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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Trace Amounts of Arsenic in Organic Industrial Chemicals[1]

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 Water[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[4]

E 200 Practice for Preparation, Standardization, and Storage of Reagent Solutions for Chemical Analysis[4]

E 300 Practice for Sampling Industrial Chemicals[4]

E 533 Test Method for Trace Amounts of Arsenic in Inorganic Industrial Chemicals[4]

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 Generator*[5]— 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.

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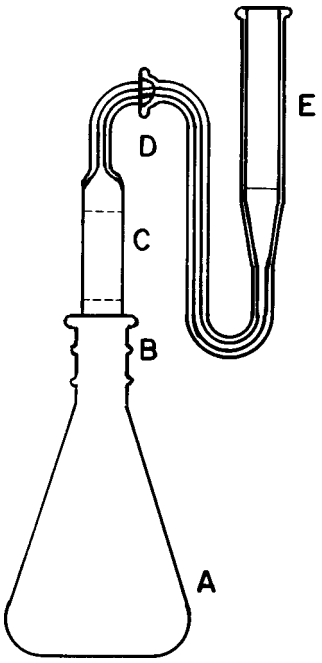
[2] Published by National Academy of Science, Washington, DC.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 15.05.

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



(*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 $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 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] (C_5H_6N), freshly distilled and colorless.

7.8 *Silver Diethyldithiocarbamate*[8] Solution (5 g/L of C_5H_6N)—Dissolve 1 g of silver diethyldithiocarbamate ($(C_2H_5)_2NSCSAg$) 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 $SnCl_2 \cdot 2H_2O$/L)— Dissolve 40 g of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) 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.

points should form a linear curve that intersects the origin. An absorbance of approximately 0.29 should be obtained for the 5 µg arsenic standard. The calibration curve must be confirmed frequently by rechecking at least one point on the curve. If satisfactory agreement is not obtained, a new calibration curve should be prepared.

10. Procedure

10.1 Transfer an accurately weighed sample, containing up to 5 µg of arsenic to an arsine generator flask (Fig. 1). Do not exceed a sample weight of 1.00 g.

10.2 Carefully add 5 mL of concentrated H_2SO_4. **Caution:** See 7.11. Add two or three small glass beads to the flask, and digest on a hot plate until the solution starts to turn brown. Use a hot plate temperature low enough (<120°C) to prevent rapid charring. This precaution applies particularly to polymeric compounds, such as polyethylene glycols. Additional concentrated H_2SO_4 may be necessary to completely wet some samples, but the total volume used should not exceed 10 mL. If halogen-containing compounds are present, use a lower hot plate temperature, do not boil the mixture, and in 10.3 add the peroxide, with caution, before charring begins, to prevent loss of trivalent arsenic.

10.3 After the sample has been initially decomposed by the acid, add 30 % H_2O_2 dropwise with caution, allowing the reaction to subside and reheating between drops. Allow the peroxide to drop down the side of the flask with swirling. The first few drops must be added very slowly with sufficient mixing to prevent a rapid reaction, and heating should be discontinued if foaming becomes excessive. Swirl the solution in the flask to prevent unreacted material from caking on the flask during the digestion. **Caution:** Some substances may react unexpectedly with explosive violence when digested with H_2O_2. Appropriate safety precautions must be employed at all times. See 7.4.

10.4 Maintain oxidizing conditions at all times during the digestion by adding small quantities of H_2O_2 whenever the mixture turns brown or darkens. Continue the digestion, gradually increasing the temperature of the hot plate from 250 to 300°C, until the organic matter is destroyed, fumes of sulfuric acid are copiously evolved, and the solution becomes colorless or retains only a light straw color.

10.5 Cool the flask, cautiously add 10 mL of water, and again evaporate to strong fumes of sulfuric acid. Start at temperatures low enough to prevent bumping or violent boiling. Cool, dissolve the residual liquid in about 10 mL of water, wash the sides of the flask with a few millilitres of water, and dilute to a volume of 35 ± 2 mL with water.

10.6 Add 20 mL of H_2SO_4 (1 + 4) to the flask.

10.7 Pipet 2 mL of the KI solution and 0.5 mL of the $SnCl_2$ solution into the flask. Swirl gently and allow the solution to stand at room temperature for 30 min.

10.8 Prepare a blank, following the procedure in 10.1 through 10.7, omitting the sample, but using the same quantities of reagents used for the sample digestion.

10.9 Pack the scrubber tube of the arsine generator (Fig. 1) with two plugs of the lead acetate-impregnated cotton in a manner to ensure that all evolved vapors will be contacted. The two plugs should have a small air space between them. Lubricate joints *B* and *D* with a suitable lubricant[9] and assemble the arsine generator, as shown in Fig. 1.

10.10 Pipet 3 mL of the silver diethyldithiocarbamate solution into the absorber tube.

10.11 Momentarily remove the scrubber and absorber tubes from the generator flask, add 3.0 g of granular zinc to the flask by means of a powder funnel, to avoid contact with the lubricated joint, and immediately reinsert the scrubber and absorber tubes.

10.12 Allow the evolution of hydrogen and the color development to proceed at room temperature (not below 25°C) for 45 min, or until gas evolution is complete, gently swirling the flask at 10-min intervals. Take care to prevent the absorber solution from being drawn back into the scrubber tube when the gas evolution is complete.

10.13 Disconnect the absorber tube from the scrubber tube and generator, and transfer the silver diethyldithiocarbamate solution to a 1-cm spectrophotometer cell.

10.14 Determine the absorbance of the sample scrubber solution at 525 nm, based on an absorbance of zero for the blank scrubber solution. Determine the micrograms of arsenic equivalent to the observed absorbance from the calibration curve.

NOTE 6—If the absorbance of the sample absorber solution is beyond the calibration range, repeat the analysis using a smaller sample size.

11. Calculation

11.1 Calculate the concentration of arsenic in the sample as follows:

$$\text{Arsenic, ppm} = \frac{A}{B} \quad (1)$$

where:

A = micrograms of arsenic in the sample, and
B = grams of sample.

12. Report

12.1 Report the arsenic content of the sample to the nearest 0.1 ppm.

13. Precision and Bias

13.1 The following criteria should be used in judging the acceptability of results (Note 7):

13.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.20 ppm absolute at 42 df. The 95 % limit for the difference between two such runs is 0.6 ppm absolute.

13.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability, Formerly Called Repeatability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.22 ppm absolute at 21 df. The 95 % limit for the difference between two such averages is 0.6 ppm absolute.

13.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by

[9] Lubricant must not be soluble in pyridine. K–Y lubricating jelly, a trademark of Johnson & Johnson, has been found satisfactory for this purpose when applied just prior to performing the evolution.

analysts in different laboratories, has been estimated to be 0.36 ppm absolute at 6 df. The 95 % limit for the difference between two such averages is 1.0 ppm absolute.

NOTE 7—The preceding precision statements are based on an interlaboratory study performed in 1978 to 1979 in which one sample each of acetic acid, 2-ethylhexanol, and triethyl phosphate containing 2 to 5 ppm arsenic was used. One analyst in each of seven laboratories performed duplicate determinations and repeated them on a second day, for a total of 84 determinations.[10] Practice E 180 was used in developing these precision estimates.

13.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials. The bias depends upon the accuracy of the calibration and the extent of many interferences. These must be determined for each application.

14. Keywords

14.1 arsenic; organic chemicals; SDDC; silver diethyldithiocarbamate

[10] Details of the interlaboratory study are available as Research Report E15:1055 from ASTM Headquarters.