Designation: E396 – 12$^{\varepsilon 1}$

Standard Test Methods for Chemical Analysis of Cadmium[1]

This standard is issued under the fixed designation E396; 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.

ε[1] NOTE—Editorial corrections were made throughout in August 2012.

1. Scope

1.1 These test methods cover the chemical analysis of cadmium having chemical compositions with the following limits:

Element	Composition, max, %
Antimony	0.001
Arsenic	0.003
Copper	0.015
Lead	0.025
Silver	0.010
Thallium	0.003
Tin	0.010
Zinc	0.035

1.2 The test methods appear in the following order:

	Sections
Antimony by the Rhodamine B Spectrophotometric Method [0.0002 % to 0.0010 %]	62-72
Arsenic by the Molybdenum Blue Spectrophotometric Method [0.001 % to 0.005 %]	40-50
Copper by the Neocuproine Spectrophotometric Method [0.002 % to 0.030 %]	10-19
Copper, Lead, Silver, and Zinc by the Atomic Absorption Method [0.004 % to 0.02 % Cu, 0.01 % to 0.05 % Pb, 0.004 % to 0.02 % Ag and 0.01 % to 0.05 % Zn]	51-61
Lead by the Dithizone Spectrophotometric Method [0.001 % to 0.05 %]	20-29
Thallium by the Rhodamine B Spectrophotometric Method [0.0003 % to 0.005%]	30-39
Tin by the 8-Quinolinol Spectrophotometric Method [0.0025 % to 0.0150 %]	73-82

1.3 *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 information is given in Section 6, 25.8, 35.2, and 35.3.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

B440 Specification for Cadmium

D1193 Specification for Reagent Water

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[3]

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E135.

4. Significance and Use

4.1 These test methods for the chemical analysis of cadmium are primarily intended to test such material for compliance with compositional specifications in Specification B440. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures

[1] These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.05 on Cu, Pb, Zn, Cd, Sn, Be, their Alloys, and Related Metals.

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[2] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

5. Apparatus, Reagents, and Spectrophotometric Practice

5.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions, and reagents shall conform to the requirements prescribed in Practices E50. Spectrophotometers shall conform to the requirements prescribed in Practice E60.

5.2 Spectrophotometric practice prescribed in these methods shall conform to Practice E60.

6. Safety Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E50.

7. Sampling

7.1 Wrought products shall be sampled in accordance with Practice E55. Cast products shall be sampled in accordance with Practice E88. However, these test methods do not supersede any sampling requirements specified in a specific ASTM material specification.

8. Rounding Calculated Values

8.1 Calculated values shall be rounded to the desired number of places as directed in Practice E29.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practices E173, unless otherwise noted in the precision section.

COPPER BY THE NEOCUPROINE SPECTROPHOTOMETRIC METHOD

10. Scope

10.1 This test method covers the determination of copper content from 0.002 % to 0.030 %.

11. Summary of Test Method

11.1 Copper is separated as cuprous copper from other metals by extraction of the copper-neocuproine complex with chloroform. Spectrophotometric measurement is made at approximately 455 nm.

12. Concentration Range

12.1 The recommended concentration range is from 0.01 mg to 0.15 mg of copper for each 25 mL of solution, using a 1-cm cell.

NOTE 1—This test method has been written for cells 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.

13. Stability of Color

13.1 The color develops within 5 min and the extracted complex is stable. However, because of the volatile nature of the solvent, it is advisable to take spectrophotometric readings promptly.

14. Interferences

14.1 The elements ordinarily present do not interfere if their contents are under the maximum limits shown in 1.1.

15. Reagents

15.1 *Chloroform* ($CHCl_3$).

15.2 *Copper, Standard Solution* (1 mL = 0.01 mg Cu)—Dissolve 0.1000 g of copper (purity: 99.9 % min) in 10 mL of HNO_3 (1 + 1). Add 25 mL of water, heat to boiling, and boil gently for 2 min to eliminate oxides of nitrogen. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Transfer 5.00 mL to a 500-mL volumetric flask. Add 1 mL of HNO_3 (1 + 1), dilute to volume, and mix.

15.3 *Hydroxylamine Hydrochloride Solution (100 g/L)*—Dissolve 5.0 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 50 mL of water. Prepare fresh as needed.

15.4 *Metacresol Purple Indicator Solution (1 g/L)*—Dissolve 0.100 g of metacresol purple together with 1 pellet of sodium hydroxide (NaOH) in about 10 mL of water by warming. Dilute to 100 mL, and mix.

15.5 *Neocuproine Solution (1 g/L)*—Dissolve 0.10 g of neocuproine (2,9-dimethyl-1,10-phenanthroline hemihydrate) in 100 mL of either methanol or 95 % ethanol.

15.6 *Sodium Citrate Solution (300 g/L)*—Dissolve 300 g of sodium citrate dihydrate in water, dilute to 1 L, and mix.

15.7 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.

16. Preparation of Calibration Curve

16.1 *Calibration Solution:*

16.1.1 Using pipets, transfer (2, 5, 10, 15, and 20) mL of copper solution (1 mL = 0.01 mg Cu) to five 150-mL beakers, and dilute to about 40 mL.

16.1.2 Add 2 drops of metacresol purple indicator solution, and then add HNO_3 (1 + 1) dropwise to the red color change of the indicator. Proceed as directed in 16.3.

16.2 *Reference Solution*—Add 40 mL of water to a 150- mL beaker. Proceed as directed in 16.1.2.

16.3 *Color Development:*

16.3.1 Add 10 mL of $NH_2OH \cdot HCl$ solution, and stir. Add 10 mL of sodium citrate solution, and stir. Add NH_4OH to the purple color of the indicator (pH about 8.5). Add 5.0 mL of neocuproine solution, stir, and allow to stand for 5 min.

NOTE 2—The precipitate that may form upon addition of sodium citrate solution will redissolve when the pH is raised to 8.5 with NH_4OH.

16.3.2 Transfer to a 125-mL separatory funnel marked at 80 mL, and dilute to the mark with water. Add 25.0 mL of $CHCl_3$. Shake vigorously for 45 s, and allow the layers to separate. Draw off and discard about 1 mL of the $CHCl_3$ layer to rinse the stem of the separatory funnel.

16.4 *Spectrophotometry:*

16.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 455 nm (Note 3). Using the test cell, take the spectrophotometric readings of the calibration solutions.

NOTE 3—Avoid transfer of water to the absorption cell in the following manner. Insert a loose plug of sterilized absorbent cotton into the stem of each separatory funnel. Just prior to filling the absorption cell with the solution in the separatory funnel, discard about 1 mL of the $CHCl_3$ layer through the cotton plug and immediately transfer a suitable portion of the $CHCl_3$ layer into the dry absorption cell.

16.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 455 nm (Note 1). While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

16.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against milligrams of copper per 25 mL of solution.

17. Procedure

17.1 *Test Solution*—Transfer a 0.5-g sample, weighed to the nearest 1 mg, to a 150-mL beaker. Add 5 mL of HNO_3 (1 + 1). When dissolution is complete, add 20 mL of water and boil gently to eliminate oxides of nitrogen. Cool, dilute to about 40 mL, and add 2 drops of metacresol purple indicator solution. Proceed as directed in 17.3.

17.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amount of all reagents with the sample omitted, for use as the reference solution.

17.3 *Color Development*—Proceed as directed in 16.3.

17.4 *Spectrophotometry*—Proceed as directed in 16.4.

18. Calculation

18.1 Convert the net spectrophotometric reading of the test solution to milligrams of copper by means of the calibration curve. Calculate the percentage of copper as follows:

$$\text{Copper, \%} = A/(B \times 10) \quad (1)$$

where:

A = copper found in the 25 mL of final test solution, mg, and

B = sample represented in 25 mL of final test solution, g.

19. Precision and Bias

19.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 1.

19.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

19.3 E173 has been replaced by Practice E1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.

TABLE 1 Statistical Information

Specimen	Copper Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1	0.0074	0.003	0.0013
2	0.0173	0.0018	0.0031

LEAD BY THE DITHIZONE SPECTROPHOTOMETRIC METHOD

20. Scope

20.1 This test method covers the determination of lead in content from 0.001 % to 0.05 %.

21. Summary of Test Method

21.1 Lead dithizonate is extracted with chloroform from a buffered cyanide solution at a pH of 8.5. The excess dithizone in the chloroform is then removed by extraction with an ammoniacal sulfite solution. spectrophotometric measurement is made at approximately 515 nm.

22. Concentration Range

22.1 The recommended concentration range is from 0.005 mg to 0.050 mg of lead for each 25 mL of solution, using a 1-cm cell (Note 1).

23. Stability of Color

23.1 The color is stable for at least 2 h if protected from direct sunlight; however, because of the volatile nature of the solvent, it is advisable to take spectrophotometric readings promptly.

24. Interferences

24.1 The elements ordinarily present in cadmium do not interfere if their contents are under the maximum limits shown in 1.1.

25. Reagents

25.1 *Ascorbic Acid.*

25.2 *Bromine Water* (*Saturated*).

25.3 *Chloroform* ($CHCl_3$).

25.4 *Dithizone Solution (0.01 g/L of $CHCl_3$)*—Dissolve 0.05 g of dithizone (diphenylthiocarbazone) in a freshly opened 700-g bottle of $CHCl_3$. Mix several times over a period of several hours. Store in a cool, dark place. Just before use, dilute 50 mL of this solution to 500 mL with $CHCl_3$ in a dry borosilicate bottle or flask, and mix.

25.5 *Lead, Standard Solution (1 mL = 0.005 mg Pb)*—Dissolve 0.1000 g of lead (purity: 99.9 % min) in 20 mL of HNO_3 (1 + 1), and boil gently to eliminate oxides of nitrogen. Cool, transfer to a 200-mL volumetric flask, dilute to volume, and mix. Transfer 5.00 mL to a 500-mL volumetric flask, dilute to volume, and mix. Prepare the final solution fresh as needed.

25.6 *Metacresol Purple Indicator Solution (1 g/L)*—Proceed as directed in 15.4.

25.7 *Potassium Cyanide Solution (200 g/L)*—Dissolve 200 g of potassium cyanide (KCN) (low in lead and sulfide) **(Warning** —See 25.8) in water, and dilute to 1 L. Bring to a boil and boil for 2 min. Cool, and store in a polyethylene bottle.

25.8 *Sodium Sulfite Wash Solution*—Dissolve 1 g of sodium sulfite (Na_2SO_3) in about 300 mL of water in a 1-L volumetric flask. Add 20 mL of the KCN solution and 475 mL of NH_4OH (1 + 1) which has been prepared from a freshly opened bottle. Dilute to volume, and mix. Store in a polyethylene bottle. (**Warning**—The preparation, storage, and use of KCN solutions require care and attention. Avoid inhalation of fumes and exposure of the skin to the chemical and its solutions. Do not allow solutions containing cyanide to come in contact with strongly acidic solutions. Work in a well-ventilated hood. Refer to Section 8 of Practices E50.)

25.9 *Sodium Tartrate Solution (250 g/L)*—Dissolve 50 g of sodium tartrate dihydrate in water, and dilute to 200 mL.

25.10 *Thioglycolic Acid Solution (1 + 99)*—Dilute 1.0 mL of thioglycolic acid (mercaptoacetic acid) to 100 mL with water. Refrigerate both the concentrated and diluted acid solutions. Do not use concentrated acid that is more than 1 year old, nor diluted acid that has stood for more than 1 week.

25.11 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.

26. Preparation of Calibration Curve

26.1 *Calibration Solutions*—Using pipets, transfer (1, 2, 3, 5, and 10)-mL volumes of lead solution (1 mL = 0.005 mg Pb) to 125-mL separatory funnels (set No. 1). Dilute to 15 mL with water and add 1 drop of metacresol purple indicator solution.

26.2 *Reference Solution*—Transfer 15 mL of water to a 125-mL separatory funnel (one of set No. 1), and add 1 drop of metacresol purple indicator solution.

26.3 *Color Development:*

26.3.1 Add NH_4OH (1 + 1) dropwise, with swirling, until the indicator color begins to change from red to yellow. Add 2 drops of HNO_3. Extract with successive 10-mL portions of dithizone solution until the color of the dithizone remains unchanged. Discard all extracts.

26.3.2 Add 2 mL of sodium tartrate solution, about 20 mg of ascorbic acid, and 2 drops of thioglycolic acid solution (1 + 99). Add NH_4OH (1 + 1), while mixing, until the solution turns yellow. Add 20 mL of KCN solution **(Warning**—see 25.8) and mix. Add 10 mL of acetic acid (1 + 4), and mix.

NOTE 4—The indicator color should be purple and the pH approximately 8.5. Some lots of KCN may give a pH lower than 8.0 or higher than 9.0. Should this occur, use NH_4OH (1 + 1) or acetic acid (1 + 4) to adjust the pH to 8.5 ± 0.5.

26.3.3 Dilute to 60 mL with water, add 15.0 mL of dithizone solution, and shake vigorously for 1 min. Allow the layers to separate for 1 min. Transfer the lower layer to another 125-mL separatory funnel (set No. 2) containing 50 mL of the sodium sulfite wash solution. Add an additional 10.0 mL of dithizone solution to the original separatory funnel (set No. 1) and shake for 1 min. Again allow the layers to separate for 1 min and add this second portion to the No. 2 separatory funnel.

26.3.4 Shake the combined organic layers in the No. 2 funnel for 1 min and allow the layers to separate for 1 min. Draw off and discard a few millilitres of the lower layer to rinse out the stem of the funnel.

26.4 *Spectrophotometry:*

26.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 515 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

26.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 515 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

26.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against milligrams of lead per 25 mL of solution.

27. Procedure

27.1 *Test Solution*—Transfer a 5-g sample, weighed to the nearest 10 mg, to a 125-mL beaker. Add 25 mL of HNO_3 (1 + 1). When dissolution is complete, add several drops of HCl and 1 mL of saturated bromine water. Boil gently to eliminate the oxides of nitrogen and to remove excess bromine. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Using a pipet, transfer a 2-mL to 10-mL portion (containing between 0.005 mg and 0.050 mg of Pb) to a 125-mL separatory funnel. Dilute to 15 mL with water, and add 1 drop of metacresol purple indicator solution. Proceed as directed in 27.3.

27.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amount of all reagents, with the sample omitted for use as the reference solution.

27.3 *Color Development*—Proceed as directed in 26.3.

27.4 *Spectrophotometry*—Proceed as directed in 26.4.

28. Calculation

28.1 Convert the net spectrophotometric reading of the test solution to milligrams of lead by means of the calibration curve. Calculate the percentage of lead as follows:

$$\text{Lead, \%} = A/(B \times 10) \quad (2)$$

where:

A = lead in the 25 mL of final test solution, mg, and
B = sample represented in 25 mL of final test solution, g.

29. Precision and Bias

29.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 2.

29.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory

TABLE 2 Statistical Information

Specimen	Lead Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1	0.0066	0.0009	0.0020
2	0.0236	0.0025	0.0053

testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

29.3 E173 has been replaced by Practice E1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.

THALLIUM BY THE RHODAMINE B SPECTROPHOTOMETRIC METHOD

30. Scope

30.1 This test method covers the determination of thallium in concentrations from 0.0003 % to 0.005 %. Higher and lower amounts can be determined by varying the sample size or the dilution within reasonable limits. However, the standard solutions used to establish the calibration curve must contain about the same amount of cadmium as the test solution.

31. Summary of Test Method

31.1 The bromothallate (III) ion is extracted from a 1-*M* hydrobromic acid solution with isopropyl ether and the red rhodamine B complex of thallium is then formed. spectrophotometric measurement is made at approximately 540 nm.

32. Concentration Range

32.1 The recommended concentration range is from 0.002 mg to 0.025 mg of thallium for each 25 mL of solution using a 1-cm cell (Note 1).

33. Stability of Color

33.1 The color develops immediately and is stable. However, transfers of the organic layer should be carried out quickly and the spectrophotometric measurements made in stoppered cells to minimize evaporation of the isopropyl ether.

34. Interferences

34.1 The elements normally present do not interfere if their contents are under the maximum limits shown in 1.1.

35. Reagents

35.1 *Cadmium Bromide Solution (1 mL = 0.05 g Cd)*—Dissolve 5.0 g of cadmium metal (thallium, max 0.001 %) with 35 mL of the HBr-Br_2 mixture. Warm, if necessary, to effect dissolution. Evaporate just to dryness but do not bake; dissolve in water, and cool. Transfer to a 100-mL volumetric flask, dilute to volume, and mix.

35.2 *Hydrobromic Acid-Bromine Mixture*—(**Warning** —Add 50 mL of bromine to 950 mL of HBr and mix. (Handle liquid bromine with care. The vapors are poisonous and the liquid causes severe burns.))

35.3 *Isopropyl Ether*—(**Warning** —Isopropyl ether that has been improperly stored or that has been stored for many years may contain peroxides. Small amounts of peroxide can cause violent explosions when the ether is distilled; larger amounts can be detonated by ordinary handling of the liquid.)

35.4 *Rhodamine B Solution (0.1 g/L)*—Dissolve 0.10 g of rhodamine B in water. Add 40 mL of HCl, and dilute to 1 L.

35.5 *Sulfatoceric Acid Solution (2 g/L)*—Dissolve 0.2 g of sulfatoceric acid (ceric sulfate) ($H_4Ce(SO_4)_4$), in 50 mL of water and 4 mL of H_2SO_4 (1 + 1). Dilute to 100 mL.

35.6 *Thallium Standard Solution (1 mL = 0.005 mg Tl)*—Remove the surface oxide from a piece of thallium metal (purity: 99.9 % min). Dissolve 0.100 g in 10 mL of H_2SO_4 (1 + 1). Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Transfer 5.00 mL to a 500-mL volumetric flask containing 250 mL of water. Add 25 mL of H_2SO_4 (1 + 1), cool, dilute to volume, and mix.

35.7 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.

36. Preparation of Calibration Curve

36.1 *Calibration Solutions*—Using pipets, transfer 1, 2, 3, and 5 mL of thallium solution (1 mL = 0.005 mg Tl) to 100-ml beakers. Add 10.0 mL of cadmium bromide solution, 5 mL of HBr-Br_2 mixture, and sufficient water to bring the volume of each solution to about 20 mL. Boil gently to eliminate excess bromine. Cool the solution (Note 5). Proceed as directed in 36.3.

NOTE 5—The solution should be colorless or at most faintly yellow and the volume should be not less than 8 mL.

36.2 *Reference Solution*—Transfer 10 mL of cadmium bromide solution, 5 mL of HBr-Br_2 mixture, and 5 mL of water to a 100-mL beaker. Boil gently to eliminate excess bromine (Note 5). Cool the solution.

36.3 *Color Development*—Transfer the solution to a 125-mL separatory funnel, add 1.0 mL of sulfatoceric acid solution, and dilute to approximately 30 mL. Mix thoroughly, and allow to stand 10 min. Add 25.0 mL of isopropyl ether. Shake for 60 s and then allow the layers to separate completely. Drain off and discard the aqueous (lower) layer. Add 20 mL of rhodamine B solution and shake for 30 s. Allow the layers to separate and again discard the aqueous (lower) layer.

36.4 *Spectrophotometry:*

36.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 540 nm (Note 1). Using the test cell, take the spectrophotometric readings of the calibration solutions.

NOTE 6—Eliminate water droplets in the organic solvent by drawing the isopropyl ether layer into a clean, dry test tube before transferring to the absorption cell.

36.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a

1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 540 nm (Note 1). While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

36.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against milligrams of thallium per 25 mL of solution.

37. Procedure

37.1 *Test Solution*—Transfer a 0.5-g sample, weighed to the nearest 1 mg, to a 100-mL beaker. Add 6 mL of HBr-Br_2 mixture, and heat gently to dissolve the sample. Add 15 mL of water, and boil (Note 5). Cool the solution. Proceed as directed in 37.3.

37.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amount of all reagents with the sample omitted for use as the reference solution.

37.3 *Color Development*—Proceed as directed in 36.3.

37.4 *Spectrophotometry*—Proceed as directed in 36.4.

38. Calculation

38.1 Convert the net spectrophotometric reading of the test solution to milligrams of thallium by the means of the calibration curve. Calculate the percentage of thallium as follows:

$$\text{Thallium, \%} = A/(B \times 10) \quad (3)$$

where:

A = thallium in 25 mL of final test solution, mg, and
B = sample represented in 25 mL of final test solution, g.

39. Precision and Bias

39.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 3.

39.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

39.3 E173 has been replaced by Practice E1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E1601.

TABLE 3 Statistical Information

Specimen	Thallium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1	0.0011	0.0001	0.0002
2	0.0030	0.0006	0.0007

ARSENIC BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD

40. Scope

40.1 This test method covers the determination of arsenic content from 0.001 % to 0.005 %. Higher and lower contents can be determined by varying the sample size within reasonable limits.

41. Summary of Test Method

41.1 Arsenic is reduced to As (III) with stannous chloride and potassium iodide, and extracted into benzene. The arsenic is stripped from the organic layer and oxidized to As (V) with potassium permanganate. The heteropoly acid is formed with molybdate and extracted into methyl isobutyl ketone. Excess molybdate is removed with sulfuric acid solution. The yellow molybdoarsenate is reduced with stannous chloride. spectrophotometric measurement of the blue complex is made at approximately 725 nm.

42. Concentration Range

42.1 The recommended concentration range is from 10 µg to 80 µg of arsenic per 25 mL of solution using a 1-cm cell (see Note 1).

43. Stability of Color

43.1 The color develops immediately and is stable for at least 1 h.

44. Interferences

44.1 The elements ordinarily present do not interfere if their contents are under the maximum limits shown in 1.1. More than 20 µg of germanium in the final sample solution will interfere. A procedure is given for eliminating this possible interference.

45. Apparatus

45.1 *Glassware,* borosilicate, having low arsenic content should be used. Before use, clean all glassware with HNO_3 or cleaning solution and rinse with water. Do not use soaps or detergents because they may contain phosphates or silicates.

46. Reagents

46.1 *Ammonium Molybdate Solution (25 g/L)*—Dissolve 25 g of ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) in about 900 mL of water. Add 70 mL of H_2SO_4 (1 + 1). Dilute to 1L, and mix. Store in a polyethylene bottle.

46.2 *Ammonium Oxalate Solution* (*Saturated*)—Add 10 g of ammonium oxalate monohydrate to 100 mL of water.

46.3 *Arsenic, Standard Solution (1 mL = 50 µg As)*—Weigh 0.0661 g of arsenic trioxide (As_2O_3) and transfer to a polyethylene beaker. Add 1 pellet of NaOH and 10 mL of water. Swirl to dissolve. Transfer to a glass beaker and dilute to about 90 mL. Add 2 mL of H_2SO_4. Heat to boiling and add $KMnO_4$ solution dropwise until a precipitate or a pink color persists. Cool the solution for 15 min. Add ammonium oxalate solution dropwise, with stirring, until a clear, colorless solution is

obtained. Transfer to a 1-L volumetric flask, add 60 mL of H_2SO_4 (1 + 1), and cool. Dilute to volume, and mix. Store in a polyethylene bottle.

46.4 *Benzene.*

46.5 *Methanol.*

46.6 *Methylene Isobutyl Ketone.*

46.7 *Potassium Iodide Solution (100 g/L)*—Dissolve 10 g of potassium iodide (KI) in water, and dilute to 100 mL. Prepare fresh as needed.

46.8 *Potassium Permanganate Solution (10 g/L)*—Dissolve 1 g of potassium permanganate ($KMnO_4$) in water and dilute to 100 mL.

46.9 *Stannous Chloride Solution A (50 g/L)*—Dissolve 5 g of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 10 mL HCl, and dilute to 100 mL with water. Prepare just before use.

46.10 *Stannous Chloride Solution B (1 g/L)*—Transfer 2.0 mL of stannous chloride Solution A (50 g/L) to a 100-mL volumetric flask. Add 20 mL of HCl, dilute to volume, and mix. Do not use a solution that has stood more than 24 h.

46.11 *Sulfuric-Hydrochloric Acid Wash Solution*—Add 160 mL of H_2SO_4 (1 + 1) to 90 mL of water, and cool. Add 750 mL of HCl, and mix.

46.12 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.

47. Preparation of Calibration Curve

47.1 *Calibration Solution*—Using pipets, transfer 1, 2, 3, 5, and 10 mL of arsenic solution (1 mL = 50 µg As) to 100-mL volumetric flasks. Add 10 mL of HNO_3, dilute to volume, and mix. Using a pipet, transfer 20 mL of each solution to 150-mL beakers. Proceed as directed in 47.3.1.

47.2 *Reference Solution*—Add 10 mL of HNO_3 to a 100-mL volumetric flask. Dilute to volume, and mix. Using a pipet, transfer 20 mL to a 150-mL beaker. Proceed as directed in 47.3.1.

47.3 *Color Development:*

47.3.1 Add 4 mL of H_2SO_4. Evaporate the solution to sulfur trioxide fumes (surface temperature of hot plate 250°C) and heat for 5 min to 10 min. Cool. Add 5 mL of ammonium oxalate solution, again evaporate to sulfur trioxide fumes and heat for at least 5 min. Cool. Add 15 mL of water and boil for 3 min.

NOTE 7—If more than 20 µg of germanium is present, it is removed at this time. Transfer the solution to a 125-mL separatory funnel. Add 20 mL of HCl, 1 drop of H_2O_2 (10 %), and mix. Add 25 mL of carbon tetrachloride (CCl_4) and shake for 1 min. Discard the CCl_4 layer. Continue as directed in 47.3.2 but add 10 mL of water instead of 10 mL of HCl.

47.3.2 Add 10 mL of HCl, 1 mL of KI solution, and 2 mL of $SnCl_2$ Solution A. Mix and allow to stand for 15 min. Transfer the solution to a 125-mL separatory funnel and add 50 mL of HCl in three portions using the HCl to rinse the beaker. Add 20 mL of benzene and shake for 1 min. Drain the aqueous phase into a 125-mL separatory funnel and extract with a second 20-mL portion of benzene. Discard the aqueous solution and combine the benzene extracts. To the organic solution, add 4 drops of $SnCl_2$ Solution A and 25 mL of H_2SO_4-HCl acid wash solution. Shake for 5 s. Allow the layers to separate for 15 min, and discard the aqueous phase. Allow the benzene layer to stand for 5 min and discard any aqueous solution that separates. Add 25 mL of water and shake for 1 min. After 15 min, transfer the aqueous layer to a 150-mL beaker.

47.3.3 Add 1 mL of H_2SO_4 (1 + 1) and 4 drops of $KMnO_4$ solution. Mix and heat for about 15 min (surface temperature of hot plate 150°C). Cool to room temperature and add 1 drop of ammonium oxalate solution. Swirl and allow to stand for 5 min. Repeat the addition of ammonium oxalate solution until a clear, colorless solution is obtained. Transfer the solution to a 125-mL separatory funnel. Rinse the beaker with two 25-mL portions of ammonium molybdate solution, add the rinsings to the funnel, and mix. Using a pipet, add 20 mL of methyl isobutyl ketone. Shake for 1 min. Allow the phases to separate and discard the aqueous phase. Add 50 mL of H_2SO_4 (1 + 9) washing the stopper and the ground glass with the acid. Shake for 30 s. Allow the layers to separate and discard the aqueous layer. Repeat the extraction with a second 50-mL portion of H_2SO_4 (1 + 9). Allow the layers to separate and discard the aqueous layer. Allow to stand for 10 min. Drain off and discard the last few drops of the aqueous phase. Add 10 mL of $SnCl_2$ Solution B and shake for 30 s. Allow the layers to separate for 10 min and discard the aqueous phase. Using a pipet, add 5 mL of methanol, and mix. Flush a small portion of the organic solution through the stopcock and stem of the separatory funnel. Dry the stem with a cotton swab.

47.4 *Spectrophotometry:*

47.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 725 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

47.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 725 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

47.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against micrograms of arsenic per 25 mL of solution.

48. Procedure

48.1 *Test Solution:*

48.1.1 Transfer a 5.0-g or 10.0-g sample, weighed to the nearest 5 mg, to a 250-mL beaker. Add 35 mL of HNO_3 (1 + 1) and cover. When dissolution is complete, add 20 mL of water and several boiling chips. Boil for 15 min, and cool. Transfer to a 100-mL volumetric flask, dilute to volume, and mix. Using a pipet, transfer a portion of the solution containing about 50 µg of arsenic to a 150-mL beaker.

48.2 *Reference Solution*—Add 4 mL of HNO_3 to a 150-mL beaker and proceed as directed in 47.3.

48.3 *Color Development*—Proceed as directed in 47.3.

48.4 *Spectrophotometry*—Take the spectrophotometric readings of the test solution as directed in 47.4.

49. Calculation

49.1 Convert the net spectrophotometric readings of the test solution to micrograms of arsenic by means of the calibration curve. Calculate the percentage of arsenic as follows:

$$\text{Arsenic, \%} = A/(B \times 10\,000) \quad (4)$$

where:

A = arsenic found in 25 mL of the final test solution, µg and
B = sample in 25 mL of the final test solution, g.

50. Precision and Bias

50.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 4.

50.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

50.3 E173 has been replaced by Practice E1601. The Reproducibility Index R_2, corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1, corresponds to the Repeatability Index r of Practice E1601.

COPPER, LEAD, SILVER, AND ZINC BY THE ATOMIC ABSORPTION METHOD

TABLE 4 Statistical Information

Specimen	Arsenic Found,	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
D60	0.0012	0.0002	0.0003
D61	0.0052	0.0010	0.0010

51. Scope

51.1 This test method covers the determination of copper in contents from 0.004 % to 0.02 %; lead in contents from 0.01 % to 0.05 %; silver in contents from 0.004 % to 0.02 %; and zinc in contents from 0.01 % to 0.05 %.

52. Summary of Test Method

52.1 A nitric acid solution of the sample is aspirated into the flame of the atomic absorption apparatus. The absorption of the resonance line energy from the spectrum of each element is measured and compared with that of calibration solutions of the same element.

53. Concentration Range

53.1 The concentration range of each element in the test solutions must be determined experimentally because the optimum range will depend upon the individual instrument. Higher or lower concentration ranges may be required for different instruments and with different radiation sources. Determine the appropriate concentration ranges of the elements as described in 53.1.1-53.1.5.

53.1.1 Prepare a dilute standard solution (see Table 5 for suggested initial concentrations).

53.1.2 Prepare the instrument for use as directed in 59.1.1-59.1.4. Measure the instrument response of the "zero," the lowest, and the two highest calibration solutions. Apply the minimum sensitivity (55.1.1) and curve linearity (55.1.2) tests.

53.1.3 If the instrument meets or surpasses the minimum sensitivity and curve linearity criteria, the initial concentration range chosen is suitable for use, and the sample size should be selected to bring the anticipated concentration of the unknown element within that range. If both criteria are met, proceed as described in 53.1.5. If either fails, proceed to 53.1.4.

53.1.4 If the minimum sensitivity is not achieved, prepare another dilute standard solution to provide a higher concentration range and repeat 53.1.2 and 53.1.3. If the calibration curve does not meet the linearity criterion, prepare another dilute standard solution to provide a lower concentration range and repeat 53.1.2 and 53.1.3. If a concentration range cannot be found for which both criteria can be met, the performance of the apparatus must be improved before this test method may be employed.

53.1.5 Apply the stability test as directed in 55.1.3. If either of the minimum stability requirements is not met, consult the manufacturer of the instrument for means of improving the repeatability of readings.

54. Interferences

54.1 Elements normally present do not interfere if their contents are below the maximum limits shown in 1.1.

55. Apparatus

55.1 *Atomic Absorption Spectrometer*—The atomic absorption spectrometer used in this test method will be satisfactory if it meets the following tests for stability.

55.1.1 *Minimum Sensitivity*—The difference between the readings of the two highest calibration solutions (that is, the highest one-fifth of the range) must be at least 40 units.

NOTE 8—The scale unit is defined as the smallest numerical interval that is estimated in taking each reading on the instrument. If the scale is non-linear, the largest unit defined in this manner is used.

55.1.2 *Curve Linearity*—The difference between the scale readings of the two highest calibration solutions must be more than 0.7 times the difference between the readings for the zero solution and the lowest calibration solution. Absorbance units must be used in this calibration.

TABLE 5 Preparation of Typical Calibration Solutions

Dilute Standard Solution, (5 mL to 25 mL)	Concentration Range of the Element, µg/mL	Cadmium Solution, mL/100 mL	Equivalent Weight of Cadmium, g
Copper	1.0 to 5.0	25.0	2.50
Lead	1.0 to 5.0	10.0	1.00
Silver	0.5 to 2.5	10.0	1.00
Zinc	0.2 to 1.0	2.00	0.200

55.1.3 *Minimum Stability*—The coefficients of variation of the readings of the highest calibration solution and of the zero calibration solution must be less than 1.5 % and 0.5 %, respectively, as calculated as follows:

$$S_c = (100/\bar{C}) \cdot \sqrt{\sum (C - \bar{C})^2/(n-1)} \quad (5)$$

$$S_o = (100/\bar{C}) \cdot \sqrt{\sum (O - \bar{O})^2/(n-1)}$$

where:

S_c = coefficient of variation of the highest calibration readings,
$\bar{C}$ = average absorbance values for the highest calibration solution,
$\sum (C - \bar{C})^2$ = sum of the squares of the n differences between each individual absorbance reading on the highest calibration solution and its average.
$\bar{O}$ = average absorbance value of the zero calibration solution,
S_o = coefficient of variation of the zero calibration readings (relative to $\bar{C}$),
$\sum (O - \bar{O})^2$ = sum of the squares of the *n* differences between each individual absorbance reading on the zero calibration solution and its average value, and
n = number of determinations.

55.2 *Instrument Parameters:*

55.2.1 Parameters will vary with each instrument. The parameters shown in Table 6 were successfully used in one laboratory for the interlaboratory testing of these test methods, and they can be used as guidelines. The solutions were aspirated into an acetylene-rich, air-acetylene flame of a premix burner.

TABLE 6 Guidelines for Instrument Parameters

Property	Copper	Lead	Silver	Zinc
Hollow cathode lamp, mA	20	30	12	15
Wavelength, nm	3248	2170	3281	2139
Air flow at 30 psi (207 kPa), L/min	7.5	7.5	9.0	8.0
Acetylene flow at 8 psi (55 kPa), L/min	7.0	7.5	8.5	8.5

56. Reagents

56.1 *Cadmium Solution (100 mg/mL)*—Transfer 200 g of cadmium metal (purity: 99.9 % min) to a 2-L beaker. Add 100 mL of water, and then add 400 mL HNO_3, in small increments to control the reaction. When dissolution is complete, boil gently to remove oxides of nitrogen and cool. Dilute to 2000 mL and mix.

56.2 *Copper, Standard Solution (1 mL = 1.00 mg Cu)*—Transfer 1.00 g of copper metal (purity: 99.9 % min) to a 400-mL beaker, and cover. Add 50 mL of HNO_3 (1 + 1). If necessary, heat gently until dissolution is complete. Boil gently to remove oxides of nitrogen, and cool. Transfer to a 1-L volumetric flask, add 100 mL of HNO_3 (1 + 1), dilute to volume, and mix. Store in a polyethylene bottle.

56.3 *Lead, Standard Solution (1 mL = 1.00 mg Pb)*—Weigh 1.00 g of lead metal (purity: 99.9 % min) and prepare the solution as directed for the copper solution in 56.2.

56.4 *Silver, Standard Solution (1 mL = 1.00 mg Ag)*—Weigh 1.00 g of silver metal (purity 99.9 % min) and prepare the solution as directed for the copper solution in 56.2.

56.5 *Zinc, Standard Solution (1 mL = 0.100 mg Zn)*—Weigh 0.100 g of zinc metal (purity: 99.9 % min) and prepare the solution as directed for the copper solution in 56.2.

56.6 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.

57. Calibration

57.1 *Dilute Standard Solutions*—Prepare a dilute standard solution for each element to be determined. The concentration of each solution should be such that when (5, 10, 15, 20, and 25)-mL portions are diluted to 100 mL, the proper range of calibration solutions is obtained. A guide for the dilution of the standard solutions, similar to those used in the interlaboratory testing of the test methods, is shown in Table 5.

57.2 *Calibration Solutions*—For each element to be determined, prepare five calibration solutions. Using pipets, transfer (5, 10, 15, 20, and 25)-mL portions of the appropriate dilute standard solution to 100-mL volumetric flasks. Select the solution in accordance with the following:

Element	Concentration, µg/mL	Standard Solution, mL/100 mL
Copper	20.0	2.00
Lead	20.0	2.00
Silver	10.0	1.00
Zinc	4.0	4.00

Using a pipet, add an appropriate portion of the cadmium solution to each flask to equal the concentration of cadmium in the corresponding test solution. A guide for the preparation of typical calibration solutions, similar to those used in the interlaboratory testing of these test methods, is shown in Table 5.

NOTE 9—The concentration ranges, which are optimum for other instruments, must be determined by applying the stability tests outlined in 55.1.1-55.1.3.

57.3 *Zero Calibration Solution*—Prepare a zero calibration solution for each level of cadmium used in the calibration solutions. Using pipets, transfer appropriate volumes of the cadmium solution to 100-mL volumetric flasks, dilute to volume, and mix.

58. Procedure

58.1 *Test Solution:*

58.1.1 Transfer a 5.00-g sample, weighed to the nearest 1 mg, to a 400-mL beaker, and cover. Cautiously add 30 mL of HNO_3 (1 + 1). If necessary, warm gently until dissolution is complete. Boil gently to remove oxides of nitrogen, and cool.

58.1.2 Transfer to a 100-mL volumetric flask, dilute to volume, and mix. Use the solution undiluted, or transfer an aliquot to an appropriate volumetric flask, dilute to volume, and mix.

NOTE 10—The final test solution should provide approximately the same concentration of each element as the dilute standard solutions. Dilutions shown in the following table correspond with the standards shown in Table 5:

Element	Expected µg of Element in Sample	Aliquot, mL	Final Volume of Test Solution, mL
Copper	40 to 200	25	50
Lead	100 to 500	10	50
Silver	50 to 250	10	50
Zinc	100 to 500	4	100

Element	Concentration Range, µg/mL	Equivalent Weight of Sample, g
Copper	1 to 5	1.25
Lead	1 to 5	0.500
Silver	0.5 to 2.5	0.500
Zinc	0.2 to 1	0.200

Reagent Blank—Transfer 30 mL of HNO_3 (1 + 1) to a 400-mL beaker, and cover. Boil gently to remove oxides of nitrogen, and cool. Proceed as directed in 58.1.2.

59. Measurements

59.1 *Instrument Adjustment*—Optimize the response of the instrument as directed in 59.1.1-59.1.4.

59.1.1 Set the instrument parameters to the values obtained in 55.2, and light the burner.

59.1.2 Set the approximate wavelength for the element to be determined (see Table 6) and complete the wavelength adjustment to obtain maximum absorption or absorbance while aspirating the highest calibration solution.

59.1.3 Optimize fuel, air, and burner adjustments while aspirating the highest calibration solution.

59.1.4 Aspirate water long enough to establish that the absorbance reading is not drifting, and then set the initial reading (zero absorption or absorbance, or 100 % transmission).

59.2 *Readings:*

59.2.1 Aspirate the test solution and note, but do not record the readings.

59.2.2 Aspirate water until the initial reading is again obtained. Aspirate the calibration and test solutions in the order of increasing instrument response starting with the reagent blank and zero calibration solutions. When a stable response is obtained for each solution, record the readings.

59.2.3 Aspirate and record the readings of the test solution at the proper points in the calibration series as determined from the preliminary readings (59.2.1).

59.2.4 Proceed as directed in 59.2.2 and 59.2.3 at least two more times.

60. Calculation

60.1 Calculate the coefficient of variation for the zero and the highest calibration solutions as directed in 55.1.3. These values should be less than 1.5 % and 0.5 %, respectively. If these criteria are not met, disregard the data, readjust the instrument, and proceed again as directed in 59.2.

60.2 If necessary, convert the average of the readings for each calibration solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the average absorbance of the zero calibration solution. In a similar manner, obtain the net absorbance of the test solution by subtracting the absorbance of the reagent blank solution.

60.3 Prepare a calibration curve by plotting the net absorbance values for the calibration solutions against micrograms of the element per millilitre.

60.4 Convert the net absorbance value of the test solution to micrograms of the element per millilitre by means of the appropriate calibration curve. Calculate the percentage of the element as follows:

$$\text{Element, \%} = (A \times B)/(C \times 10\,000) \quad (6)$$

where:

A = element per millilitre, µg
B = final volume of test solution, and
C = sample represented in final volume of test solution, g.

61. Precision and Bias

61.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 7.

61.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

61.3 E173 has been replaced by Practice E1601. The Reproducibility Index R_2, corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1, corresponds to the Repeatability Index r of Practice E1601.

TABLE 7 Statistical Information

	Sample	Average	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
Cu	D-62	0.0112	0.0009	0.0011
	63	0.0192	0.0006	0.0025
	64	0.0076	0.0006	0.0007
Pb	D-62	0.034	0.002	0.005
	63	0.030	0.002	0.005
	64	0.018	0.001	0.003
Ag	D-62	0.0199	0.0005	0.0015
	63	0.0098	0.0008	0.0013
	64	0.0056	0.0003	0.0007
Zn	D-62	0.028	0.004	0.007
	63	0.022	0.002	0.003
	64	0.065	0.008	0.008

ANTIMONY BY THE RHODAMINE B SPECTROPHOTOMETRIC METHOD

62. Scope

62.1 This test method covers the determination of antimony in contents from 0.0002 % to 0.0010 %. Higher and lower contents can be determined by varying the sample size within reasonable limits.

63. Summary of Test Method

63.1 Antimony (V) is extracted with isopropyl ether from a chloride solution. The organic solution is washed with dilute hydrochloric acid containing sodium sulfite to remove thallium and iron. The red complex of antimony with rhodamine B is formed. Spectrophotometric measurement is made at approximately 550 nm.

64. Concentration Range

64.1 The recommended concentration range is from 2 µg to 10 µg of antimony per 15 mL of solution, using a 1-cm cell (see Note 1).

65. Stability of Color

65.1 The color develops immediately and remains stable for at least 30 min. Care must be taken to avoid loss of solvent before and during the measurement.

66. Interferences

66.1 The elements ordinarily present in cadmium do not interfere if their contents are under the maximum limits shown in 1.1.

67. Apparatus

67.1 *Separatory Funnels,* 125-mL and 1-L capacity.

68. Reagents

68.1 *Antimony, Standard Solution A (1 mL = 0.5 mg Sb)*—Dissolve 100 mg of antimony metal (purity: 99.9 % min) in 20 mL of H_2SO_4. Fume for 5 min, cool, and dilute carefully to about 150 mL with H_2SO_4 (1 + 9). Transfer to a 200-mL volumetric flask, cool, dilute to volume with H_2SO_4 (1 + 9), and mix.

68.2 *Antimony, Standard Solution B (1 mL = 2.5 µg Sb)*—Using a pipet, transfer 5 mL of antimony solution A (1 mL = 0.5 mg Sb) to a 1-L volumetric flask containing 200 mL of H_2SO_4 (1 + 1). Dilute nearly to volume, cool, dilute to volume, and mix.

68.3 *Isopropyl Ether, Washed*—Transfer 500 mL of isopropyl ether to a 1-L separatory funnel. Add 200 mL of HCl and shake for 1 min. Add 200 mL of water and shake for 30 s. Allow the layers to separate and discard the aqueous layer. Wash the organic layer twice with 200 mL of water. Do not use a solution that has stood more than 24 h.

68.4 *Rhodamine B Solution (100 mg/L)*—Dissolve 100 mg of rhodamine B in water. Transfer to a 1-L volumetric flask, add 42 mL of HCl, dilute to volume, and mix.

68.5 *Sodium Sulfite Solution (1 g/L)*—Dissolve 100 mg of sodium sulfite (Na_2SO_3) in water. Transfer to a 100-mL volumetric flask, dilute to volume, and mix. Do not use a solution that has stood more than 8 h.

68.6 *Sulfatoceric Acid Solution (10 g/L)*—Dissolve 1.0 g of sulfatoceric acid ($H_4Ce(SO_4)_4$) in water containing 5 mL of H_2SO_4. Transfer to a 100-mL volumetric flask, dilute to volume, and mix.

68.7 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.

69. Preparation of Calibration Curve

69.1 *Calibration Solutions:*

69.1.1 Using pipets, transfer (1, 2, 3, 4, and 5) mL of antimony solution B (1 mL = 2.5 µg Sb) to 150-mL beakers.

69.1.2 Add 10 mL of HNO_3 and 2 mL of H_2SO_4, cover, and boil the solutions at 100 °C to 120 °C to evaporate the water and HNO_3. Gradually increase the temperature until the solution fumes, and continue fuming for 5 min. Cool for about 5 min. Add about 10 mL of water, wash the cover and sides of the beaker with water, evaporate to fumes, and continue fuming for 5 min. Cool to room temperature. Add 10.0 mL of HCl and mix to dissolve the salts. Proceed as directed in 69.3.

69.2 *Reference Solution*—Transfer 20 mL of HNO_3 (1 + 1) and 2 mL of H_2SO_4 to a 150-mL beaker. Proceed as directed in 69.1.2.

69.3 *Color Development:*

69.3.1 Transfer the solution to a 125-mL separatory funnel. Rinse the beaker twice using 4.0 mL of HCl each time, and add the rinsings to the separatory funnel. Add 1.0 mL of sulfatoceric acid solution and mix. Add 15.0 mL of washed isopropyl ether and shake for 30 s. Add 10.0 mL of water and shake for 30 s. Allow the layers to separate for 5 min and discard the aqueous layer.

69.3.2 Add 20.0 mL of HCl (1 + 11) and 1.0 mL of Na_2SO_3 solution to the separatory funnel, and shake for 30 s. Allow the layers to separate for not more than 5 min and discard the aqueous layer. Add 20.0 mL of HCl (1 + 11) and shake for 30 s. Allow the layers to separate for not more than 5 min and discard the aqueous layer. Add 20.0 mL of rhodamine B solution and shake for 30 s. Allow the layers to separate for 5 min and discard the aqueous layer. Eliminate water droplets in the organic solution by transferring the isopropyl ether solution to a clean, dry test tube before transferring to the absorption cell.

69.4 *Spectrophotometry:*

69.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 550 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

69.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 550 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

69.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against micrograms of antimony per 15 mL of solution.

70. Procedure

70.1 *Test Solution:*

70.1.1 Transfer a 1.0-g sample, weighed to the nearest 1 mg, to a 150-mL beaker. Proceed as directed in 69.1.2.

70.2 *Reference Solution*—Proceed as directed in 69.2.

70.3 *Color Development*—Proceed as directed in 69.3.

70.4 *Spectrophotometry*—Take the spectrophotometric reading of the test solution as directed in 69.4.

71. Calculation

71.1 Convert the net spectrophotometric reading of the test solution to micrograms of antimony by means of the calibration curve. Calculate the percentage of antimony as follows:

$$\text{Antimony, \%} = A/(B \times 10000) \quad (7)$$

where:

A = antimony found in 15 mL of the final test solution, µg, and
B = sample used, g.

72. Precision and Bias

72.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 8.

72.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

72.3 E173 has been replaced by Practice E1601. The Reproducibility Index R_2, corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1, corresponds to the Repeatability Index r of Practice E1601.

TIN BY THE 8-QUINOLINOL SPECTROPHOTOMETRIC METHOD

73. Scope

73.1 This test method covers the determination of tin in contents from 0.0025 % to 0.0150 %.

74. Summary of Test Method

74.1 An 8-quinolinol complex of tin is extracted with chloroform from a chloride solution at a pH of 0.90. Spectrophotometric measurement is made at approximately 385 nm.

75. Concentration Range

75.1 The recommended concentration range is from 50 µg to 300 µg of tin per 20 mL of solution, using a 1-cm cell (see Note 1).

TABLE 8 Statistical Information

Test Specimen	Antimony Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. D-66	0.00092	0.00008	0.00016
2. D-67	0.00137	0.00004	0.00024

76. Stability of Color

76.1 The color is stable for at least 2 h. Care must be taken to avoid loss of solvent before and during the measurement.

77. Interferences

77.1 The elements ordinarily present do not interfere if their contents are under the maximum limits shown in 1.1. More than 0.05 µg of molybdenum will interfere. A procedure for eliminating this interference is incorporated in this test method.

78. Reagents

78.1 *Ammonium Chloride Solution (200 g/L)*—Dissolve 100 g of ammonium chloride (NH_4Cl) in water and dilute to 500 mL.

78.2 *Ammonium Chloride Wash Solution (40 g/L)*—Dissolve 40 g of NH_4Cl in water, add 10 mL of HCl, and dilute nearly to 1 L. Adjust the pH to 0.90 ± 0.05 with HCl (1 + 1), and dilute to 1 L.

78.3 *Hydrogen Peroxide Solution (30 %)*—This reagent must not be stabilized by tin compounds.

78.4 *Platinum,* sheet, 5 by 5 by 0.05-mm pieces.

78.5 *8-Quinolinol Solution (40 g/L)*—Dissolve 40 g of 8-quinolinol in about 900 mL of H_2SO_4 (1 + 45), cool, and dilute to 1 L with water.

78.6 *Sulfuric Acid Wash Solution (pH 0.90)*—Add 10 mL of H_2SO_4 to about 1 L of water and cool. Adjust the pH to 0.90 ± 0.05 with H_2SO_4 (1 + 1).

78.7 *Tin, Standard Solution A (1 mL = 2 mg Sn)*—Dissolve 400 mg of tin metal (purity: 99 % min) in 10 mL of H_2SO_4 and fume strongly. Add 30 mL of H_2SO_4, cool carefully, dilute to about 150 mL, and cool. Transfer to a 200-mL volumetric flask, dilute to volume, and mix.

78.8 *Tin, Standard Solution B (1 mL = 40 µg Sn)*—Using a pipet, transfer 10 mL of tin solution A (1 mL = 2 mg Sn) to a 500-mL volumetric flask containing about 350 mL of water and 25 mL of H_2SO_4. Cool, dilute to volume, and mix. Do not use a solution that has stood more than 8 h.

78.9 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water as defined by Type II of Specification D1193. Other Types may be used if they effect no measurable change in the reference solution or sample.

79. Preparation of Calibration Curve

79.1 *Calibration Solutions:*

79.1.1 Using pipets, transfer (1, 2, 3, 5, and 10) mL of tin solution B (1 mL = 40 µg Sn) to 150-mL beakers. Add 8 mL of H_2SO_4 (1 + 1), a piece of platinum metal, and 6 drops to 8 drops of H_2O_2 solution, and dilute to 20 mL with water.

79.1.2 Boil vigorously for 30 min maintaining the volume with water. Cool to room temperature in a water bath. Proceed as directed in 79.3.

79.2 *Reference Solution*—To 12 mL of water in a 150-mL beaker add 8 mL of H_2SO_4 (1 + 1), a piece of platinum metal, and 6 drops to 8 drops of H_2O_2 solution. Proceed as directed in 79.1.2.

79.3 *Color Development:*

79.3.1 Add 5 mL of NH_4Cl solution and 10 mL of NH_4OH (1 + 1), and cool. Add 25 mL of 8-quinolinol solution, and adjust the pH to 0.90 ± 0.05 with H_2SO_4 (1 + 1) or NH_4OH (1 + 1). Transfer the solution to a 125-mL conical separatory funnel, using the H_2SO_4 wash solution to rinse the beaker and the platinum. Adjust the volume to 75 mL with H_2SO_4 wash solution. Reserve the platinum for the next determination.

79.3.2 Using a pipet, add 20 mL of $CHCl_3$. Shake for 2 min, and allow the layers to separate for 10 min. Drain the organic layer into a second 125-mL separatory funnel containing 50 mL of NH_4Cl wash solution. Shake for 2 min, and allow the layers to separate for 10 min. Insert a loose cotton plug in the stem of the separatory funnel and drain the organic layer into a 25-mL glass-stoppered flask.

79.4 *Spectrophotometry:*

79.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 385 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

79.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 385 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

79.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against micrograms of tin per 20 mL of solution.

80. Procedure

80.1 *Test Solution*—Transfer a 2.0-g sample, weighed to the nearest 2 mg, to a 150-mL beaker. Add 8 mL of H_2SO_4 (1 + 1), a piece of platinum metal, and 6 drops to 8 drops of H_2O_2 solution. Dilute to 20 mL and heat. If dissolution stops add more H_2O_2 dropwise until dissolution of the sample is complete. Boil vigorously for 30 min, maintaining the volume with water, and cool. (Note 11). Add 10 mL of NH_4OH (1 + 1) and cool. Add 25 mL of 8-quinolinol solution and adjust the pH to 0.90 ± 0.05 with H_2SO_4 (1 + 1) or NH_4OH (1 + 1). Transfer the solution to a 125-mL separatory funnel using the H_2SO_4 wash solution to rinse the beaker and the platinum. Adjust the volume to about 75 mL with the H_2SO_4 wash solution and extract the molybdenum complex with two 10-mL portions of $CHCl_3$. Discard the organic solutions and reserve the platinum for the next determination. Add 5 mL of NH_4Cl solution to the aqueous solution and proceed as directed in 80.3.

NOTE 11—If 0.05 µg or less of molybdenum is known to be present, proceed as directed in 79.3.1 after dissolving the sample, boiling the solution, and cooling.

80.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents but with the sample omitted.

80.3 *Color Development*—Proceed as directed in 79.3.2.

80.4 *Spectrophotometry*—Take the spectrophotometric measurement of the test solution as directed in 79.4.

81. Calculation

81.1 Convert the net spectrophotometric reading of the test solution to micrograms of tin by means of the calibration curve. Calculate the percentage of tin as follows:

$$\text{Tin, \%} = A/(B \times 10\,000) \quad (8)$$

where:

A = tin found in 20 mL of the final test solution, µg, and
B = sample used, g.

82. Precision and Bias

82.1 *Precision*—Seven laboratories cooperated in testing this test method and obtained eight sets of data summarized in Table 9.

82.2 *Accuracy*—No certified reference materials suitable for testing this test method were available when the interlaboratory testing program was conducted. The user of this test method is encouraged to employ accepted reference materials, if available, to determine the accuracy of this test method as applied in a specific laboratory.

82.3 E173 has been replaced by Practice E1601. The Reproducibility Index R_2, corresponds to the Reproducibility Index R of Practice E1601. Likewise the Repeatability Index R_1, corresponds to the Repeatability Index r of Practice E1601.

83. Keywords

83.1 antimony; arsenic; atomic absorption; cadmium; copper; lead; silver; spectrophotometry; thallium; tin; zinc

TABLE 9 Statistical Information

Test Specimen	Tin Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. D-42	0.0012	0.0005	0.0005
2. D-65	0.0171	0.0007	0.0016