



Designation: E 819 – 98

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for Trace Amounts of Arsenic in Organic Industrial Chemicals¹

This standard is issued under the fixed designation E 819; 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 the colorimetric determination of arsenic in organic industrial chemicals with diethyldithiocarbamate. This test method is applicable to samples containing 1 ppm or more of arsenic.

NOTE 1—Test Method E 533 describes the use of the same reagent for determining trace amounts of arsenic in inorganic chemicals. Annexes to this test method describe ways for conducting a preliminary evaluation to determine if the general method is directly applicable to a sample and for eliminating specific interferences. These should be equally helpful in the application of this test method.

NOTE 2—This test method is based on data described in “Food Chemicals Codex.”²

1.2 *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 hazards statements are given throughout this test method.

1.3 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 Water³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

E 200 Practice for Preparation, Standardization, and Storage of Reagent Solutions for Chemical Analysis⁴

E 300 Practice for Sampling Industrial Chemicals⁴

E 533 Test Method for Trace Amounts of Arsenic in Inorganic Industrial Chemicals⁴

3. Summary of Test Method

3.1 The organic matter in the sample is digested in concentrated sulfuric acid, and further treated with 30 % hydrogen peroxide to destroy the organic matter. The arsenic is then

reduced to arsine gas, which is absorbed in a pyridine solution of silver diethyldithiocarbamate, forming an amber to red color, 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 concentrations of arsenic in a wide variety of organic chemicals, provided that appropriate digestion of the organic matter is accomplished without loss of arsenic.

4.2 This test method assumes that the amount of color developed is proportional to the amount of arsenic in the test solution. The calibration curve is linear over the specified range.

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 (Note 1).

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 (Note 1).

5.3 Nitrates and sulfides, in excess of trace amounts, will cause a distortion of the color of the silver diethyldithiocarbamate complex (Note 1).

6. Apparatus

6.1 Absorption Cell, 1-cm light path.

NOTE 3—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. Amounts of sample greater than 1 g may be difficult to digest completely.

6.2 Arsine Generator⁵— See Fig. 1.

NOTE 4—All new glassware must be cleaned with chromic acid cleaning solution, then thoroughly rinsed with water, then acetone, and dried. If the glassware is used for arsenic determinations exclusively, the chromic acid cleaning solution treatment may be omitted in subsequent washings. **Caution:** Concentrated sulfuric acid and potassium dichromate, used to prepare chromic acid cleaning solutions, are hazardous. See 7.11 for safety precautions in the use of sulfuric acid. Potassium dichromate is highly toxic by ingestion and inhalation, and is a strong oxidizing agent and a dangerous fire risk in contact with organic materials.

⁵ Fisher Scientific Co., 01-405 has been found satisfactory for this purpose.

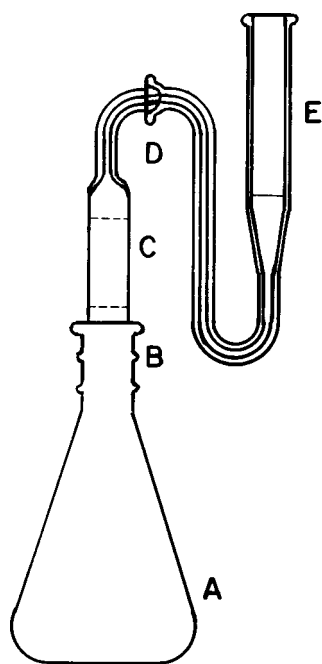
¹ This test method is under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and is the direct responsibility of Subcommittee E15.21 on Elements.

Current edition approved Sept. 10, 1998. Published February 1999. Originally published as E 819 – 81. Last previous edition E 819 – 93.

² Published by National Academy of Science, Washington, DC.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 15.05.



- (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

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

7. Reagents

NOTE 5—All reagents used in this test method must be very low in trace arsenic content. It is especially important that the metal be arsenic-free.

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.⁶ Other grades may be used provided it is first ascertained that the reagent is of sufficient 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)—Prepare in accordance with Practice E 200. Prepare the final dilution at the time of use. Do not retain longer than 3 days.

7.4 *Hydrogen Peroxide* (30 %)—**Caution:** Concentrated solutions of hydrogen peroxide are highly toxic and strong

irritants. They are strong oxidizing agents and dangerous fire and explosive risks. Avoid body contact.

7.5 *Lead Acetate Impregnated Absorbent Cotton*—Prepare a saturated solution of lead acetate (approximately 50 g of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in 100 mL of water). Soak a sufficient amount of cotton in the saturated solution, squeeze out the excess solution, and dry under vacuum at room temperature. **Caution:** Lead acetate is highly toxic by ingestion, inhalation, and skin absorption.

7.6 *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.

7.7 *Pyridine*⁷ ($\text{C}_5\text{H}_5\text{N}$), freshly distilled and colorless.

7.8 *Silver Diethyldithiocarbamate*⁸ Solution (5 g/L of $\text{C}_5\text{H}_5\text{N}$)—Dissolve 1 g of silver diethyldithiocarbamate ($(\text{C}_2\text{H}_5)_2\text{NSCSAg}$) in 200 mL of redistilled pyridine. Store in an amber bottle.

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

7.10 *Stannous Chloride Solution* (400 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O/L}$)—Dissolve 40 g of stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 100 mL of hydrochloric acid (sp gr 1.19). Store in an all-glass container and use within 3 months.

7.11 *Sulfuric Acid, Concentrated* (sp gr 1.84)—**Caution:** Concentrated sulfuric acid is corrosive; contact with the body is to be avoided at all times. Use proper protective equipment, including adequate eye protection.

7.12 *Sulfuric Acid* (1 + 4)—Cautiously, while stirring, add 200 mL of concentrated sulfuric acid (H_2SO_4 , sp gr 1.84) to 800 mL of water.

7.13 *Zinc, Granular*, 20-mesh, arsenic-free. The metal should be free of any surface oxide or film.

8. Sampling

8.1 Sampling is not within the scope of this test method. It should be understood, however, that reference to a “sample” means a representative portion of the chemical being tested, contained in a single container, submitted for test. For details on sampling, reference should be made to Practice E 300.

9. Calibration

9.1 Into a series of arsine generator flasks, pipet 0, 1, 3, and 5 mL of the standard arsenic solution (1 mL = 1.0 µg As). (**Caution:** See 7.3.) Perform the oxidation procedure described in 10.2 through 10.5, using 5 mL of concentrated H_2SO_4 and 5 mL of 30 % H_2O_2 .

9.2 Develop the color of each standard solution as described in 10.6 through 10.13. Determine the absorbance of each standard at 525 nm, based on an absorbance of zero for the blank aliquot.

9.3 Plot on coordinate paper, the absorbances of the standard solutions against the micrograms of arsenic. The

⁶ 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.

⁷ Impurities in pyridine may cause rapid fading of the developed color. Fisher certified ACS grade has been found satisfactory as supplied.

⁸ Silver diethyldithiocarbamate reagent powder is unstable. Good reagent is a bright yellow powder. Darker or off-color reagent may prove unsuitable with the result that the developed color fades rapidly.