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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 Inorganic Industrial Chemicals[1]

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 Water[2]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

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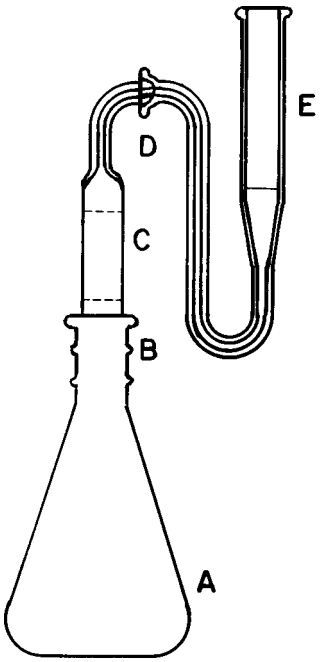
[2] *Annual Book of ASTM Standards,* Vol 11.01.

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

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



(*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 (As_2O_3) in 10 mL of sodium hydroxide solution (NaOH, 100 g/L), neutralize with sulfuric acid (H_2SO_4, 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 H_2SO_4 (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 ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$) 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* (C_5H_6N), freshly distilled and colorless.

7.7 *Silver Diethyldithiocarbamate Solution* (5 g/L of pyridine)—Dissolve 1 g of silver diethyldithiocarbamate ($(C_2H_5)_2$-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 $SnCl_2 \cdot 2H_2O$/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.

7.10 *Sulfuric Acid* (1 + 8)—Cautiously with stirring, add 109 mL of concentrated sulfuric acid (H_2SO_4, 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 H_2SO_4.

9.2 Transfer the prepared sample to the arsine generator (Fig. 1), and add by pipet 20 mL of dilute H_2SO_4, 2 mL of KI solution, and 0.5 mL of the $SnCl_2$ 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.

The packing should not protrude into the small bore tubing at the top of scrubber or extend below the dotted line shown at the top of the large bore section of scrubber. Pipet 3.0 mL of the silver diethyldithiocarbamate solution into the absorber. Lubricate joints *D*[6] and connect scrubber. By means of a powder funnel, add quickly 5.0 g of the 20-mesh zinc to the generator flask. Immediately attach the scrubber-absorber unit to the generator flask and allow the evolution of hydrogen to proceed at room temperature for 45 min. Swirl the assembly gently at 10-min intervals.

9.5 Transfer a portion of the scrubber solution from the blank determination to the 1-cm absorption cell. Set the spectrophotometer at a wavelength of 525 nm and adjust the absorbance to zero. Determine the absorbance on the sample scrubber solution. Determine from the calibration curve the micrograms of arsenic equivalent to the observed absorbance.

NOTE 5—If the intensity of the complex color is beyond the calibration range, reduce the sample size and repeat the determination.

NOTE 6—If the intensity of the complex color falls in the lower range of the calibration curve, less than 0.1 µg arsenic, increase the sample size and repeat the determination. The only limitation on the amount of sample that can be used is (*1*) the sample must remain in solution, and (*2*) the final volume of the sample preparation should not exceed 85 mL (7.2).

NOTE 7—The volume of the neutralized sample solution can be reduced by heating on a steam bath without loss of arsenic.

10. Calculation

10.1 By means of the calibration curve determine the micrograms of arsenic found in the sample.

10.2 Calculate the parts per million arsenic as follows:

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

where:

A = arsenic in the sample, µg, and
B = sample, g.

11. Report

11.1 Report the arsenic content of the sample to the nearest 0.01 ppm.

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

12. Precision and Bias

12.1 The following criteria should be used in judging the acceptability of results (Note 8):

12.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be the amount shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is also shown in Table 1.

12.1.2 *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 the amount shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is also shown in Table 1.

12.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the amount shown in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is also shown in Table 1.

NOTE 8—The preceding precision statements are based on an interlaboratory study concluded in 1974 on five inorganic chemicals: phosphoric acid, hydrochloric acid, potassium hydroxide, and sodium hydroxide. Two samples of each chemical containing approximately 0.2 and 1.0 ppm arsenic, a total of ten samples, were used in the study. One analyst in each of eight laboratories performed duplicate determinations and repeated them on a second day for a total of 320 determinations.[7] Practice E 180 was used in obtaining these precision estimates.

12.2 *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 any interferences. These must be determined for each specific application.

13. Keywords

13.1 arsenic; inorganic compounds; SDDC; silver diethyldithiocarbamate; spectrophotometric

[7] Details of the interlaboratory study are available as Research Report E15-1021 from ASTM Headquarters.

TABLE 1 Arsenic Precision

	Repeatability			Laboratory Precision			Reproducibility		
Level, ppm	Coefficient of Variation, % Relative	Degrees of Freedom	95 % Limit, % Relative	Coefficient of Variation, % Relative	Degrees of Freedom	95 % Limit, % Relative	Coefficient of Variation, % Relative	Degress of Freedom	95 % Limit, % Relative
0.2	11.4	66	32	8.33	33	23	22.5	6	63
1.0	5.03	66	14	5.80	33	16	15.4	6	43

ANNEXES

(Mandatory Information)

A1. PROCEDURE FOR A PRELIMINARY EVALUATION TO DETERMINE THE VALIDITY OF THE DIRECT APPLICATION OF THE GENERAL METHOD

A1.1 Procedure

A1.1.1 Weigh to the nearest 0.1 mg two identical portions of the test sample containing 1 to 2 µg of arsenic. To one of the duplicate samples add 5.0 mL of the arsenic standard solution (7.3). Neutralize the sample solution to the phenolphthalein end point with either dilute NaOH solution or dilute H_2SO_4.

A1.1.2 Proceed with the determination of arsenic as described in Section 9 beginning with 9.2.

A1.2 Calculation

A1.2.1 By means of the calibration curve determine the micrograms of arsenic in the two samples, as follows:

μ_1 = arsenic found in the unspiked sample, µg, and
μg_2 = arsenic found in the sample spiked with 5 µg of arsenic, µg.

A1.3 Interpretation of Results

A1.3.1 If the color of the absorbing solution is typical of the arsenic-silver diethyldithiocarbamate complex, amber to red, and if the added arsenic is recovered ($\mu g_2 - \mu g_1$) within the limits of Section 12 the determination is considered to be valid.

A1.3.2 If the amount of arsenic recovered ($\mu g_2 - \mu g_1$) is less than the amount added and the difference exceeds that indicated by Section 12, the low recovery is probably due to metal interference. The metals and metal salts of the elements listed in 5.1 amalgamate with the zinc which results in reduction in the rate and amount of hydrogen evolved. This usually results in the failure to evolve all of the arsenic as arsine. In this case the sample preparation recommended in Annex A2 should be used in conjunction with Test Method E 533.

A1.3.3 If the absorbing solution has an off-color (see Note A1.1), the validity of the absolute value of the amount of arsenic found in the unspiked sample is suspect even though the recovery of the added arsenic ($\mu g_2 - \mu g_1$) is acceptable. If this situation is encountered proceed as follows:

NOTE A1.1—NO_2 produces a green discoloration while H_2S causes a black discoloration.

A1.3.3.1 If NO_3 is known to be present in the sample, use the sample preparation recommended in Annex A3 in conjunction with Test Method E 533.

A1.3.3.2 If sulfides are known to be present in the sample, use the sample preparation recommended in Annex A4 in conjunction with Test Method E 533.

A1.3.3.3 If the off-color of the arsenic and silver diethyldithiocarbamate complex is found to be due to some interference other than nitrates or sulfides, the procedure in Annex A5 recommends a method of separating and reclaiming the arsenic from the absorbing solution for reanalysis by Test Method E 533.

A2. METHOD OF SEPARATING ARSENIC FROM INTERFERENCES DUE TO METALS AND METAL SALTS

A2.1 Summary

A2.1.1 The sample solution is evaporated to dryness. The arsenic is evolved as arsenious chloride by nascent hydrogen chloride formed from the reaction of sodium chloride and concentrated sulfuric acid. The arsenious chloride is recovered in water and the arsenic determined in the water solution as described in Test Method E 533.

A2.2 Apparatus: (See Fig. A2.1.)

A2.2.1 *Magnetic Stirrer* (*A*).
A2.2.2 *Flat-Bottom Boiling Flask*, 250-mL (*B*).
A2.2.3 *Delivery Tube and Reservoir* (*C*).
A2.2.4 *Condenser* (*D*).
A2.2.5 *Erlenmeyer Flask with Dust Cover*, 125-mL (*E*).
A2.2.6 *Flowmeter*[8] (*F*).

A2.3 Procedure

A2.3.1 Prepare the sample solution as described in 7.1 of Test Method E 533.

A2.3.2 Transfer the sample solution to the boiling flask shown in Fig. A2.1 and evaporate to dryness at steam bath temperature.

A2.3.3 Transfer 5.0 g of NaCl to the boiling flask and 60 mL of water to the absorber *E* in Fig. A2.1.

A2.3.4 Assemble the apparatus shown in Fig. A2.1. Add 15 mL of concentrated H_2SO_4 to the delivery tube reservoir *C*. Commence adding the concentrated H_2SO_4 acid drop by drop. Immediately after the addition of the H_2SO_4 attach the air purge to the reservoir and adjust the air flow to approximately 0.5 L/min. Continue the air purge for 20 min.

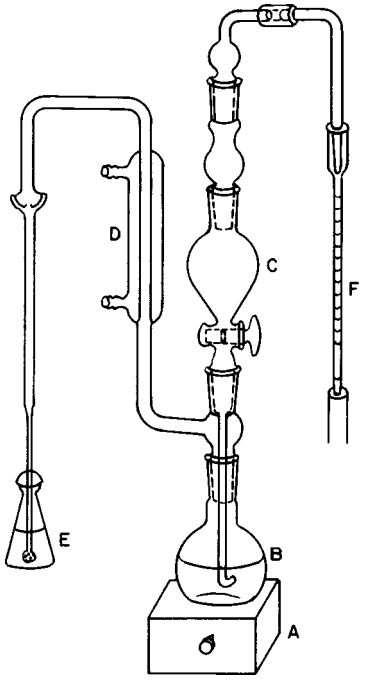
A2.3.5 Run a blank using the same reagents as described under procedure beginning with A2.3.3.

A2.3.6 Neutralize the water solution to the phenolphthalein end point using dilute NaOH solution. Proceed as described under 9.2.

A2.4 Calibration

A2.4.1 Into a series of boiling 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). Run the standard solutions as described

[8] Matheson Flowraton Catalog No. 24890-50 has been found suitable.



(*A*)	Magnetic stirrer.
(*B*)	Flat-bottom boiling flask, 250-mL.
(*C*)	Delivery tube and reservoir.
(*D*)	Condenser.
(*E*)	Erlenmeyer-flask with dust cover, 125-mL.
(*F*)	Flowmeter.

FIG. A2.1 Apparatus

under A2.3 beginning with A2.3.3.

NOTE A2.1—See Section 7.

A2.4.2 Plot on coordinate paper the absorbance of the standard solutions against the micrograms of arsenic.

A2.5 Calculation

A2.5.1 By means of the calibration curve determine the micrograms of arsenic found in the sample.

A2.5.2 Calculate the parts per million arsenic as described in 10.2.

A3. RECOMMENDED METHOD OF SAMPLE PREPARATION IN CASE OF INTERFERENCE FROM NITRATE

A3.1 Procedure

A3.1.1 Weigh to the nearest 0.1 mg a portion of sample containing 1 to 8 µg of arsenic. Dissolve the sample and neutralize to the phenolphthalein end point with either dilute NaOH solution or dilute sulfuric acid.

A3.1.2 Transfer the sample to the arsine generator flask *A* in Fig. 1. Add 20 mL of dilute sulfuric acid and evaporate the sample to fumes of sulfur trioxide.

A3.1.3 Cool and carefully dilute with 75 mL of water. Add 2 mL of KI solution and 0.5 mL of $SnCl_2$ solution, mix, and allow to digest at room temperature for 30 min.

A3.1.4 Proceed with the determination of arsenic as described in Section 9 beginning with 9.4.

NOTE A3.1—See Sections 6 and 7.

NOTE A3.2—This method of sample preparation is not applicable to samples containing chloride. The arsenic could be volatilized as arsenious chloride in the evaporation step. If the sample contains both anions the method of sample preparation recommended in Annex A2 should be used.

A4. RECOMMENDED METHOD OF SAMPLE PREPARATION IN CASE OF INTERFERENCE FROM SULFIDES

A4.1 Weigh to the nearest 0.1 mg a portion of sample containing 1 to 8 µg of arsenic. Dissolve the sample and neutralize to the phenolphthalein end point with either dilute NaOH solution (7.8) or dilute sulfuric acid (7.10).

A4.2 Transfer the sample solution to the arsine generator flask *A* in Fig. 1. Add 20 mL of dilute sulfuric acid. Add 2.0 g of potassium persulfate and evaporate to fumes of sulfur trioxide.

NOTE A4.1—See Sections 6 and 7.

NOTE A4.2—This method of sample preparation is not applicable to samples containing chloride. The arsenic could be volatilized as arsenious chloride in the evaporation step. If the sample contains both anions the sample preparation recommended in Annex A2 should be used.

A5. RECOMMENDED PROCEDURE FOR SEPARATING AND RECLAIMING THE ARSENIC FROM THE ABSORBING SOLUTION FOR RE-ANALYSIS BY THE GENERAL METHOD

A5.1 Summary

A5.1.1 The absorbing solution from the original analysis is evaporated to dryness. The organic phase is destroyed by oxidation with potassium persulfate in the presence of concentrated sulfuric acid. The arsenic is redetermined in the sulfuric acid solution as described in Test Method E 533.

A5.2 Procedure

A5.2.1 Transfer the absorbing solution to a 150-mL beaker. Rinse the absorbing tube with three 5-mL portions of acetone and add washings to the 150-mL beaker. Evaporate the solution to dryness at steam bath temperature.

A5.2.2 Add 20 mL of dilute H_2SO_4 to the residue. Add 2.0 g of potassium persulfate and evaporate to fumes of sulfur trioxide.

A5.2.3 Cool and carefully add 75 mL of water. Pipet 2 mL of KI solution 7.5 and 0.5 mL of $SnCl_2$ solution 7.9, mix, and allow to digest at room temperature for 30 min.

A5.2.4 Proceed with the determination of arsenic as directed in Section 9 beginning with 9.4.

A5.3 Calibration

A5.3.1 Prepare a series of standards as described in 8.1.

A5.3.2 Treat the standard solutions reserved from A5.3.1 as described under A5.2.

A5.3.3 Plot on coordinate paper the absorbance of the standard solutions against micrograms of arsenic.

A5.4 Calculation

A5.4.1 By means of the calibration curve determine the micrograms of arsenic found in the sample.

A5.4.2 Calculate the parts per million arsenic as described in 10.2.