* (1.00 mL = 1.00 µg As)—Dilute 10.0 mL of arsenic intermediate solution and 1 mL of $HNO_3$ (sp gr 1.42) to 100 mL. This standard is used to prepare working standards at the time of analysis.

31.3 *Filter Paper*—See 11.4.

31.4 *Hydrogen Peroxide* (30 %)—Hydrogen peroxide ($H_2O_2$).

31.5 *Nickel Nitrate Solution* (1.0 mL = 10 mg Ni)—Dissolve 5.0 g of nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] in water and dilute to 100 mL.

31.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ($HNO_3$).

31.7 *Nitric Acid* (1 + 9)—Add 1 mL of $HNO_3$ (sp gr 1.42) to 9 mL of water.

31.8 *Support Gas*—Prepurified argon is the usual support gas. Nitrogen may be used if recommended by the instrument manufacturer.

## 32. Standardization

32.1 Set the instrumental parameters to the manufacturer's specifications. Follow the general instructions as provided in Practice D3919.

32.2 Prepare a calibration curve using a blank and a series of standards in accordance with Practice D3919. Analyze at least three working standards containing known concentrations of arsenic that bracket the expected sample known concentration, prior to analysis of samples, to calibrate the instrument.

NOTE 12—It is essential that the concentrations of the nickel nitrate and the nitric acid be equal for both standards and samples.

## 33. Procedure

33.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by rinsing first with $HNO_3$ (1 + 1) and then with water. If possible, soak the glassware overnight in $HNO_3$ (1 + 1).

33.2 If only dissolved arsenic is to be determined, add 8.0 mL of a filtered (31.3) and acidified sample to a beaker or flask. Then add 1.0 mL of $HNO_3$ (1 + 9) (31.7) and 1.0 mL of nickel nitrate solution (31.5). Mix the solution thoroughly and proceed to 33.6.

33.3 For total arsenic, measure 30 mL of each standard and well-mixed sample to a 150-mL beaker. Add 0.25 mL of $HNO_3$ (31.6) (sp gr 1.42) and 2 mL of hydrogen peroxide (30 %) (31.4) to the sample and mix thoroughly. Heat the samples at 95°C on a hot-plate or steam bath (see Note 13), in a well-ventilated fume hood, until the volume has been reduced to approximately 10 mL.

NOTE 13—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

33.4 Cool and quantitatively transfer the sample to a 15-mL centrifuge tube. Dilute to volume with water, cap the tube, and mix the solution thoroughly. If undissolved material is present, centrifuge the sample for a few minutes to obtain a clear solution.

33.5 Pipette 5.0 mL of the supernatant liquid into a 10-mL volumetric flask. Add 1 mL of nickel solution (31.5) and dilute to volume.

33.6 Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D3919.

**TABLE 3 Precision and Bias for Arsenic by Test Method C, Atomic Absorption-Graphite Furnace**

| Water | Amount Added, µg/L | Amount Found, µg/L | $S_t$ | Bias, % |
|---|---|---|---|---|
| Reagent Type II | 6.0 | 5.35 | 1.14 | −11.0 |
| | 22.0 | 23.10 | 2.96 | + 5.0 |
| | 72.0 | 71.30 | 6.68 | −1.0 |
| Water of Choice | 6.0 | 5.21 | 0.89 | −13.0 |
| | 22.0 | 23.20 | 3.28 | + 5.4 |
| | 72.0 | 71.30 | 6.21 | −1.0 |

## 34. Calculation

34.1 Determine the concentration of arsenic in each sample by referring to Practice D3919.

## 35. Precision and Bias[9]

35.1 The precision of this test method was tested by 12 laboratories in reagent water, lake water, river water, well water, filtered tap water, and condensate from a medium Btu coal gasification process. Two laboratories reported data from two operators. Although multiple injections may have been made, the report sheets provided allowed only for reporting single values. Thus, no single operator precision data can be calculated.

35.1.1 The overall precision of this test method, within its designated range for reagent water and selected water matrices, varies with the quantity tested as shown in Table 3.

35.1.2 Recovery and precision data for this test method are listed in Table 3.

35.2 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.

35.3 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

## 36. Quality Control

36.1 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.

36.2 *Calibration and Calibration Verification:*

36.2.1 Analyze at least three working standards containing known concentrations of arsenic that bracket the expected sample known concentration, prior to analysis of samples, to calibrate the instrument (see 32.2). The calibration correlation coefficient shall be equal to or greater than 0.990.

[9] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1108. Contact ASTM Customer Service at service@astm.org.

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

36.2.3 If calibration cannot be verified, recalibrate the instrument.

36.2.4 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 ±15 % of the known concentration.

36.3 *Initial Demonstration of Laboratory Capability:*

36.3.1 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.

36.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range known 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.

36.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 3. This study should be repeated until the recoveries are within the limits given in Table 3. If a known concentration other than the recommended known 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.

36.4 *Laboratory Control Sample (LCS):*

36.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of arsenic with each batch (laboratory defined or twenty 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 ±15 % of the known concentration.

36.4.2 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.

36.5 *Method Blank:*

36.5.1 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.

36.6 *Matrix Spike (MS):*

36.6.1 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.

36.6.2 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.

36.6.3 Calculate the percent recovery of the spike ($P$) using the following equation:

$$P = 100[A(V_s + V) - B\,V_s]/C\,V \quad (5)$$

where:

$A$ = analyte known concentration (µg/L) in spiked sample,
$B$ = analyte known concentration (µg/L) in unspiked sample,
$C$ = known concentration (µg/L) of analyte in spiking solution,
$V_s$ = volume (mL) of sample used, and
$V$ = volume (mL) of spiking solution added.

36.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte known concentration, listed in Guide D5810, Table 3. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 14—Acceptable spike recoveries are dependent on the known concentration of the component of interest. See Guide D5810 for additional information.

36.7 *Duplicate:*

36.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the known concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

36.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

36.7.3 If the result exceeds the precision limit, 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.

36.8 *Independent Reference Material (IRM):*

36.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the

laboratory at least once per quarter. The known concentration of the IRM should be in the known concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

## 37. Keywords

37.1 arsenic; atomic absorption; colorimetric (Test Method A); graphite furnace (Test Method C); hydride (Test Method B); water

## SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D2972 – 08) that may impact the use of this standard. (Approved Feb. 1, 2015.)

*(1)* Section 2 was updated to include Test Method D5673.
*(2)* Section 3 was updated.
*(3)* Section 6 was modified to allow for pH of the samples in the laboratory.
*(4)* Sections 11, 21, and 31 were modified to allow for commercial standards and filter paper information was added.
*(5)* Sections 12, 22, and 32 were modified with standard and calibration information.
*(6)* Sections 12, 13, 23, and 33 were modified to add reagent references.
*(7)* 16.2.1, 16.2.4, 16.6.3, 26.2.4, 26.6.3, 36.2.4, and 36.6.3were modified.
*(8)* Section 22 was modified to allow for using a computer.
*(9)* Section 27 was modified to inform the user of the possibility of using an ICP-MS.
*(10)* Section 33 was modified to include note about the use of block digestion systems.
*(11)* Section 30 content on Strip Chart Recorder was replaced with Data Storage and Reduction Devices.