Designation: E 396 – 04

Standard Test Methods for Chemical Analysis of Cadmium[1]

This standard is issued under the fixed designation E 396; 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 These test methods cover the chemical analysis of cadmium having chemical compositions with the following limits:

Element	Concentration, 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 Photometric Method [0.0002 to 0.0010%]	62-72
Arsenic by the Molybdenum Blue Photometric Method [0.001 to 0.005%]	40-50
Copper by the Neocuproine Photometric 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 Photometric Method [0.001 to 0.05%]	20-29
Thallium by the Rhodamine B Photometric Method [0.0003 to 0.005%]	30-39
Tin by the 8-Quinolinol Photometric Method [0.0025 to 0.0150%]	73-82

1.3 *This standard does not purport to address all of the safety problems, 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 and 25.8.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

B 440 Specification for Cadmium
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals
E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition
E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals
E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition
E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E 173 Practices for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals
E 1601 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 E 135

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 B 440. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory.

5. Apparatus, Reagents, and Photometric 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 E 50. Photometers shall conform to the requirements prescribed in Practice E 60.

5.2 Photometric practice prescribed in these methods shall conform to Practice E 60.

6. Safety Hazards

6.1 For precautions to be observed in the use of certain reagents in these test methods, refer to Practices E 50.

[1] These test methods are under the jurisdiction of ASTM Committee E-1 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.

7. Sampling

7.1 Wrought products shall be sampled in accordance with Practice E 55. Cast products shall be sampled in accordance with Practice E 88. 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 E 29.

9. Interlaboratory Studies

9.1 These test methods have been evaluated in accordance with Practices E 173, unless otherwise noted in the precision section.

COPPER BY THE NEOCUPROINE PHOTOMETRIC METHOD

10. Scope

10.1 This test method covers the determination of copper in concentrations 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. Photometric measurement is made at approximately 455 nm.

12. Concentration Range

12.1 The recommended concentration range is from 0.01 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 photometric readings promptly.

14. Interferences

14.1 The elements ordinarily present do not interfere if their concentrations 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.

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 *Photometry*:

16.4.1 *Multiple-Cell Photometer*—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 photometric 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 Photometer*—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 455 nm (Note 1). While maintaining this adjustment, take the photometric readings of the calibration solutions.

16.5 *Calibration Curve*—Plot the net photometric 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 *Photometry*—Proceed as directed in 16.4.

18. Calculation

18.1 Convert the net photometric 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 E 173 has been replaced by Practice E 1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E 1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E 1601.

LEAD BY THE DITHIZONE PHOTOMETRIC METHOD

20. Scope

20.1 This test method covers the determination of lead in concentrations 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. Photometric measurement is made at approximately 515 nm.

22. Concentration Range

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

TABLE 1 Statistical Information

Specimen	Copper Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1	0.0074	0.003	0.0013
2	0.0173	0.0018	0.0031

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 photometric readings promptly.

24. Interferences

24.1 The elements ordinarily present in cadmium do not interfere if their concentrations 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 6 of Practices E 50.)

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.

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 *Photometry*:

26.4.1 *Multiple-Cell Photometer*—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 photometric readings of the calibration solutions.

26.4.2 *Single-Cell Photometer*—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 515 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

26.5 *Calibration Curve*—Plot the net photometric 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 to 10-mL portion (containing between 0.005 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 *Photometry*—Proceed as directed in 26.4.

28. Calculation

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

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

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 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 E 173 has been replaced by Practice E 1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E 1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E 1601.

THALLIUM BY THE RHODAMINE B PHOTOMETRIC METHOD

30. Scope

30.1 This test method covers the determination of thallium in concentrations from 0.0003 to 0.005 %. Higher and lower concentrations 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. Photometric measurement is made at approximately 540 nm.

32. Concentration Range

32.1 The recommended concentration range is from 0.002 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

TABLE 2 Statistical Information

Specimen	Lead Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E<usb> 173)
1	0.0066	0.0009	0.0020
2	0.0236	0.0025	0.0053

quickly and the photometric 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 concentrations 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.

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 *Photometry*:

36.4.1 *Multiple-Cell Photometer*—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 photometric 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 Photometer*—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 540 nm (Note 1). While maintaining this adjustment, take the photometric readings of the calibration solutions.

36.5 *Calibration Curve*—Plot the net photometric 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 *Photometry*—Proceed as directed in 36.4.

38. Calculation

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

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

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 E 173 has been replaced by Practice E 1601. The reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E 1601. Likewise the Repeatability Index R_1 corresponds to the Repeatability Index r of Practice E 1601.

ARSENIC BY THE MOLYBDENUM BLUE PHOTOMETRIC METHOD

40. Scope

40.1 This test method covers the determination of arsenic in concentrations from 0.001 to 0.005 %. Higher and lower

TABLE 3 Statistical Information

Specimen	Thallium Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1	0.0011	0.0001	0.0002
2	0.0030	0.0006	0.0007

concentrations 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. Photometric measurement of the blue complex is made at approximately 725 nm.

42. Concentration Range

42.1 The recommended concentration range is from 10 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 concentrations 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 $(NH)_4)_6Mo_7O_{24}\cdot H_2O)$ 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.

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 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.