



Designation: E 533 – 98

AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Trace Amounts of Arsenic in Inorganic Industrial Chemicals¹

This standard is issued under the fixed designation E 533; 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 This test method covers colorimetric determination of arsenic in inorganic industrial chemicals containing 1 to 8 µg of arsenic, using silver diethyldithiocarbamate.

1.2 Annex A1 contains a method for conducting a preliminary evaluation to determine if the general method is directly applicable to the sample or if some special precaution must be observed to achieve proper accuracy and precision (see Section 5).

1.3 Annex A2 recommends a method of separating arsenic from the interference of metals or salts of metals such as chromium, cobalt, copper, etc. (see 5.1).

1.4 Annex A3 recommends a sample preparation to eliminate the interference due to nitrate (5.3).

1.5 Annex A4 recommends a sample preparation to eliminate the interference due to sulfide, in excess of trace amounts (5.3).

1.6 Annex A5 recommends a method for confirming the validity of the arsenic value if the result is suspect due to a distortion of the color of the arsenic silver diethyldithiocarbamate complex.

1.7 The values stated in SI units are to be regarded as the standard.

1.8 *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.* Specific precautionary statements are given in Note 4.

1.9 Review the current material safety data sheets (MSDS) for detailed information concerning toxicity, first-aid procedures, and safety precautions.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals³

3. Summary of Test Method

3.1 The arsenic is reduced to arsine gas which is absorbed in a pyridine solution of silver diethyldithiocarbamate forming an amber to red colored complex, the intensity of which is measured at a wavelength of 525 nm with a spectrophotometer.

4. Significance and Use

4.1 This test method is suitable for determining trace amounts of arsenic in a wide variety of inorganic materials. A procedure to determine the validity of the direct method for a given sample is described in Annex A1.

4.2 This test method assumes that the arsenic is quantitatively reduced to arsine, evolved and absorbed in the scrubber solution where the color developed is proportional to the arsenic content. Possible interferences are listed in Section 5 and methods to circumvent them are given in Annex A2, Annex A3, and Annex A4.

5. Interferences

5.1 Metals or salts of metals such as chromium, cobalt, copper, mercury, molybdenum, nickel, palladium, and silver, in excess of 50 ppm, may prevent the complete recovery of arsenic as arsine (see Annex A1).

5.2 Antimony interferes by forming stibine which distills along with the arsine. Stibine reacts with the color-forming reagent to form a red color having a maximum absorbance at 510 nm.

5.3 Nitrates and sulfides, in excess of trace amounts, will cause a distortion of the color of the silver diethyldithiocarbamate complex (see Annex A1).

6. Apparatus

6.1 *Absorption Cell*, 1-cm light path.

NOTE 1—The procedure has been written for a cell having a 1-cm light path. Cells having other dimensions may be used provided suitable adjustments can be made in the amounts of sample and reagents used.

6.2 *Arsine Generator*⁴ (Fig. 1) (Note 2).

6.3 *Photometer*—Use a suitable photoelectric spectrophotometer that will measure the absorbance of the solutions at 525 nm.

NOTE 2—All new glassware must be cleaned with chromic acid cleaning solution, then thoroughly rinsed with water, then with acetone,

¹ This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.21 on Elements.

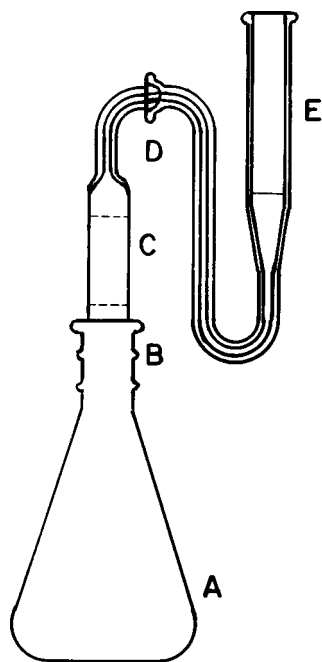
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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 15.05.

⁴ Fisher Scientific Co. No. 1-405 has been found satisfactory for this purpose.

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- (A) Generator, 125-mL Erlenmeyer,
(B) Standard-taper joint, 24/40,
(C) Scrubber,
(D) Ball-joint, 12/2,
(E) Absorber, 12-mL heavy-walled, centrifuge tube with extended arm capillary connection, 2-mm inside diameter.

FIG. 1 Arsine Generator

and dried. If the glassware is used for arsine determinations exclusively, the chromic acid cleaning solution treatment may be omitted in subsequent washings.

7. Reagents

NOTE 3—All reagents used in the determination of arsenic by this test method must be very low in arsenic, particularly the zinc.

7.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II or III reagent water conforming to Specification D 1193.

7.3 *Arsenic Standard Solution* (1.0 µg As/mL)—Dissolve 0.1320 g of reagent grade arsenic trioxide (As₂O₃) in 10 mL of sodium hydroxide solution (NaOH, 100 g/L), neutralize with sulfuric acid (H₂SO₄, 1 + 15) add 10 mL of the acid in excess and dilute with water to 1 L. Transfer 10 mL of the stock

solution to a 1-L volumetric flask, add 10 mL of H₂SO₄ (1 + 15) and dilute to 1 L with water. The diluted stock solution contains 1.0 µg As/mL. Prepare the final dilution at the time of use. Do not retain longer than 3 days.

NOTE 4—**Caution:** Arsenic trioxide is extremely toxic, avoid ingestion.

7.4 *Lead Acetate Moistened Absorbent Cotton*—Dissolve 100 g of lead acetate trihydrate (Pb(C₂H₃O₂)₂·3H₂O) in 200 mL of water. Saturate a sufficient amount of absorbent cotton with the solution, remove excess solution by gentle squeezing, and place in the scrubber section (C) of the apparatus. Prepare at the time of use.

7.5 *Potassium Iodide Solution* (165 g/L)—Dissolve 16.5 g of potassium iodide (KI) in water to make 100 mL. Store in an amber glass bottle.

7.6 *Pyridine* (C₅H₅N), freshly distilled and colorless.

7.7 *Silver Diethyldithiocarbamate Solution* (5 g/L of pyridine)—Dissolve 1 g of silver diethyldithiocarbamate ((C₂H₅)₂-NSCSAg) in 200 mL of redistilled pyridine. Store in an amber glass bottle.

7.8 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 L with water.

7.9 *Stannous Chloride Solution* (400 g SnCl₂·2H₂O/L)—Dissolve 40 g of stannous chloride dihydrate (SnCl₂·2H₂O) in 100 mL of hydrochloric acid (sp gr 1.19). Store in an all glass container and use within 3 months.

7.10 *Sulfuric Acid* (1 + 8)—Cautiously with stirring, add 109 mL of concentrated sulfuric acid (H₂SO₄, sp gr 1.84) to 800 mL of water.

7.11 *Zinc, Granular*, 20-mesh, arsenic-free.

8. Calibration

8.1 Into a series of arsine generator flasks pipet 0, 1.0, 3.0, 5.0, and 8.0 mL of the diluted standard arsenic solution (1 mL = 1.0 µg As). **Caution:** See Note 1. Add 60 mL of distilled water. Process the standards as described in Section 9 beginning with 9.2.

8.2 Plot on coordinate paper the absorbance of the standard solutions against the micrograms of arsenic. The absorbance for 8 µg of arsenic employing the conditions described varies between 0.42 to 0.46 depending on the instrument used.

9. Procedure

9.1 Weigh to the nearest 0.1 mg a portion of sample containing 1 to 8 µg of arsenic, expressed as As. Dissolve the sample and adjust the volume to 25 mL with water. Neutralize the sample solution to the phenolphthalein end point with either dilute NaOH solution or dilute H₂SO₄.

9.2 Transfer the prepared sample to the arsine generator (Fig. 1), and add by pipet 20 mL of dilute H₂SO₄, 2 mL of KI solution, and 0.5 mL of the SnCl₂ solution. Adjust the volume to 85 mL with water, and mix. Allow the mixture to stand for 30 min at room temperature.

9.3 Run a blank following the same procedure with the same quantities of all the reagents used for the sample preparation.

9.4 Place the absorbent cotton moistened with the lead acetate in the top section of scrubber. Pack the cotton loosely

⁵ *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.