Designation: E478 – 08 (Reapproved 2017)

Standard Test Methods for Chemical Analysis of Copper Alloys[1]

This standard is issued under the fixed designation E478; 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 copper alloys having chemical ranges within the following limits:[2]

Element	Composition, %
Aluminum	12.0 max
Antimony	1.0 max
Arsenic	1.0 max
Cadmium	1.5 max
Cobalt	1.0 max
Copper	40.0 min
Iron	6.0 max
Lead	27.0 max
Manganese	6.0 max
Nickel	50.0 max
Phosphorus	1.0 max
Silicon	5.0 max
Sulfur	0.1 max
Tin	20.0 max
Zinc	50.0 max

1.2 The test methods appear in the following order:

	Sections
Aluminum by the Carbamate Extraction-Ethylenedinitrilotetraacetate Titrimetric Test Method [2 % to 12 %]	71 – 78
Copper by the Combined Electrodeposition Gravimetric and Oxalyldihydrazide Spectrophotometric Test Method [50 %, minimum]	10 – 18
Iron by the 1,10-Phenanthroline Spectrophotometric Test Method [0.003 % to 1.25 %]	19 – 28
Lead by Atomic Absorption Spectrometry [0.002 % to 15 %]	90 – 100
Lead by the Ethylenedinitrilotetraacetic Acid (EDTA) Titrimetric Test Method [2.0 % to 30.0 %]	29 – 36
Nickel by the Dimethylglyoxime Extraction Sprectophotometric Test Method [0.03 % to 5.0 %]	37 – 46
Nickel by the Dimethylglyoxime Gravimetric Test Method [4 % to 50 %]	55 – 62
Silver in Silver-Bearing Copper by Atomic Absorption Spectrometry [0.01 % to 0.12 %]	101 – 112
Tin by the Iodotimetric Titration Test Method [0.5 % to 20 %]	63 – 70
Tin by the Phenylfluorone Spectrophotometric Test Method [0.01 % to 1.0 %]	113 – 123
Zinc by Atomic Absorption Spectrometry [0.2 % to 2 %]	79 – 89
Zinc by the Ethylenedinitrilotetraacetic Acid (EDTA) Titrimetric Test Method [2 % to 40 %]	47 – 54

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

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

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

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)[4]

E255 Practice for Sampling Copper and Copper Alloys for the Determination of Chemical Composition

E1601 Practice for Conducting an Interlaboratory Study to

[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, Precious Metals, their Alloys, and Related Metals.

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[2] The actual limits of application of each test method are presented in 1.2.

[3] 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.

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

Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definitions of terms used in these test methods, refer to Terminology E135.

4. Significance and Use

4.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with composition specifications. It is assumed that all who use these 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 Spectrophotometric Practice

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

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

6. Hazards

6.1 Specific hazard statements are given in 33.7, 51.13, and 107.1.

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

7. Sampling

7.1 For procedures for sampling the material, refer to Practice E255. However, this practice does 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 were evaluated in accordance with Practice E173 unless otherwise noted in the precision section. Practice E173 has been replaced by Practice E1601. The Reproducibility R_2 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability R_1 of Practice E173 corresponds to the Repeatability Index r of Practice E1601.

COPPER BY THE COMBINED ELECTRODEPOSITION GRAVIMETRIC AND OXALYLDIHYDRAZIDE SPECTROPHOTOMETRIC TEST METHOD

10. Scope

10.1 This test method covers the determination of copper in compositions greater than 50 %.

10.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

11. Summary of Test Method

11.1 After dissolution of the sample in HNO_3 and HF, the oxides of nitrogen are reduced with hydrogen peroxide, and the copper deposited electrolytically. Loss of platinum from the anode is minimized by the addition of lead. The copper oxalyldihydrazide complex is formed with the copper remaining in the electrolyte. Photometric measurement is made at approximately 540 nm.

12. Interferences

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

13. Apparatus

13.1 *Polytetrafluoroethylene or Polypropylene Beakers,* 250-mL capacity.

13.2 *Polytetrafluoroethylene or Polypropylene Split Covers.*

13.3 *Electrodes for Electroanalysis*—Recommended stationary type platinum electrodes are described in 13.3.1 and 13.3.2. The surface of the platinum electrode should be smooth, clean, and bright to promote uniform deposition and good adherence. Deviations from the exact size and shape are allowable. In instances where it is desirable to decrease the time of deposition and agitation of the electrolyte is permissible, a generally available rotating type of electrode may be employed. Cleaning of the electrode by sandblasting is not recommended.

13.3.1 *Cathodes*—Platinum cathodes may be either open or closed cylinders formed from sheets that are plain or perforated, or from gauze. Gauze cathodes are recommended; preferably from 50-mesh gauze woven from approximately 0.21-mm diameter wire. The top and bottom of gauze cathodes should be reinforced by doubling the gauze about 3 mm onto itself, or by the use of platinum bands or rings. The cylinder should be approximately 30 mm in diameter and 50 mm in height. The stem should be made from a platinum alloy wire such as platinum-iridium, platinum-rhodium, or platinum-ruthenium, having a diameter of approximately 1.3 mm. It should be flattened and welded the entire length of the gauze. The overall height of the cathode should be approximately 130 mm. A cathode of these dimensions will have a surface area of 135 cm^2 exclusive of the stem.

13.3.2 *Anodes*—Platinum anodes may be a spiral type when anodic deposits are not being determined, or if the deposits are small (as in the electrolytic determination of lead when it is present in compositions below 0.2 %). Spiral anodes should be made from 1.0 mm or larger platinum wire formed into a spiral of seven turns having a height of approximately 50 mm and a diameter of 12 mm with an overall height of approximately 130 mm. A spiral anode of these dimensions will have a surface area of 9 cm^2. When both cathode and anode plates are to be determined, the anode should be made of the same material and design as the electrode described in 13.3.1. The anode cylinder

should be approximately 12 mm in diameter and 50 mm in height and the overall height of the anode should be approximately 130 mm. A gauze anode of these dimensions will have a surface area of 54 cm^2 exclusive of the stem.

13.3.3 Gauze cathodes are recommended where rapid electrolysis is used.

14. Reagents

14.1 *Ammonium Chloride Solution* (0.02 g/L)—Dissolve 0.02 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L.

14.2 *Hydrogen Peroxide* (3 %)—Dilute 100 mL of 30 % hydrogen peroxide to 1 L.

14.3 *Lead Nitrate Solution* (10 g/L) —Dissolve 10.0 g of lead nitrate ($Pb(NO_3)_2$) in water and dilute to 1 L.

15. Procedure

15.1 Transfer a 2.000-g sample, weighed to the nearest 0.1 mg, to a 250-mL polytetrafluoroethylene or polypropylene beaker, add 2 mL of HF, and 30 mL of HNO_3 (1 + 1). Cover with a cover glass and allow to stand for a few minutes until the reaction has nearly ceased. Warm but do not heat over 80 °C. When dissolution is complete, add 25 mL of 3 % H_2O_2 and 3 mL of $Pb(NO_3)_2$ solution. Rinse the cover glass and dilute to approximately 150 mL with NH_4Cl solution.

15.2 With the electrolyzing current off, position the anode and the accurately weighed cathode in the solution so that the gauze is completely immersed. Cover the beaker with a split plastic cover.

15.3 Start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1.0 A/dm^2 and electrolyze overnight. Alternatively electrolyze at a current density of 4 A/dm^2 for 1.5 h. (The more rapid procedure requires the use of gauze electrodes).

15.4 Slowly withdraw the electrodes (or lower the beaker) with the current still flowing, and rinse with a stream of water from a wash bottle. Quickly remove the cathode, rinse it in water, and then dip into two successive baths of ethanol or methanol. Dry in an oven at 110 °C for 3 min to 5 min.

15.5 Return the voltage to zero and turn off the switch. Reserve the electrolyte.

15.6 Allow the electrode to cool to room temperature and weigh.

16. Calculation

16.1 Calculate the percentage of copper as follows:

$$\text{Copper, \%} = [(A+B)/C] \times 100 \quad (1)$$

where:

A = deposited copper, g,
B = copper in the electrolyte as calculated in 17.10, g, and
C = sample used, g.

17. Spectrophotometric Determination of the Residual Copper in the Electrolyte

17.1 *Interferences*—The elements ordinarily present do not interfere if their composition is under the maximum limits shown in 1.1.

17.2 *Concentration Range*—The recommended concentration is from 0.0025 mg to 0.07 mg of copper per 50 mL of solution, using a 2-cm cell.

NOTE 1—This procedure has been written for cells having a 2-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

17.3 *Stability of Color*—The color fully develops in 20 min and is stable for 1 h.

17.4 *Reagents:*

17.4.1 *Acetaldehyde Solution* (40 %)—Dilute 400 mL of acetaldehyde to 1 L with water.

17.4.2 *Boric Acid Solution (50 g/L)*—Dissolve 50 g of boric acid (H_3BO_3) in hot water, cool, and dilute to 1 L.

17.4.3 *Citric Acid Solution (200 g/L)*—Dissolve 200 g of citric acid in water and dilute to 1 L.

17.4.4 *Copper, Standard Solution A (1 mL = 1.0 mg Cu)*—Transfer a 1.000-g sample of electrolytic copper (purity: 99.9 % minimum) to a 250-mL beaker and add 10 mL of HNO_3 (1 + 1). Evaporate nearly to dryness. Add 5 mL of water to dissolve the residue. Transfer to a 1-L volumetric flask, dilute to volume, and mix.

17.4.5 *Copper, Standard Solution B (1 mL = 0.010 mg Cu)*—Using a pipet, transfer 10 mL of Copper Solution A (1 mL = 1.0 mg Cu) to a 1-L volumetric flask, dilute to volume, and mix.

17.4.6 *Oxalyldihydrazide Solution (2.5 g/L)*—Dissolve 2.5 g of oxalyldihydrazide in warm water and dilute to 1 L.

17.5 *Preparation of Calibration Curve:*

17.5.1 *Calibration Solutions:*

17.5.1.1 Transfer 25 mL of boric acid solution to a 250-mL volumetric flask and then add a solution containing 150 mL of water, 2 mL of HF, and 30 mL of HNO_3 (1 + 1). Dilute to volume and mix.

17.5.1.2 Transfer 10 mL of this solution to each of four 50-mL volumetric flasks. Using pipets, transfer (1, 3, 5, and 7) mL of Copper Solution B (1 mL = 0.010 mg Cu) to the flasks. Proceed as directed in 17.5.3.

17.5.2 *Reference Solution*—Add 10 mL of boric acid solution prepared as directed in 17.5.1.1 to a 50-mL volumetric flask and proceed as directed in 17.5.3.

17.5.3 *Color Development*—Add in order, and with mixing after each addition, 5 mL of citric acid solution, 6 mL of NH_4OH, 10 mL of acetaldehyde solution, and 10 mL of oxalyldihydrazide solution. Cool, dilute to volume, and mix. Allow to stand for 30 min and proceed as directed in 17.5.4.

17.5.4 *Spectrophotometry:*

17.5.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 2-cm light path and a light band centered at approximately 540 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

17.5.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the spectrophotometer to the initial setting using a light band centered at approximately 540 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

17.5.5 *Calibration Curve*—Plot the net spectrophotometric-readings of the calibration solutions against milligrams of copper per 50 mL of solution.

17.6 *Test Solution*—Transfer the reserved electrolyte to a 250-mL volumetric flask containing 25 mL of boric acid solution, dilute to volume, and mix. Using a pipet, transfer 10 mL to a 50-mL volumetric flask. Proceed as directed in 17.8. If the solution shows a permanganate color, add sodium nitrite solution (20 g/L) dropwise until the color is discharged, and then proceed as directed in 17.8.

17.7 *Reference Solution*—Proceed as directed in 17.5.2.

17.8 *Color Development*—Proceed as directed in 17.5.3.

17.9 *Spectrophotometry*—Take the spectrophotometric reading of the test solution as directed in 17.5.4.

17.10 *Calculation*—Convert the net spectrophotometric reading of the test solution to milligrams of copper by means of the calibration curve. Calculate the grams of copper in the total electrolyte as follows:

$$\text{Copper, g} = (A \times 25)/1000 \quad (2)$$

where:

A = copper found in 50 mL of the final test solution, mg.

18. Precision and Bias

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

18.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the certified reference material in Table 1. Users are encouraged to use this or similar reference materials to verify that the method is performing accurately in their laboratories.

IRON BY THE 1,10-PHENANTHROLINE SPECTROPHOTOMETRIC TEST METHOD

19. Scope

19.1 This test method covers the determination of iron in compositions from 0.003 % to 1.25 %.

19.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

TABLE 1 Statistical Information

Test Specimen	Copper Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Bronze ounce metal (NIST 124d, 83.60 Cu)	83.56	0.09	0.13
2. AAB 521	91.98	0.03	0.08
3. AAB 655	95.38	0.09	0.14
4. AAB 681	57.60	0.10	0.09
5. AAB 715	68.95	0.08	0.21

20. Summary of Test Method

20.1 The sample is dissolved in HCl and hydrogen peroxide, and the excess oxidant removed by evaporation. The iron is extracted with methyl isobutyl ketone-benzene mixture. The iron is extracted from the organic phase into a hydroxylamine hydrochloride solution and the red-colored 1,10-phenanthroline complex is formed. Spectrophotometric measurement is made at approximately 510 nm.

21. Concentration Range

21.1 The recommended concentration range is from 0.005 mg to 0.12 mg of iron per 50 mL of solution, using a 2-cm cell.

NOTE 2—This test method has been written for cells having a 2-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

22. Stability of Color

22.1 The color develops within 5 min and is stable for at least 4 h.

23. Interferences

23.1 Elements ordinarily present do not interfere if their composition range is under the maximum limits shown in 1.1.

24. Reagents

24.1 *Hydroxylamine Hydrochloride Solution (10 g/L)*—Dissolve 5.0 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 500 mL of water. Prepare fresh as needed.

24.2 *Iron, Standard Solution A (1 mL = 0.125 mg Fe)*—Transfer 0.125 g of iron (purity: 99.9 % minimum) to a 100-mL beaker. Add 10 mL of HCl (1 + 1) and 1 mL of bromine water. Boil gently until the excess bromine is removed. Add 20 mL of HCl, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

24.3 *Iron, Standard Solution B (1 mL = 0.00625 mg Fe)*—Using a pipet, transfer 50 mL of Iron Solution A to a 1-L volumetric flask, dilute to volume with HCl (1 + 49), and mix.

24.4 *Methyl Isobutyl Ketone-Benzene Mixture*—Mix 200 mL of methyl isobutyl ketone (MIBK) and 100 mL of benzene.

24.5 *1,10-Phenanthroline-Ammonium Acetate Buffer Solution*—Dissolve 1.0 g of 1,10-phenanthroline monohydrate in 5 mL of HCl in a 600-mL beaker. Add 215 mL of acetic acid, and, while cooling, carefully add 265 mL of NH_4OH. Cool to room temperature. Using a pH meter, check the pH; if it is not between 6.0 and 6.5, adjust it to that range by adding acetic acid or NH_4OH as required. Dilute to 500 mL.

24.6 *Sodium Nitrite Solution (20g/L)*—Dissolve 20.0 g of dry sodium nitrite ($NaNO_2$) in approximately 500 mL of water, transfer to a 1-L volumetric flask, dilute to volume and mix.

25. Preparation of Calibration Curve

25.1 *Calibration Solutions:*

25.1.1 Using pipets, transfer (1, 2, 5, 10, 15, and 20) mL of Iron Solution B (1 mL = 0.00625 mg Fe) to 50-mL volumetric flasks. Dilute to 20 mL.

25.1.2 Add 20 mL of $NH_2OH·HCl$ solution, mix, and allow to stand 1 min. Proceed as directed in 25.3.

25.2 *Reference Solution*—Transfer 20 mL of water to a 50-mL volumetric flask and proceed as directed in 25.1.2.

25.3 *Color Development*—Add 5 mL of 1,10-phenanthroline-ammonium acetate buffer solution, dilute to volume, and mix. Allow to stand at least 5 min but not more than 4 h.

25.4 *Spectrophotometry:*

25.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 2-cm light path and a light band centered at approximately 510 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

25.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 510 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

25.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against milligrams of iron per 50 mL of solution.

26. Procedure

26.1 *Test Solution:*

26.1.1 Select and weigh a sample as follows:

Iron, %	Sample Weight, g	Tolerance in Sample Weight, mg	Aliquot Volume, mL
0.003 to 0.02	2.0	2.0	25
0.02 to 0.10	1.0	1.0	10
0.05 to 0.20	0.5	0.5	10
0.10 to 0.40	0.5	0.5	5
0.25 to 1.25	0.2	0.5	5

Transfer it to a 400-mL beaker or to a polytetrafluoroethylene beaker if HF is to be used.

26.1.2 Carry a reagent blank through the entire procedure, using the same amounts of all reagents but with the sample omitted.

26.1.3 Add 12 mL of HCl (7 + 3) per gram of sample, and then H_2O_2 as needed to completely dissolve the alloy. Add HF as needed to decompose high-silicon alloys. When dissolution is complete, add 10 mL of concentrated HCl per gram of sample and heat carefully to decompose excess peroxide. Cool to room temperature, transfer to a 100-mL volumetric flask, dilute to volume with HCl (1 + 1), and mix.

26.1.4 Using a pipet, transfer an aliquot in accordance with 26.1.1 to a 125-mL conical separatory funnel. Add HCl (1 + 1), as required, to adjust the volume to 25 mL.

26.1.5 Add 20 mL of MIBK-benzene mixture to the separatory funnel and shake 1 min. Allow the phases to separate, discard the aqueous phase, wash the organic phase three times with 3-mL to 5-mL portions of HCl (1 + 1) to remove copper, and discard the washings. Extract the iron from the organic phase by shaking vigorously 30 s with 10 mL of $NH_2OH·HCl$ solution. Transfer the aqueous phase to a 50-mL volumetric flask. Repeat the extraction with a second 10-mL portion of $NH_2OH·HCl$ solution, and transfer the extract to the 50-mL flask.

26.2 *Reference Solution*—Use the reagent blank solution prepared as directed in 26.1.2.

26.3 *Color Development*—Proceed as directed in 25.3.

26.4 *Spectrophotometry*—Proceed as directed in 25.4.

27. Calculation

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

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

where:

A = iron found in 50 mL of the final test solution, mg, and

B = sample represented in 50 mL of the final test solution, g.

28. Precision and Bias

28.1 *Precision*—Seven laboratories cooperated in testing this method, submitting nine pairs of values, and obtained the data summarized in Table 2.

28.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the certified reference materials in Table 2. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

LEAD BY THE ETHYLENEDINITRILOTETRAACETIC ACID (EDTA)TITRIMETRIC TEST METHOD

29. Scope

29.1 This test method covers the determination of lead in composition range from 2.0 % to 30.0 %.

29.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the*

TABLE 2 Statistical Information

Test Specimen	Iron Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Cast bronze (NIST 52c, 0.004 Fe)	0.0034	0.0005	0.0010
2. Ounce metal (NIST 124d, 0.18 Fe)	0.187	0.012	0.017
3. Cupro Nickel, 30 Ni	0.60	0.015	0.044
4. Silicon bronze (NIST 158a, 1.23 Fe)	1.24	0.019	0.037

Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

30. Summary of Test Method

30.1 Lead diethyldithiocarbamate is extracted with chloroform from an alkaline tartrate-cyanide solution. After the removal of organic material, lead is titrated with disodium ethylenedinitrilotetraacetic acid (EDTA) solution.

31. Interferences

31.1 Elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1.

32. Apparatus

32.1 *Separatory Funnels,* 250-mL capacity.

32.2 *Magnetic Stirrer and Polytetrafluoroethylene-Covered Magnetic Stirring Bar.*

33. Reagents

33.1 *Ascorbic Acid.*

33.2 *Chloroform* ($CHCl_3$).

33.3 *Disodium Ethylenedinitrilotetraacetic Acid (EDTA), Standard Solution* (0.025 *M*)—Dissolve 9.3 g of disodium ethylenedinitrilo tetraacetate dihydrate in water, transfer to a 1-L volmetric flask, dilute to volume, and mix. The solution is stable for several months when stored in plastic or borosilicate glass bottles. Standardize as follows: Using a pipet, transfer 25 mL of lead solution (1 mL = 6.0 mg Pb) to a 250-mL beaker and dilute to 100 mL. Proceed as directed in 34.7. Calculate the lead equivalent of the solution as follows:

$$\text{Lead equivalent, g/mL} = A/B \quad (4)$$

where:

A = weight of lead, g, and
B = EDTA solution required for titration of the lead solution, mL.

33.4 *Fluoroboric Acid* (37 % to 40 %).

33.5 *Hexamethylenetetramine.*

33.6 *Lead, Standard Solution (1 mL = 6.0 mg Pb)*—Transfer 1.500 g of lead (purity 99.9 % minimum) to a 150-mL beaker. Add 10 mL of HNO_3 (1 + 1) and heat until dissolution is complete. Boil to remove oxides of nitrogen, cool, transfer to a 250-mL volumetric flask, dilute to volume, and mix.

33.7 *Sodium Cyanide Solution (200 g/L)*—Dissolve 200 g of sodium cyanide (NaCN) in water and dilute to 1 L. Store in a plastic bottle. (**Warning—**The preparation, storage, and use of NaCN solutions require care and attention. Avoid inhalation of fumes and exposure of skin to the chemical and its solutions. Work in a well-ventilated hood. Refer to the Hazards Section of Practices E50.)

33.8 *Sodium Diethyldithiocarbamate Solution (100 g/L)*—Dissolve 10 g of sodium diethyldithiocarbamate in water and dilute to 100 mL. Do not use a solution that is more than 24 h old.

33.9 *NaOH (250 g/L)*—Dissolve 250 g of NaOH in water and dilute to 1 L. Store in a plastic bottle.

33.10 *Sodium Tartrate Solution (250 g/L)*—Dissolve 250 g of sodium tartrate dihydrate in water and dilute to 1 L.

33.11 *Xylenol Orange Indicator Solution (1 g/L)*—Dissolve 0.050 g of xylenol orange powder in a mixture of 25 mL of water and 25 mL of ethanol.

34. Procedure

34.1 Select a sample as follows:

Lead, %	Sample Weight, g
2.0 to 20.0	1.00
20.0 to 30.0	0.60

Weigh the sample to the nearest 0.5 mg, and transfer it to a 250-mL beaker.

34.2 Add 5 mL of HBF_4 and then 10 mL of HNO_3 (1 + 1). Cover the beaker and heat until dissolution is complete. Boil until oxides of nitrogen have been expelled and cool.

34.3 Wash the cover and walls of the beaker. Add 25 mL of sodium tartrate solution, 25 mL of NaOH solution, and 25 mL of NaCN solution (**Warning—**See 33.7.), mixing after each addition. Cool to room temperature.

34.4 Transfer to a 250-mL separatory funnel. Add 15 mL of sodium diethyldithiocarbamate solution and 15 mL of $CHCl_3$, and shake for 30 s. Allow the layers to separate; draw off the lower organic layer into a 250-mL beaker, retaining the aqueous layer. Add 5 mL more of diethyldithiocarbamate solution to the separatory funnel and mix. If no precipitate forms, proceed as directed in 34.5. If a precipitate does form, add 5 mL of diethyldithiocarbamate solution and 10 mL of $CHCl_3$, shake for 30 s, and draw off the organic layer into the 250-mL beaker containing the extract.

34.5 Extract twice with additional 10-mL portions of $CHCl_3$, adding the extracts to the extracts in the 250-mL beaker.

34.6 Add 10 mL of HCl (1 + 1) to the combined extracts and place on a hot plate. Cover the beaker with a raised cover glass, and evaporate the solution to a volume of 2 mL to 3 mL. Wash the cover and walls of the beaker, dilute to 100 mL, and heat to dissolve salts.

34.7 Place the beaker on a magnetic stirrer and stir (Note 3). Add 10 mg to 20 mg of ascorbic acid and three or four drops of xylenol orange solution. Add enough hexamethylenetetramine to color the solution purple. Add four or five drops of NaCN solution (**Warning—**See 33.7.) and titrate with the EDTA solution. When a yellow color begins to appear, stop the titration and add 2 g to 3 g of hexamethylenetetramine and a drop of xylenol orange solution. Titrate dropwise until the color changes from purplish-red to yellow.

NOTE 3—The titration may be performed in either a hot or cold solution.

35. Calculation

35.1 Calculate the percentage of lead as follows:

$$\text{Lead, \%} = [(C \times D)/E] \times 100 \quad (5)$$

where:

C = standard EDTA solution used, mL,
D = equivalent of EDTA solution, g/mL, and
E = sample used, g.

36. Precision and Bias

36.1 *Precision*—Due to limited data, a precision statement conforming to the requirements of Practice E173 cannot be furnished. However, in a cooperative program conducted by six laboratories, the between-laboratory range was 3.13 % to 3.20 % lead on a sample averaging 3.16 %, and 14.05 % to 14.23 % on a sample averaging 14.15 %.

36.2 *Bias*—No information on the accuracy of this method is known, because at the time it was tested, no certified reference materials were available. Users are encouraged to employ suitable reference materials, if available, to verify the accuracy of the method in their laboratories.

NICKEL BY THE DIMETHYLGLYOXIME-EXTRACTION SPECTROPHOTOMETRIC TEST METHOD

37. Scope

37.1 This test method covers the determination of nickel in composition range from 0.03 % to 5.0 %.

37.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

38. Summary of Test Method

38.1 A dimethylglyoxime complex of nickel is formed in the presence of copper and extracted with chloroform. Spectrophotometric measurement is made at approximately 405 nm.

39. Concentration Range

39.1 The recommended concentration range is 0.015 mg to 0.3 mg of nickel per 20 mL of solution, using a 2-cm cell.

NOTE 4—This procedure has been written for a cell having a 2-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

40. Stability of Color

40.1 The color is stable for at least 2 h.

41. Interferences

41.1 The elements ordinarily present do not interfere if their composition is under the maximum limits shown in 1.1.

42. Reagents

42.1 *Chloroform* ($CHCl_3$).

42.2 *Complexing Solution*—Mix 240 mL of sodium tartrate solution, 90 mL of NaOH solution, 480 mL of sodium acetate solution, and 200 mL of $Na_2S_2O_3$ solution.

42.3 *Dimethylglyoxime Solution (10 g/L in alcohol)*—Dissolve 10 g of dimethylglyoxime in ethanol, methanol, or denatured alcohol and dilute to 1 L with alcohol. Filter before using. This solution keeps almost indefinitely.

42.4 *Hydroxylamine Hydrochloride Solution (10 g/L)*—Dissolve 10 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in water and dilute to 1 L. Adjust the pH to 7.0 with NH_4OH.

42.5 *Nickel, Standard Solution A (1 mL = 1.0 mg Ni)*—Dissolve 1.000 g of nickel metal (purity, 99.8 % minimum) in 10 mL of HNO_3. When dissolution is complete, boil gently to expel oxides of nitrogen, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

42.6 *Nickel, Standard Solution B (1 mL = 0.2 mg Ni)*—Using a pipet, transfer 100 mL of Nickel Solution A (1 mL = 1.0 mg Ni) to a 500-mL volumetric flask, dilute to volume, and mix.

42.7 *Sodium Acetate Solution (200 g/L)*—Dissolve 200 g of sodium acetate trihydrate ($CH_3COONa{\cdot}3H_2O$) in about 600 mL of water, filter, and dilute to 1 L.

42.8 *NaOH (1 N)*—Dissolve 40 g of NaOH in water, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Store in a plastic bottle.

42.9 *Sodium Sulfate,* anhydrous (Na_2SO_4).

42.10 *Sodium Tartrate Solution (100 g/L)*—Dissolve 100 g of sodium tartrate dihydrate in water and dilute to 1 L.

42.11 *Sodium Thiosulfate Solution (200 g/L)*—Dissolve 200 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) in water and dilute to 1 L.

43. Preparation of Calibration Curve

43.1 *Calibration Solutions:*

43.1.1 Transfer 1.000 g of copper (purity, 99.99 % minimum) to each of five 250-mL beakers, add 20 mL of HCl (1 + 1), and add 10 mL of H_2O_2 in small portions. When dissolution is complete, boil for 1 min to destroy excess peroxide, and cool.

43.1.2 Using pipets, transfer (2, 5, 10, 20, and 30) mL of Nickel Solution B (1 mL = 0.2 mg Ni) to the beakers. Transfer the solutions to 500-mL volumetric flasks, dilute to volume, and mix.

43.1.3 Using a pipet, transfer 25 mL to a 250-mL conical separatory funnel. Add 5 mL of $NH_2OH{\cdot}HCl$ solution and 50 mL of complexing solution, shaking after each addition. Using indicator paper, check the pH, which should be between 6.5 and 7.2. If necessary, adjust the pH with HCl (1 + 1) or dilute NaOH solution.

43.2 *Reference Solution*—Transfer 1.000 g of copper (purity, 99.99 % minimum) to a 250-mL beaker and proceed as directed in 43.1, omitting the addition of nickel solution.

43.3 *Color Development:*

43.3.1 Add 3 mL of dimethylglyoxime solution and shake for 1 min. Using a pipet, transfer 20 mL of $CHCl_3$ to the solution and shake again for 40 s. Allow the phases to separate.

43.3.2 Transfer the yellow-colored chloroform phase to a 25-mL Erlenmeyer flask fitted with a ground-glass stopper and

containing about 1 g of Na_2SO_4. Shake to stir the Na_2SO_4 into the $CHCl_3$. Decant the clear $CHCl_3$ solution into an absorption cell and cover immediately to prevent loss of solvent.

43.4 *Spectrophotometry:*

43.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 2-cm light path and a light band centered at approximately 405 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

43.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 405 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

43.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against milligrams of nickel per 20 mL of solution.

44. Procedure

44.1 *Test Solution:*

44.1.1 Select and weigh a sample as follows:

Nickel, %	Sample Weight, g	Tolerance in Sample Weight, mg	Weight of Copper, g	Aliquot Volume, mL
0.03 to 0.6	1.0	1.0	...	25
0.55 to 1.5	0.4	0.5	0.6	25
1.45 to 3.5	0.4	0.5	0.6	10
3.45 to 5.0	0.25	0.2	0.75	10

Transfer it to a 250-mL beaker. Add to the beaker the weight of copper (purity, 99.99 % minimum) indicated in the table.

44.1.2 Add 20 mL of HCl (1 + 1), and add 10 mL of H_2O_2 in small portions. Cool until the violent reaction has ceased. When dissolution is complete, boil for approximately 1 min to destroy excess peroxide. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix.

44.1.3 Proceed as directed in 43.1.3, using an aliquot volume in accordance with 44.1.1. If a 10-mL aliquot is used, add 3 mL of HCl (1 + 9) to the aliquot in the separatory funnel.

44.2 *Reference Solution*—Proceed as directed in 43.2.

44.3 *Color Development*—Proceed as directed in 43.3.

44.4 *Spectrophotometry*—Proceed as directed in 43.4.

45. Calculation

45.1 Convert the net spectrophotometric readings of the test solution to milligrams of nickel by means of the calibration curve. Calculate the percentage of nickel as follows:

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

where:

A = nickel found in 20 mL of the final test solution, mg, and
B = sample represented in 20 mL of the final test solution, g.

46. Precision and Bias

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

TABLE 3 Statistical Information

Test Specimen	Nickel Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. 816-12	0.107	0.010	0.028
2. Sheet Brass (NIST 37c, 0.53 Ni)	0.531	0.010	0.036
3. Ounce Metal (NIST 124d, 0.99 Ni)	0.997	0.021	0.037
4. 844-J	4.90	0.071	0.33

46.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the certified reference materials in Table 3. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

ZINC BY THE ETHYLENEDIAMINE TETRAACETATE (TITRIMETRIC) TEST METHOD

47. Scope

47.1 This test method covers the determination of zinc in the range from 2 % to 40 %.

47.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

48. Summary of Test Method

48.1 The zinc is converted to the zinc thiocyanate complex and extracted with methyl isobutyl ketone. The zinc is then stripped from the organic phase as the ammonia complex, which is further treated with potassium cyanide to complex bivalent metals as well as the zinc. Finally, the zinc is released from the cyanide complex by means of formaldehyde and titrated with disodium ethylenedinitrilotetraacetic acid (EDTA) solution.

49. Interferences

49.1 None of the elements ordinarily present interfere. The extraction procedure also affords a separation of the zinc from cadmium.

50. Apparatus

50.1 *Electrodes for Electroanalysis*—Platinum anode and cathode described in 13.3.

50.2 *Separatory Funnels,* conical, 500-mL capacity.

50.3 *Magnetic Stirrer,* with polytetrafluoroethylene-covered magnetic stirring bar.

51. Reagents

51.1 *Ammonium Chloride Solution (0.02 g/L)*—Dissolve 0.20 g of ammonium chloride (NH_4Cl) in water and dilute to 10 L.

51.2 *Ammonium Fluoride Solution (200 g/L)*—Dissolve 200 g of ammonium fluoride (NH_4F) in water and dilute to 1 L. Store in a polyethylene bottle.

51.3 *Ammonium Thiocyanate Solution (500 g/L)*—Dissolve 500 g of ammonium thiocyanate (NH_4SCN) in water and dilute to 1 L. Filter, if necessary, and store in a polyethylene bottle.

51.4 *Ascorbic Acid,* powdered.

51.5 *Buffer Solution* (*pH 10*)—Dissolve 54 g of ammonium chloride (NH_4Cl) in 200 mL of water. Add 350 mL of NH_4OH and dilute to 1 L. Store in a polyethylene bottle.

51.6 *Disodium—Ethylenedinitrilotetraacetic Acid* (*EDTA*), *Standard Solution* (0.05 *M*) *:*

51.6.1 Dissolve 18.6125 g of disodium ethylenedinitrilo tetraacetate dihydrate in water, transfer to a 1-L volumetric flask, dilute to volume, and mix. The solution is stable for several months when stored in plastic or borosilicate glass bottles.

51.6.2 *Standardization*—Dissolve 0.1 g of zinc in 10 mL of HNO_3 (1 + 1) in a 400-mL beaker. Dilute the solution to 150 mL and proceed as directed in 52.4 – 52.7.

$$\text{Zinc equivalent, mg/mL} = (A \times 1000)/(B - C) \quad (7)$$

where:

A = grams of zinc,
B = final buret reading, mL, and
C = initial buret reading, mL.

51.7 *Eriochrome Black-T Indicator Solution*—Dissolve 0.4 g of the sodium salt of 1-(1-hydroxy-2 naphtholazo)-5 nitro-2 naphthol-4 sulfonic acid in a mixture of 20 mL of ethanol and 30 mL of triethanolamine. Store in a tightly closed polyethylene dropping bottle. Do not use a solution that is older than three months.

51.8 *Formaldehyde Solution* (37 %).

51.9 *Hydrogen Peroxide Solution (3 %)*—Dilute 100 mL of 30 % H_2O_2 to 1 L.

51.10 *Indicator Ion Solution* (0.05 *M* $MgCl_2$ Solution)—Dissolve 1.02 g of magnesium chloride hexahydrate ($MgCl_2 \cdot 6 H_2O$) in water and dilute to 100 mL.

51.11 *Lead Nitrate Solution (10 g/L)*—Dissolve 10 g of lead nitrate ($Pb(NO_3)_2$) in water and dilute to 1 L.

51.12 *Methyl Isobutyl Ketone.*

51.13 *Potassium Cyanide Solution (100 g/L)*—Dissolve 100 g of potassium cyanide (KCN) in water and dilute to 1 L. 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 the Hazards Section of Practices E50.))

51.14 *NaOH (200 g/L)*—Dissolve 200 g of NaOH in water, cool, and dilute to 1 L. Store the solution in a polyethylene bottle.

51.15 *Thiocyanate Wash Solution*—Dissolve 100 g of sodium chloride (NaCl) in 600 mL of water. Add 10 mL of the NH_4SCN solution and mix. Add 10 mL of HCl and dilute to 1 L.

51.16 *Zinc Metal* (purity: 99.9 % minimum)—Do not use finely divided powder or surface oxidized material.

52. Procedure

52.1 Transfer a 2.00-g sample, weighed to the nearest 1 mg, to a 250-mL polytetrafluoroethylene or polypropylene beaker and add 2 mL of HF followed by 30 mL of HNO_3 (1 + 1). Cover the beaker with a plastic cover and allow the sample to dissolve. Do not place the beaker on a hot plate unless the temperature is less than 80 °C. When dissolution is complete, add 25 mL of H_2O_2 solution and 3 mL of $Pb(NO_3)_2$ solution. Rinse the plastic cover glass and dilute to approximately 150 mL with NH_4Cl solution.

52.2 Insert the electrodes into the solution and cover the beaker with a pair of split cover glasses. Electrolyze for 2 h at a current density of 4 A/dm^2 using gauze electrodes. When deposition is complete, slowly withdraw the electrodes (or lower the beaker) with the current still flowing and rinse them with a stream of water from a wash bottle. Reserve the electrolyte.

52.3 Depending on the amount of zinc present, transfer the whole electrolyte or an aliquot portion, containing not more than 100 mg of zinc, to a 400-mL beaker. If an aliquot of the sample is to be taken, add 25 mL of saturated boric acid (H_3BO_3) solution to the volumetric flask, add the electrolyte, dilute to volume, and mix. Dilute the aliquot to 150 mL and proceed as directed in 52.4. If the entire electrolyte is to be used, proceed directly with the neutralization.

52.4 Neutralize with NaOH solution using litmus paper as an indicator; then add 10 mL of HCl (1 + 1) and cool.

52.5 Transfer to a 500-mL separatory funnel and dilute to about 250 mL. Add 30 mL of NH_4SCN solution, 20 mL of NH_4F solution, and mix. Add 50 mL of methyl isobutyl ketone and shake vigorously for 1 min. Allow the layers to separate; then draw off the lower aqueous layer into a second separatory funnel. Retain the organic layer. Add an additional 50 mL of methyl isobutyl ketone to the second funnel and shake for 1 min. Allow the layers to separate. Draw off and discard the aqueous layer. Add the organic layer to that retained in the first separatory funnel. To the combined extracts, add 40 mL of thiocyanate wash solution, shake, and allow the layers to separate. Draw off and discard the aqueous layer.

52.6 To the organic layer add 20 mL buffer solution, 30 mL of water, and shake to strip the zinc from the organic phase. Allow the layers to separate, and drain off the lower ammoniacal layer into a 600-mL beaker. Repeat the extraction of zinc with another 20 mL of buffer solution and 30 mL of water, followed by a final wash with 50 mL of water, combining all the aqueous extracts in the 600-mL beaker. Discard the organic layer.

52.7 Dilute to about 300 mL. Place a polytetrafluoroethylene-covered stirring bar into the beaker,

add 20 mL of KCN solution, and then add 10 mg to 20 mg of ascorbic acid powder. Add 1.0 mL of indicator ion solution and about five drops of eriochrome black-T indicator. Transfer the beaker to the magnetic stirring apparatus and titrate with EDTA solution to a pure blue end point. Record the initial buret reading. Cautiously add formaldehyde solution, 1 mL to 2 mL at a time, until the color has changed again to wine red. Titrate with EDTA solution to a pure blue end point. Make further additions of formaldehyde and each time titrate to the blue end point to ensure that all the zinc has been released. Avoid adding excessive amounts of formaldehyde. Record the final buret reading.

53. Calculation

53.1 Calculate the percentage of zinc as follows:

$$\text{Zinc, \%} = (A - B)C/(D \times 10) \quad (8)$$

where:

A = final buret reading, mL,
B = initial buret reading, mL,
C = zinc equivalent of standard EDTA solution, mg/mL, and
D = grams of sample represented in portion of electrolyte taken.

54. Precision and Bias

54.1 *Precision*—Eight laboratories cooperated in testing this method and obtained the data shown in Table 4.

54.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the certified reference materials in Table 4. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC TEST METHOD

55. Scope

55.1 This test method covers the determination of nickel in composition range from 4 % to 50 %.

55.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

TABLE 4 Statistical Information

Test Specimen	Zinc Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Ounce Metal (NIST 124d, 5.06 Zn)	5.08	0.02	0.18
2. Sheet Brass (NIST 37c, 27.85 Zn)	27.87	0.13	0.27
3. AAB Alloy 681	40.84	0.23	0.40

56. Summary of Test Method

56.1 After dissolution of the sample, the nickel is precipitated from an alkaline citrate solution with sodium dimethylglyoximate; this precipitate is subsequently weighed as nickel dimethylglyoxime.

57. Interferences

57.1 The elements ordinarily present do not interfere if their composition range is under the maximum limits shown in 1.1.

58. Apparatus

58.1 *Electrodes for Electroanalysis*—Platinum anode and cathode described in 13.3.

58.2 *Filtering Crucibles*—Gooch crucible (35 mL) fitted with a glass microfiber pad, or fritted glass crucible (30 mL) of medium porosity.

59. Reagents

59.1 *Citric Acid (250 g/L)*—Dissolve 250 g of citric acid in water and dilute to 1 L. The addition of 1 g of benzoic acid per litre will prevent bacterial growth.

59.2 *Sodium Dimethylglyoximate Solution (25 g/L)*—Dissolve 25 g of sodium dimethylglyoximate $[(CH_3)_2C_2(NONa)_2 \cdot 8H_2O]$ in water and dilute to 1 L. Do not use a solution that is more than 24 h old.

59.3 *Sulfamic Acid Solution (100 g/L)*—Dissolve 100 g of sulfamic acid $[H(NH_2)SO_3]$ in water and dilute to 1 L.

60. Procedures

60.1 Transfer a sample, weighed to the nearest 0.1 mg, which contains between 40 mg and 150 mg of nickel, to a 250-mL beaker. Dissolve the sample in 25 mL of HNO_3 (1 + 1) and when dissolution is complete, boil gently to expel oxides of nitrogen. Add 50 mL of hot water and, if the solution is clear, proceed as described in 60.4. If enough tin is present at this point to cause turbidity, proceed as directed to 60.2 and 60.3.

60.2 Maintain the temperature of the solution at about 80 °C for 1 h, or until the precipitate has coagulated. Add paper pulp and filter through a fine paper into a 250-mL beaker to remove the metastannic acid. Wash several times with hot HNO_3 (1 + 99), and reserve the filtrate and washings.

60.3 Transfer the filter paper and precipitate to the original beaker, add 15 mL to 20 mL of HNO_3 and 10 mL to 15 mL of $HClO_4$. Heat to copious white fumes and boil to destroy organic matter. Cool, wash the cover glass and sides of the beaker, and add 15 mL of HBr. Heat to copious white fumes to volatilize the tin. If the solution is not clear, repeat the treatment with HBr. Evaporate the solution to near dryness, cool, and dissolve the residue in a few millilitres of water. Combine with the filtrate reserved in 60.2.

60.4 Add one drop of HCl (1 + 99) and 5 mL of sulfamic acid solution. Insert the electrodes into the solution, cover with a pair of split cover glasses, and electrolyze overnight at a current density of 0.5 A/dm^2, or for a short period at a current density of 4 A/dm^2 while stirring. After the blue color due to copper has disappeared, wash the cover glasses, electrodes, and

the sides of the beaker, and continue the electrolysis until deposition of the copper is complete, as indicated by failure to plate on a new surface when the level of the solution is raised. Rotating electrodes must be used at the higher current densities. The more rapid procedure requires the use of gauze electrodes.

60.5 When deposition of the copper is complete, with the current still flowing, lower the beaker slowly while washing the electrodes with water. Reserve the electrolyte.

60.6 Add 5 mL of HNO_3 and 10 mL of $HClO_4$ to the reserved electrolyte and evaporate to copious white fumes. Cool, add 100 mL of water, and heat to dissolve the soluble salts. If insoluble matter is present, filter the solution through a medium paper into a 600-mL beaker. If there is no insoluble matter, transfer the solution to a 600-mL beaker.

60.7 Add 10 mL of citric acid solution. Add NH_4OH until the blue color is formed, and then add 1 mL in excess. Dilute to 400 mL and heat to 60 °C to 70 °C.

60.8 Add 0.4 mL of sodium dimethylglyoximate solution for each milligram of nickel, plus 10 mL in excess. Stir the mixture vigorously and allow to cool to room temperature while stirring occasionally. Filter on a Gooch or fritted glass crucible of medium porosity which has been dried at 150 °C for 1 h and weighed. Wash with water 10 times to 12 times. Add 5 mL of sodium dimethylglyoximate solution to the filtrate and let stand overnight to make certain that the separation of the nickel is complete.

60.9 Dry the precipitate at 150 °C to constant weight. Cool in a desiccator and weigh as nickel dimethylglyoxime.

61. Calculation

61.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = [(A \times 0.2032)/B] \times 100 \quad (9)$$

where:

A = nickel dimethylglyoxime, g, and
B = sample used, g.

62. Precision and Bias

62.1 *Precision*—Eight laboratories cooperated in testing this test method, submitting eight pairs of values, and obtained the data summarized in Table 5. Although samples with nickel value near the upper limit of the scope were not available for testing, the precision data obtained for the other specimens should apply.

62.2 *Bias*—No information on the accuracy of this method is known, because at the time it was tested, no certified reference materials were available. Users are encouraged to employ suitable reference materials, if available, to verify the accuracy of the method in their laboratories.

TABLE 5 Statistical Information

Test Specimen	Nickel Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Cupro-nickel	29.74	0.12	0.14
2. Nickel-aluminum bronze	5.00	0.05	0.04

TIN BY THE IODOMETRIC TITRATION TEST METHOD

63. Scope

63.1 This test method covers the determination of tin in ranges from 0.5 % to 20 %.

63.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

64. Summary of Test Method

64.1 After dissolution of the sample in HCL and HNO_3, iron is added as a collector and tin is separated from copper by double precipitation with NH_4OH. The precipitate is dissolved in HCl and the tin is reduced with iron and nickel and titrated with a standard potassium iodate solution in an inert atmosphere. Starch is used to indicate the end point.

65. Interferences

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

66. Apparatus

66.1 *Apparatus for Reduction of Tin*—When tin is to be reduced to the stannous state and determined by titration with standard iodine or iodate solution, air must be excluded during the reduction and titration to prevent oxidation of the stannous tin. This exclusion of air is usually accomplished by keeping the solution under a blanket of gaseous CO_2 and may be accomplished in a variety of ways. One of the simplest methods is by means of the apparatus in which the reduction of the tin solution is made in a flask capped with a rubber stopper containing an L-shape siphon tube. When reduction is complete, the end of the siphon is dipped into a saturated solution of $NaHCO_3$ and set aside to cool. When cool, the stopper is removed and the solution titrated.

67. Reagents

67.1 *Ammonium Chloride Solution (10 g/L)*—Dissolve 10 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L.

67.2 *Ferric Chloride Solution (50 g/L)*—Dissolve 50 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in 5 mL of HCl and 995 mL of water.

67.3 *Iron,* metal powder, containing less than 0.001 % tin.

67.4 *Nickel,* sheet, containing less than 0.001 % tin and having an exposed surface area of at least 65 cm^2.

67.5 *Potassium Iodate, Standard Solution* (0.05 *N*)—Dry the crystals of potassium iodate (KIO_3) at 180 ºC to constant weight. Dissolve 1.785 g of the KIO_3 in 200 mL of water containing 1 g of sodium hydroxide (NaOH) and 10 g of potassium iodide (KI). When dissolution is complete, transfer

to a 1-L volumetric flask, dilute to volume, and mix. Standardize the solution as follows:

67.5.1 Using a pipet, transfer 50 mL of the tin solution (1 mL = 0.001 g Sn) to a 500-mL Erlenmeyer flask. Add 75 mL of HCl, 200 mL of water, and 2 g to 3 g of iron powder. Insert a roll of sheet nickel. Stopper the flask as described in 66.1. Boil the solution gently for 45 min.

67.5.2 Cool to about 10 °C while maintaining an atmosphere of CO_2 as described under the apparatus for the reduction of tin.

67.5.3 Add 5 mL of starch solution and titrate with KIO_3 solution until a blue color persists.

67.5.4 Determine a blank using the same amounts of all reagents but with the tin omitted. Calculate the tin equivalent of the KIO_3 solution as follows:

$$\text{Tin equivalent, g Sn/mL} = A/(B - C) \quad (10)$$

where:

A = tin titrated, g,
B = KIO_3 solution required to titrate tin, mL, and
C = KIO_3 solution required to titrate the blank, mL.

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

67.7 *Starch Solution (10 g/L)*—Add about 5 mL of water gradually to 1 g of soluble (or arrowroot) starch, with stirring, until a paste is formed, and add this to 100 mL of boiling water. Cool, add 5 g of potassium iodide (KI), and stir until the KI is dissolved. Prepare fresh as needed.

67.8 *Tin, Standard Solution (1 mL = 0.001 g Sn)*—Transfer 1.0000 g of tin (purity, 99.9 % minimum) to a 400-mL beaker, and cover. Add 300 mL of HCl (1 + 1) and warm gently until the metal is dissolved. If dissolution is difficult, add 0.5 g to 1.0 g of potassium chlorate ($KClO_3$). Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

68. Procedure

68.1 Select and weigh a sample as follows:

Tin, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.5 to 2.5	2	4
2.5 to 10.0	1	2
10.0 to 20.0	0.5	1

Transfer it to a 400-mL beaker.

68.2 Carry a reagent blank through the entire procedure using the same amount of all reagents, but with the sample omitted.

68.3 Add 5 mL of HCl and 20 mL of HNO_3 (1 + 1), plus an additional 5 mL of HCl and 5 mL of HNO_3 (1 + 1) for each gram of sample. Heat until dissolution is complete and then boil the solution for 2 min to 3 min. Add 100 mL of water and 10 mL of $FeCl_3$ solution.

68.4 Add NH_4OH (1 + 1) until the salts, which initially form, have been dissolved and the solution becomes clear dark blue. Heat to boiling to coagulate the precipitate. Filter on a 12.5-cm coarse paper and wash the beaker and paper alternately five times each with hot slightly ammoniacal NH_4Cl solution and water. Discard the filtrate. Place the original beaker beneath the funnel and dissolve the precipitate with hot HCl (1 + 1). Wash the paper several times with hot water and reserve the filter paper. Precipitate the iron and tin as before and heat to boiling to coagulate the precipitate. Wash the reserved filter paper three times with hot NH_4OH (1 + 99), collecting the washings in a 400-mL beaker, and then filter the hot solution containing the precipitated hydroxides of iron and tin into the 400-mL beaker containing the NH_4OH washings. Wash alternately five times each with hot, slightly ammoniacal NH_4Cl solution and water. Discard the filtrate. Transfer the paper and precipitate to a 500-mL Erlenmeyer flask.

68.5 Add 75 mL of HCl and gently swirl the flask to partially disintegrate the paper and to dissolve the precipitate. Add 200 mL of water and 2 g to 3 g of iron powder. Insert a roll of sheet nickel. Stopper the flask as described in 66.1. Boil the solution gently for 45 min.

68.6 Cool the solution to about 10 °C while maintaining an atmosphere of CO_2 as described in 66.1. Add 5 mL of KI solution and 5 mL of starch solution and titrate with KIO_3 solution until a blue color persists.

69. Calculation

69.1 Calculate the percentage of tin as follows:

$$\text{Tin, \%} = \frac{(A - B) \times C}{D} \times 100 \quad (11)$$

where:

A = KIO_3 solution required to titrate the tin in the sample, mL,
B = KIO_3 solution required to titrate the blank, mL,
C = the tin equivalent of the KIO_3 solution, and
D = sample used, g.

70. Precision and Bias

70.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 6. Although samples with tin values near the upper limit of the scope were not available for testing, the precision data obtained for the other specimens should apply.

70.2 *Bias*—No information on the accuracy of this method is known, because at the time it was tested, no certified reference materials were available. Users are encouraged to employ suitable reference materials, if available, to verify the accuracy of the method in their laboratories.

TABLE 6 Statistical Information

Test Specimen	Tin Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Tin bronze AAB521	7.51	0.14	0.23
2. Yellow brass AAB681	0.93	0.04	0.04
3. Yellow brass AAB681 + 20 % Pb	0.93	0.03	0.05

ALUMINUM BY THE CARBAMATE EXTRACTION-ETHYLENEDINITRILO TETRAACETATE TITRIMETRIC TEST METHOD

71. Scope

71.1 This test method covers the determination of aluminum in ranges from 2 % to 12 %.

71.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

72. Summary of Test Method

72.1 A diethyldithiocarbamate extraction at pH 5.5 removes antimony, cadmium, copper, iron, lead, manganese, nickel, tin, and zinc. Aluminum is chelated with an excess of a standard solution of disodium ethylenedinitrilo tetraacetate (EDTA) and then determined by back-titration with standard zinc solution.

73. Interferences

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

74. Apparatus

74.1 *Separatory Funnels,* 250-mL capacity with polytetrafluoroethylene stopcocks.

75. Reagents

75.1 *Buffer Solution*—Dissolve 250 g of ammonium acetate (CH_3COONH_4) in 600 mL of water and add 30 mL of glacial acetic acid (CH_3COOH). Dilute to 1 L and mix. Add 10 mL of buffer solution to 100 mL of water. Using a pH meter, check the pH of the solution which should be between 5.3 and 5.6. If it is not in the range, add sufficient CH_3COOH or NH_4OH to provide the desired pH.

75.2 *Diethyldithiocarbamate (DDC) Solution (100 g/L)*—Dissolve 100 g of diethyldithiocarbamic acid, disodium salt, in water, dilute to 1 L, and mix. Do not use a solution that is more than 24 h old.

75.3 *Disodium Ethylenedinitrilotetraacetate Dihydrate (EDTA), Standard Solution (0.05 M)*—Dissolve 18.613 g of disodium ethylenedinitrilo tetraacetate dihydrate in water, transfer to a 1-L volumetric flask, dilute to volume, and mix. The solution is stable for several months when stored in plastic or borosilicate glass bottles. Standardize the solution as follows:

75.3.1 Using a pipet, transfer 25 mL of the EDTA solution to a 400-mL beaker. Add 150 mL of water and 30 mL of the buffer solution. Add six drops to eight drops of xylenol orange indicator solution and titrate with standard zinc solution until the color changes from yellow to orange or pink.

75.3.2 Calculate the volume of EDTA standard solution equivalent to 1 mL of zinc standard solution as follows:

$$EDTA \text{ equivalent} = (A/B) \quad (12)$$

where:

A = EDTA solution, mL, and
B = zinc solution (0.0500 M), mL.

75.3.3 Calculate the molarity of the EDTA solution as follows:

$$Molarity,\ EDTA \text{ solution} = C \times 0.002 \quad (13)$$

where:

C = millilitres of zinc standard solution required to titrate 25.00 mL of EDTA standard solution.

75.4 *Sodium Tartrate Solution (250 g/L)*—Dissolve 250 g of sodium tartrate ($Na_2C_4H_4O_6{\cdot}2H_2O$) in water. Dilute to 1 L and mix.

75.5 *Xylenol Orange Indicator Solution (2 g/L)*—Dissolve 0.100 g of xylenol orange tetrasodium salt in 50 mL of water. Store in and dispense from a polyethylene dropping bottle.

75.6 *Zinc, Standard Solution (0.0500 M)*—Transfer 3.2690 g of zinc (purity: 99.9 % minimum) to a 1 L borosilicate volumetric flask. Add 50 mL of water and 20 mL of HCl and heat to dissolve. Cool, dilute to volume, and mix.

76. Procedure

76.1 Select and weigh a sample as follows:

Aluminum, %	Sample Weight, g	Tolerance in Sample Weight, mg
2.0 to 3.0	1.0	3.0
2.9 to 4.3	0.7	2.0
4.0 to 6.0	0.5	1.0
5.0 to 7.5	0.4	0.5
7.0 to 10.0	0.3	0.5
8.0 to 12.0	0.25	0.5

76.2 Transfer the sample to a 250-mL beaker, and add 5 mL of HCl (1 + 1), plus an additional 1 mL for each 0.1 g of sample over 0.25 g. Add H_2O_2 in 1-mL portions until the sample has been completely dissolved. Cover the beaker with a ribbed cover glass.

76.3 Boil gently and evaporate the excess acid until the color turns from a clear green to a brown-green. Cool. Remove and rinse the cover glass.

76.4 Add 50 mL of water and 5 mL of sodium tartrate solution. With swirling, add NH_4OH dropwise until the color changes from a clear green to a turquoise-green color (pH approximately 5.5). Add 30 mL of the buffer solution and mix.

76.5 Transfer the solution to a 500-mL separatory funnel and dilute to 125 mL to 150 mL. Add 8 mL of the DDC solution for each 0.1 g of sample used. Add 50 mL of $CHCl_3$. Shake the separatory funnel vigorously for 30 s and allow the phases to separate. Draw off the organic phase and discard, being careful to avoid any losses of the aqueous solution in this operation and the subsequent phase separations.

76.6 Add 5 mL of the DDC solution and 25 mL of $CHCl_3$ to the separatory funnel. Shake the separatory funnel vigorously for 30 s and allow the phases to separate. Add an additional 2 mL to 3 mL of the DDC solution to ensure that an excess of DDC has been added. If a precipitate appears, shake again, add 5 mL of the DDC solution, shake vigorously for 30 s and allow

the phases to separate. Repeat this extraction until no further precipitation occurs. Draw off and discard the organic phase.

76.7 Add 25 mL of the $CHCl_3$ and shake the separatory funnel for 15 s. Allow the phases to separate. Draw off and discard the organic phase. Repeat this step.

76.8 Transfer the aqueous layer quantitatively to a 500-mL Erlenmeyer flask. Rinse the separatory funnel with distilled water and transfer the rinsings to the flask.

76.9 Using a pipet, add 25 mL of EDTA solution, and mix. Boil gently for 3 min to 5 min to completely decompose any residual DDC and to chelate the aluminum. Cool to below 20 °C.

76.10 Add six drops to eight drops of xylenol orange indicator solution and mix.

76.10.1 If the solution is red, add CH_3COOH dropwise until the color just turns from red to yellow. Proceed as directed in 76.11.

76.10.2 If the solution is yellow, add NH_4OH dropwise just to the transition color from yellow to red. Then add acetic acid dropwise until the color just turns from red to yellow.

76.11 Titrate the excess EDTA with the standard zinc solution (0.0500 *M*) to the first color change from yellow to orange or pink.

77. Calculation

77.1 Calculate the percentage of aluminum as follows:

$$\text{Aluminum, \%} = \frac{[25.00 - (A \times B)] \times C \times 2.698}{D} \qquad (14)$$

where:

A = zinc solution required to titrate the excess EDTA in 76.11, mL,
B = EDTA equivalent to 1.00 millilitre of zinc standard solution, mL, 75.3.2,
C = molarity of EDTA solution, and
D = sample used, g.

78. Precision and Bias

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

78.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the certified reference material in Table 7. Users are encouraged to used this or similar reference materials to verify that the method is performing accurately in their laboratories.

TABLE 7 Statistical Information

Test Specimen	Aluminum Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
High tensile brass (BCS 179/1, 2.54 Al)	2.52	0.05	0.08
Manganese bronze, high tensile	5.29	0.04	0.08
Nickel-aluminum bronze	11.58	0.05	0.18

ZINC BY ATOMIC ABSORPTION SPECTROMETRY

79. Scope

79.1 This test method covers the determination of zinc in ranges from 0.02 % to 2 %.

79.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

80. Summary of Test Method

80.1 An acid solution of the sample is aspirated into the air-acetylene flame of an atomic absorption spectrometer. The absorption by the sample solution of the zinc resonance line energy of 213.8 nm is measured and compared with the absorption of calibration solutions containing known amounts of zinc.

81. Concentration Range

81.1 The concentration range of zinc must be determined experimentally because the optimum range will depend on the characteristics of the instrument used. Determine the appropriate concentration range as directed in 81.1.1 – 81.1.5.

81.1.1 Prepare a dilute standard solution as directed in 84.3.

81.1.2 Prepare the instrument for use as directed in 87.1. Measure the instrument response while aspirating a reference solution, the lowest, and the two highest calibration solutions. Apply the sensitivity test and curve linearity test as directed in 83.1.1 and 83.1.2, respectively.

81.1.3 If the criteria of sensitivity and of curve linearity are met, the initial concentration range may be considered acceptable. Proceed as directed in 81.1.5.

81.1.4 If the minimum response is not obtained, prepare a dilute standard solution to provide a higher concentration range and repeat 81.1.1 and 81.1.2. If the linearity criterion is not met, prepare a dilute standard solution to provide a concentration lower than that of the original standard solution and repeat 81.1.1 and 81.1.2. If a concentration range cannot be found for which both criteria are met, the instrument's performance must be improved before this method is used.

81.1.5 Perform the stability test as directed in 83.1.3. If the minimum requirements are not met with the selected calibration solutions, do not use this method until the desired stability is obtained.

82. Interferences

82.1 The elements ordinarily present do not interfere if their ranges are under the maximum limits shown in 1.1

83. Apparatus

83.1 *Atomic Absorption Spectrometer*—Determine that the atomic absorption spectrometer is satisfactory for use in this test method by proceeding as directed in 83.1.1 – 83.1.3. Optimum settings for the operating parameters of the atomic absorption spectrometer vary with the instrument used; use the

213.8 nm zinc line, a band pass of approximately 0.5 nm, and a lean air-acetylene flame.

83.1.1 *Sensitivity*—The difference between the readings of the two highest of eight equally spaced calibration solutions must be sufficient to permit an estimation equivalent to one fifth of the difference between the concentrations of the two solutions.

83.1.2 *Curve Linearity*—The difference between the readings of the two highest of eight equally spaced calibration solutions must be more than 0.7 times the difference between the reference solution and the lowest of the calibration solutions. Absorbance values shall be used in this calculation.

83.1.3 *Minimum Stability*—Obtain the readings of the reference solution and the highest calibration solution. Repeat at least twice with no change in parameters. The variability of the readings of the highest calibration solution and of the reference solution must be less than 3.0 % and 1.5 %, respectively, as calculated as follows:

$$V_C = \frac{100}{\bar{C}} \times \sqrt{\frac{\sum (C - \bar{C})^2}{n - 1}} \quad (15)$$

$$V_O = \frac{100}{\bar{C}} \times \sqrt{\frac{\sum (O - \bar{O})^2}{n - 1}} \quad (16)$$

where:

V_C = percent variability of the highest calibration readings,

$\bar{C}$ = average absorbance value for the highest calibration solution,

$\sum (C - \bar{C})^2$ = sum of the squares of the n differences between the absorbance readings of the highest calibration solution and their average,

$\bar{O}$ = average absorbance value of the reference solution,

V_O = percent variability of the readings on the reference solution relative to $\bar{C}$,

$\sum (O - \bar{O})^2$ = sum of the squares of the n difference between the absorbance readings of the reference solution and their average, and

n = number of determinations.

84. Reagents

84.1 *Dissolving Solution*—Add 250 mL of HNO_3 to 500 mL of water, mix, add 250 mL of HCl, and mix. Store in a plastic bottle. All plastic bottles used in the method must be well rinsed with the dissolving solution before use.

84.2 *Zinc, Standard Solution A (1 mL = 1.00 mg Zn)*—Dissolve 1.00 g of zinc metal (purity: 99.95 % minimum) in a covered 600-mL beaker with 50 mL of dissolving solution. Boil gently to remove gases, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Store in a plastic bottle.

84.3 *Zinc, Standard Solution B (1 mL = 0.004 mg Zn)*—Using a pipet, transfer 4 mL of Zinc Solution A to a 1-L volumetric flask, add 10 mL of dissolving solution, dilute to volume, and mix. Store in a plastic bottle. Do not use a solution that is more than 24 h old.

85. Calibration

85.1 *Calibration Solutions*—Using a 50-mL buret, transfer (4, 8, 12, 16, 20, 24, 28, and 32) mL of Zinc Solution B to 100-mL volumetric flasks. Add 2 mL of dissolving solution to each flask, dilute to volume, and mix.

85.2 *Reference Solution*—Add 2 mL of dissolving solution to a 100-mL volumetric flask, dilute to volume, and mix.

85.3 Determine the suitability of the selected composition range and apparatus as directed in Section 83.

86. Procedure

86.1 *Test Solution:*

86.1.1 Transfer a 1.00-g sample to a 400-mL beaker, cover, and add 20 mL of dissolving solution. Allow the initial reaction to subside. Heat gently to remove gases and to complete the dissolution. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Store in a plastic bottle.

86.1.2 Select the appropriate aliquot from the following table, and, using a pipet, transfer it to a 100-mL volumetric flask, add 2 mL of dissolving solution, dilute to volume, and mix.

Zinc Composition, %	Aliquot
0.02 to 0.1	use as prepared
0.1 to 0.25	50 mL
0.25 to 1.0	10 mL
1.0 to 2.0	5 mL

87. Measurements

87.1 *Instrument Adjustments:*

87.1.1 Set the parameters to the values suggested in 83.1 and light the burner.

87.1.2 Aspirate the highest calibration solution and optimize all adjustments to obtain maximum absorption.

87.1.3 Aspirate the reference solution to ensure stability and set the initial reading above, but near, zero.

87.2 Aspirate the test solution to determine its place in order of increasing value in the calibration solutions.

87.3 Aspirate the reference solution and adjust to the base reading. Aspirate the reference solution, the test solution, and calibration solutions, in the order of increasing readings.

87.4 Repeat 87.3 at least twice.

88. Calculation

88.1 Calculate the variability of the readings for the reference solution and the highest calibration solution as directed in 83.1.3 to determine whether they are less than 1.5 % and 3.0 %, respectively. If they are not, disregard the data, readjust the instrument, and proceed again as directed in 87.2.

88.2 If necessary, convert the average of the readings for each calibration solution to absorbance.

88.3 Prepare a calibration curve by plotting the average absorbance values for the calibration solutions against milligrams of zinc/100 mL.

88.4 Convert the absorbance value of the test solution to milligrams of zinc per 100 mL by means of the calibration curve.

TABLE 8 Statistical Information

Test Specimen	Zinc Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. 70-30 cupro-nickel alloy	0.965	0.0306	0.0391
2. Aluminum-bronze alloy (78 Cu-9 Al-5 Fe-5 Ni)	0.034	0.0009	0.003
3. NIST 52c, 2.12 % zinc	2.10	0.025	0.078
4. NIST 158a, 2.08 % zinc	2.09	0.039	0.108
5. 70-30 cupro-nickel alloy	0.129	0.007	0.017

88.5 Calculate the percentage of zinc as follows:

$$\text{Zinc, \%} = \frac{A}{B} \times 100 \quad (17)$$

where:

A = zinc/100 mL of the final test solution, mg, and
B = sample represented in 100 mL of the test solution taken for analysis, mg.

89. Precision and Bias

89.1 *Precision*—Eight laboratories cooperated in the testing of this test method and obtained the data summarized in Table 8. Supporting data are available from ASTM Headquarters.[5]

89.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the certified reference materials in Table 8. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

LEAD BY ATOMIC ABSORPTION SPECTROMETRY

90. Scope

90.1 This test method covers the determination of lead in rangesd from 0.002 % to 15 %.

90.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

91. Summary of Test Method

91.1 An acid solution of the sample is aspirated into the air-acetylene flame of an atomic absorption spectrometer. The absorption by the sample solution of the lead resonance line energy at 283.3 nm is measured and compared with the absorption of calibration solutions containing known amounts of lead.

92. Concentration Range

92.1 If the optimum concentration range is not known; determine it as directed in 92.2 – 92.4.3.

92.2 Prepare the reference and calibration solutions as directed in 96.1 and 96.2.

92.3 Prepare the instrument as directed in 94.1.1 – 94.1.6.

92.4 Perform the following instrument performance checks. Two pairs of calibration solutions are required for the instrument performance check. One pair of calibration solutions is at the low end of the calibration graph, where the lower one is the reference solution containing no analyte (S_0), and the other one is the calibration solution containing the lowest amount of analyte (S_1). For the other pair, the two calibration solutions containing the two highest amounts of analyte are used (S_4 and S_5). The difference in the analyte contents between S_1 and S_0 must be identical to the difference in the analyte contents between S_4 and S_5.

92.4.1 *Readability:*

92.4.1.1 Aspirate the two calibration solutions having the highest amounts of the analyte. Record the instrument readings and calculate the difference.

92.4.1.2 Divide the difference between the readings by 20. The readability of the instrument is acceptable for the procedure if this result is not less than the smallest effective interval which can be read or estimated on the instrument readout.

92.4.2 *Linearity of Instrument Response:*

92.4.2.1 Aspirate the two calibration solutions at the low end of the calibration graph. Record the readings and calculate the difference.

92.4.2.2 Divide the difference in the readings for the two calibration solutions of the highest value, as determined in 92.4.1.1, by the difference in the readings obtained between the two lowest value calibration solutions, as obtained in 92.4.2.1.

92.4.2.3 The linearity of the instrument response for the procedure is acceptable if this ratio is 0.70 or greater.

92.4.2.4 If the ratio is less than 0.70, further adjustments to the instrument may give acceptable results. Otherwise the operation range of the method shall be reduced by lowering the concentration of the calibration solution of the highest concentration.

92.4.3 If the criteria for readability and linearity are met, the initial concentration range may be considered acceptable. A sensitivity of 0.5 µg/mL at 0.0044 absorbance is widely obtained.

92.5 If adequate instrument response is not obtained, prepare a calibration solution to provide a higher value and repeat 92.4.1 – 92.4.1.2. If the linearity criterion is not met, prepare dilute standard solutions to provide a concentration range lower than that of the original standard solution and repeat 92.4.2 – 92.4.2.4.

92.6 *Stability:*

92.6.1 Aspirate HCl (1 + 19) and zero the instrument.

92.6.2 Aspirate the calibration solution with the highest analyte concentration and record the absorbance reading.

92.6.3 Aspirate HCl (1 + 19), HNO_3 (1 + 19), or deionized water. Observe the absorbance reading on this solution. The absorbance reading should return to zero. If it does not return to zero, re-zero the instrument.

92.6.4 Repeat the measurement of the calibration solution with the highest analyte concentration six times, aspirating HCl (1 + 19), HNO_3 (1 + 19), or deionized water between the readings but not adjusting any of the instrument settings.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1071.

92.6.5 The variability (*VA*), expressed as a percentage of the readings of the calibration solution with the highest analyte concentration is given by the following equation:

$$VA = \frac{100[0.40(A_h - A_l)]}{A} \quad (18)$$

where:

A = average instrument reading for the calibration solution with the highest matrix concentration, calculated from the six readings,
A_h = highest of the six instrument readings, and
A_l = lowest of the six instrument readings.

NOTE 5—$0.40\ (A_h - A_l)$ is an estimation of the standard deviation.

92.6.6 The instrument meets the stability requirements if the variability is less than 1.5 %.

NOTE 6—This test can also be applied to the other points on the calibration graph. It may also be applied to the evaluation of the stability of the instrument zero.

93. Interferences

93.1 The elements normally present do not interfere if their composition ranges are under the maximum limits shown in 1.1.

94. Apparatus

94.1 *Atomic Absorption Spectrometer*—Determine that the instrument is suitable for use by performing the steps in Section 92.

94.1.1 Set up the atomic absorption spectrometer to operate with the appropriate single slot laminar flow burner head in accordance with the manufacturer's instructions.

94.1.2 Use a single-element radiation source (hollow cathode or electrodeless discharge lamp) as the light source. Operate the lamp as directed by the manufacturer.

94.1.3 Light the burner and aspirate water until a thermal equilibrium is reached. Pass a cleaning wire through the nebulizer. Check the burner slot for any buildup which may clog the burner.

94.1.4 Aspirate a mid-range calibration solution and adjust the instrument to give optimum absorption. Use the wavelength setting specified in 94.1.7. Use the slit setting or bandpass recommended by the instrument manufacturer. Adjust the burner height and alignment for optimum absorption. The use of scale expansion may be necessary.

94.1.5 Adjust the nebulizer for maximum absorption.

94.1.6 Flush the burner system with HCl (1 +19), HNO_3 (1 + 19), or deionized water and zero the instrument.

94.1.7 *Operating Parameters:*

Wavelength	283.3 nm (Note 7)
Bandpass	about 0.5 nm
Gas mixture	air-acetylene
Flame type	lean

NOTE 7—For very low lead values, the resonance line energy at 217.0 nm may be used provided the criteria set forth in 92.1 are met.

95. Reagents

95.1 *Fluoroboric Acid* (37 % to 40 %).

95.2 *Lead, Standard Solution A (1 mL = 1.00 mg Pb)*—Dissolve 1.000 g of lead metal (purity: 99.9 % minimum) in a covered 150-mL beaker with 15 mL of HNO_3 (1 + 2). Transfer to a 1-L volumetric flask, add 100 mL of HNO_3 (1 + 2), dilute to volume, and mix. Store in a plastic bottle.

95.3 *Lead, Standard Solution B (1 mL = 0.200 mg Pb)*—Using a pipet, transfer 50 mL of Lead Solution A to a 250-mL volumetric flask. Dilute to volume and mix.

96. Calibration

96.1 Using pipets, transfer into individual 100-mL volumetric flasks (1, 2, 3, 4, and 5) mL of Lead Solution B. Add 5 mL of HNO_3 (1 + 2) to each flask, dilute to volume, and mix. These calibration solutions are S_1 through S_5 for the purpose of determining the optimum concentration range in Section 92.

96.2 *Reference Solution*—Add 5 mL of HNO_3 (1 + 2) to a 100-mL volumetric flask, dilute to volume, and mix. The reference solution is S_0 for the purpose of determining the optimum concentration range in Section 92.

96.3 Determine the suitability of the selected concentration range and apparatus as directed in Section 92.

97. Procedure

97.1 *Test Solution:*

97.1.1 Transfer a 1-g sample, weighed to the nearest 1 mg, to a 150-mL beaker, add 5 mL of HBF_4 and 15 mL of HNO_3 (1 + 2), and cover. Allow the initial reaction to subside. Heat gently to complete the dissolution and remove gases. Cool, transfer to a 1-L volumetric flask, add 50 mL of HNO_3 (1 + 2), dilute to volume, and mix.

97.1.2 Select an appropriate aliquot (nominal values) from the following table, and, using a pipet, transfer it to a 100-mL volumetric flask, add 5 mL HNO_3 (1 + 2), dilute to volume, and mix.

Lead Composition, %	Aliquot
0.002 to 0.60	use as prepared
0.50 to 3.00	20 mL
2.0 to 12.0	5 mL

98. Measurements

98.1 Optimize the response of the instrument and take preliminary readings; complete the analysis and calculate theamount of lead in the test solution by the procedure in 98.3, 98.4, or 98.5. For low levels of lead, expanded scale readout is advisable.

98.2 *Instrument Adjustments:*

98.2.1 Set the parameters to the values obtained in 94.1, light the burner, and aspirate water until the instrument comes to thermal equilibrium.

98.2.2 Aspirate a high-calibration solution and adjust parameters to obtain optimum absorption.

98.2.3 Aspirate the reference solution and adjust the instrument to zero. Aspirate the calibration solutions and make a preliminary record of the readings.

98.2.4 Aspirate the test solution to determine its place in the order of increasing concentration of the calibration solutions. Proceed as specified in 98.3 or 98.4.

98.3 *Graphical Procedure:*

98.3.1 Aspirate the reference solution until a steady signal is obtained and adjust the instrument to zero. Aspirate the calibration solutions and test solution in order of increasing absorbance and record the reading for each.

98.3.2 Aspirate water to flush the system and proceed as directed in 98.3.1 at least twice more.

98.3.3 Prepare a calibration curve by plotting the averages of the values obtained for the calibration solutions against the amounts of analyte.

98.3.4 Determine the amount of analyte in the test solution from the calibration curve.

98.4 *Ratio Procedure:*

98.4.1 Prepare two more calibration solutions (one only, if the absorbance reading for the test solution falls close to one of the earlier calibration solutions) such that they closely bracket the test solution. The portion of the analytical graph between the two calibration solution should effectively be a straight line.

98.4.2 With the instrument adjusted as in 98.2, aspirate the test solution and the closely bracketing calibration solutions in order of increasing absorbance without intervening water aspirations. Repeat at least twice and calculate the average absorbance values.

98.4.3 The concentration of the test solution may now be calculated by ratio:

$$C_t = C_l + \left[\frac{(A_t - A_l)}{(A_h - A_l)} \times (C_h - C_l) \right] \quad (19)$$

where:

C_t = concentration of analyte in the test solution,
C_h = concentration of analyte in the higher calibration solution,
C_l = concentration of analyte in the lower calibration solution,
A_t = absorbance reading of the test solution,
A_h = absorbance reading of the higher calibration solution, and
A_t = absorbance reading of the lower calibration solution.

98.5 *Computerized Procedure:*

98.5.1 If the instrument is provided with a microprocessor or a computer to calculate results, follow the instrument manufacturer's instructions.

TABLE 9 Statistical Information

Material	Average of Lead, %	Lowest Value of Lead Obtained, %	Highest Value of Lead Obtained, %
Copper (C102)	0.0037	0.0028	0.0052
Bronze (C544)	4.22	4.14	4.35
Bronze (C922)	2.00	1.93	2.06
Bronze (C939)	14.43	14.27	14.67

99. Calculation

99.1 Calculate the percentage of lead as follows:

$$\text{Lead, \%} = \frac{A}{B} \times 100 \quad (20)$$

where:

A = lead/100 mL of the final test solution, mg, and
B = sample represented in 100 mL of the test solution taken for analysis, mg.

100. Precision and Bias

100.1 *Precision*—Due to limited data, a precision statement conforming to the requirements of Practice E173 cannot be furnished. However, in a cooperative program conducted by six laboratories, the results reported in Table 9 were obtained. Supporting data are available from ASTM Headquarters.[6]

100.2 *Bias*—No information on the accuracy of this method is known, because at the time it was tested, no certified reference materials were available. Users are encouraged to employ suitable reference materials, if available to verify the accuracy of the method in their laboratories.

SILVER IN SILVER-BEARING COPPER BY ATOMIC ABSORPTION SPECTROMETRY

101. Scope

101.1 This test method covers the determination of silver in composition ranges from 0.01 % to 0.12 %.

101.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

102. Summary of Test Method

102.1 An acid solution of the sample is aspirated into the air-acetylene flame of an atomic absorption spectrometer. The absorption by the sample solution of the silver resonance line energy at 328.1 nm is measured and compared with the absorption by calibration solutions containing known amounts of silver.

103. Concentration Range

103.1 If the optimum concentration range is not known determine it as directed in 103.2 – 103.4.3.

103.2 Prepare the reference and calibration solutions as directed in 108.1 and 108.2.

103.3 Prepare the instrument as directed in 105.1.1 – 105.1.6.

103.4 Perform the following instrument performance checks. Two pairs of calibration solutions are required for the instrument performance check. One pair of calibration solutions is at the low end of the calibration graph, where the lower one is the reference solution containing no analyte (S_0), and the other one is the calibration solution containing the lowest amount of analyte (S_1). For the other pair, the two calibration solutions containing the two highest amounts of analyte are used (S_4 and S_5). The difference in the analyte contents

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1272.

between S_1 and S_0 must be identical to the difference in the analyte contents between S_4 and S_5.

103.4.1 *Readability:*

103.4.1.1 Aspirate the two calibration solutions having the highest amounts of the analyte. Record the instrument readings and calculate the difference.

103.4.1.2 Divide the difference between the readings by 20. The readability of the instrument is acceptable for the procedure if this result is not less than the smallest effective interval which can be read or estimated on the instrument readout.

103.4.2 *Linearity of Instrument Response:*

103.4.2.1 Aspirate the two calibration solutions at the low end of the calibration graph. Record the readings and calculate the difference.

103.4.2.2 Divide the difference in the readings for the two calibration solutions of the highest concentration, as determined in 103.4.1.1 by the difference in the readings obtained between the two low concentration calibration solutions, as obtained in 103.4.2.1.

103.4.2.3 The linearity of the instrument response for the procedure is acceptable if this ratio is 0.70 or greater.

103.4.2.4 If the ratio is less than 0.70, further adjustments to the instrument may give acceptable results. Otherwise the operation range of the method shall be reduced by lowering the amount in the calibration solution of the highest concentration.

103.4.3 If the criteria for readability and linearity are met, the initial concentration range may be considered acceptable.

103.5 If adequate instrument response is not obtained, prepare a calibration solution to provide a higher concentration and repeat 103.4.1 – 103.4.1.2. If the linearity criterion is not met, prepare dilute standard solutions to provide a concentration range lower than that of the original standard solution and repeat 103.4.2 – 103.4.2.4.

103.6 *Stability:*

103.6.1 Aspirate HNO_3 (1 + 19) and zero the instrument.

103.6.2 Aspirate the calibration solution with the highest analyte concentration and record the absorbance reading.

103.6.3 Aspirate HNO_3 (1 + 19) or deionized water. Observe the absorbance reading on this solution. The absorbance reading should return to zero. If it does not return to zero, re-zero the instrument.

103.6.4 Repeat the measurement of the calibration solution with the highest analyte concentration six times, aspirating HNO_3 (1 + 19) or deionized water between the readings but not adjusting any of the instrument settings.

103.6.5 The variability (*VA*), expressed as a percentage of the readings of the calibration solution with the highest analyte concentration is given by the following equation:

$$VA = \frac{100\left[0.40\left(A_h - A_l\right)\right]}{A} \qquad (21)$$

where:

A = average instrument reading for the calibration solution with the highest matrix concentration, calculated from the six readings,

A_h = highest of the six instrument readings, and

A_l = lowest of the six instrument readings.

NOTE 8—0.40 $(A_h - A_l)$ is an estimation of the standard deviation.

103.6.6 The instrument meets the stability requirements if the variability is less than 1.5 %.

NOTE 9—This test can also be applied to the other points on the calibration graph. It may also be applied to the evaluation of the stability of the instrument zero.

104. Interferences

104.1 Elements normally present in silver-bearing copper do not interfere. Contamination of the calibration or test solutions by halides may lead to the loss of silver. (Note that copper that has been soldered may contain a flux residue with a chloride constituent).

105. Apparatus

105.1 *Atomic Absorption Spectrometer*—Determine that the instrument is suitable for use as prescribed in Section 103.

105.1.1 Set up the atomic absorption spectrometer to operate with the appropriate single slot laminar flow burner head in accordance with the manufacturer's instructions.

105.1.2 Use a single-element radiation source (hollow cathode or electrodeless discharge lamp) as the light source. Operate the lamp as directed by the manufacturer.

105.1.3 Light the burner and aspirate water until a thermal equilibrium is reached. Pass a cleaning wire through the nebulizer. Check the burner slot for any buildup which may clog the burner.

105.1.4 Aspirate a mid-range calibration solution and adjust the instrument to give optimum absorption. Use the wavelength setting specified in 105.1.7. Use the slit setting or bandpass recommended by the instrument manufacturer. Adjust the burner height and alignment for optimum absorption. The use of scale expansion may be necessary.

105.1.5 Adjust the nebulizer for maximum absorption.

105.1.6 Flush the burner system with HNO_3 (1 + 19) or deionized water and zero the instrument.

105.1.7 *Operating Parameters:*

Wavelength	328.1 nm
Gas mixture	air – acetylene
Flame type	lean

106. Reagents

106.1 *Mercury Solution (3 g/L)*—Dissolve 3 g of mercury in 10 mL of HNO_3 (1 + 1). Warm gently to remove fumes, cool, add 25 mL HNO_3, and dilute to 1 L. Store in a plastic bottle.

106.2 *Silver, Standard Solution A (1 mL = 0.2 mg Ag)*—Dissolve 0.3150 g of silver nitrate ($AgNO_3$) (purity, 99.7 % minimum) in water. Transfer to a 1-L volumetric flask, add 100 mL of mercury solution (3 g/L) and 25 mL of HNO_3. Dilute to volume and mix. Store in a tightly sealed plastic bottle in a dark place. The solution is stable for one year.

106.3 *Silver, Standard Solution B (1 mL = 0.02 mg Ag)*—Using a pipet, transfer 25 mL of Silver Solution A to a 250-mL volumetric flask. Dilute to volume and mix. Prepare fresh prior to use.

107. Hazards

107.1 **Warning—**Mercury is a health hazard. Handling and disposal should be done in a safe manner.

108. Calibration

108.1 *Calibration Solutions*—Using pipets, transfer (1, 2, 3, 4, and 5) mL of Silver Solution B to 100-mL volumetric flasks. Add 10 mL of mercury solution (3 g/L) and 5 mL of HNO_3 (1 + 1) to each flask, dilute to volume, and mix. Store away from the light. These calibration solutions are S_1 through S_5 for the purpose of determining the optimum concentration range in Section 103.

108.2 *Reference Solution*—Add 10 mL of mercury solution (3 g/L) and 5 mL HNO_3 (1 + 1) to a 100-mL volumetric flask. Dilute to the mark and mix. The reference solution is S_0 for the purpose of determining the optimum concentration range in Section 103.

108.3 Determine the suitability of the selected concentration range and apparatus as directed in Section 103.

109. Procedure

109.1 *Test Solution*—Accurately weigh a sample (0.5 g or less) to contain up to 100 µg Ag. Transfer to a 150-mL beaker, add 8 mL of HNO_3 (1 + 1), and allow to dissolve. Warm gently to remove gasses, cool, and transfer to a 100-mL volumetric flask. Add 10 mL of mercury solution (3 g/L), dilute to volume, and mix.

110. Measurements

110.1 Optimize the response of the instrument and take preliminary readings; complete the analysis and calculate the amount of silver in the test solution by the procedure in 110.3, 110.4, or 110.5.

110.2 *Instrument Adjustments:*

110.2.1 Set the parameters to the values obtained in 105.1, light the burner, and aspirate water until the instrument comes to thermal equilibrium.

110.2.2 Aspirate a high-calibration solution and adjust parameters to obtain optimum absorption.

110.2.3 Aspirate the reference solution and adjust the instrument to zero. Aspirate the calibration solutions and make a preliminary record of the readings.

110.2.4 Aspirate the test solution to determine its place in the order of increasing concentration of the calibration solutions. Proceed as specified in 110.3 or 110.4.

110.3 *Graphical Procedure:*

110.3.1 Aspirate the reference solution until a steady signal is obtained and adjust the instrument to zero. Aspirate the calibration solutions and test solution in order of increasing absorbance and record the reading for each.

110.3.2 Aspirate water to flush the system and proceed as directed in 110.3.1 at least twice more.

110.3.3 Prepare a calibration curve by plotting the averages of the values obtained for the calibration solutions against the amount of analyte.

110.3.3.1 Determine the amount of analyte in the test solution from the calibration curve.

110.4 *Ratio Procedure:*

110.4.1 Prepare two more calibration solutions (one only, if the absorbance reading for the test solution falls close to one of the earlier calibration solutions) such that they closely bracket the test solution. The portion of the analytical graph between the two calibration solutions should effectively be a straight line.

110.4.2 With the instrument adjusted as in 110.2, aspirate the test solution and the closely bracketing calibration solutions in order of increasing absorbance without intervening water aspirations. Repeat at least twice and calculate the average absorbance values.

110.4.3 The concentration of the test solution may now be calculated by ratio:

$$C_t = C_l + \left[\frac{(A_t - A_l)}{(A_h - A_l)} \times (C_h - C_l) \right] \quad (22)$$

where:

C_t = concentration of analyte in the test solution,
C_h = concentration of analyte in the higher calibration solution,
C_l = concentration of analyte in the lower calibration solution,
A_t = absorbance reading of the test solution,
A_h = absorbance reading of the higher calibration solution, and
A_t = absorbance reading of the lower calibration solution.

110.5 *Computerized Procedure:*

110.5.1 If the instrument is provided with a microprocessor or a computer to calculate results, follow the instrument manufacturer's instructions.

111. Calculation

111.1 Calculate the percentage of silver as follows:

$$\text{Silver, \%} = \frac{A}{B} \times 100 \quad (23)$$

where:

A = silver per 100 mL of the final test solution, mg, and
B = sample represented in 100 mL of the test solution taken for analysis, mg.

111.2 If required, convert to troy ounces per short ton:

$$\text{Silver, \%} \times 291.7 = \text{silver, oz/ton} \quad (24)$$

112. Precision and Bias

112.1 *Precision*—Seven laboratories cooperated in testing this test method and obtained 9 sets of data summarized in Table 10. Supporting data are available from ASTM Headquarters.[7]

TABLE 10 Statistical Information

Test Specimen (Alloy Number)	Silver Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. C11600	0.0959	0.0039	0.0077
2. C11400	0.0383	0.0020	0.0038

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1088.

112.2 *Bias*—No information on the accuracy of this method is known, because at the time it was tested, no certified reference materials were available. Users are encouraged to employ suitable reference materials, if available, to verify the accuracy of the method in their laboratories.

TIN BY THE PHENYLFLUORONE SPECTROPHOTOMETRIC TEST METHOD

113. Scope

113.1 This test method covers the determination of tin in composition ranges from 0.01 % to 1.0 %.

113.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

114. Summary of Method

114.1 The sample is dissolved in HNO_3 and fluoroboric acids. Phenylfluorone in a $HClO_4$-sodium citrate-buffered solution reacts with the tin to form an orange-red complex. Spectrophotometric measurement is made at approximately 510 nm.

115. Concentration Range

115.1 The recommended concentration range is from 0.02 mg to 0.16 mg of tin in 100 mL of solution, using a 1-cm cell.

NOTE 10—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.

116. Stability of Color

116.1 Spectrophotometric measurement is made after 75 min ± 10 min.

117. Interferences

117.1 The elements ordinarily present do not interfere if their composition ranges are under the maximum limits shown in 1.1.

118. Apparatus

118.1 *pH Meter.*

119. Reagents

119.1 *Ascorbic Acid, Powder.*

119.2 *Boric Acid Solution (50 g/L)*—Dissolve 50 g of boric acid (H_3BO_3) in hot water, cool, and dilute to 1 L.

119.3 *Copper, High-Purity*—Use copper containing less than 0.0001 % tin.

119.4 *Fluoroboric Acid (HBF_4)* (49 % to 50 %).

119.5 *Gelatin Solution (10 g/L)*—While stirring, add 1 g of gelatin to 100 mL of boiling water. Do not use a solution that is more than one day old.

119.6 *$HClO_4$ Solution (9 + 31)*—Slowly add 225 mL of $HClO_4$ to a 1-L volumetric flask containing 500 mL of water, cool, dilute to volume, and mix.

119.7 *Phenylfluorone Solution (0.2 g/L)*—Dissolve 0.200 g of phenylfluorone (2,6,7-trihydroxy-9-phenylisoxanthene3-one)[8] in a mixture of 600 mL of 2-ethoxy-ethanol (ethylene glycol monoethyl ether), 30 mL of water, and 30 mL of $HClO_4$, while stirring with a magnetic stirrer. Dilute to 1 L with water. Do not use a solution that is more than one week old.

119.8 *Potassium Permanganate Solution (20 g/L)*—Dissolve 20 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L.

119.9 *Sodium Citrate Solution (100 g/L)*—Dissolve 100 g of sodium citrate dihydrate in water and dilute to 1 L.

119.10 *NaOH (250 g/L)*—Dissolve 250 g of NaOH in about 100 mL of water. When dissolution is complete, cool, and dilute to 1 L. Store in a plastic bottle.

119.11 *Tin, Standard Solution A (1 mL = 1.0 mg Sn)*—Dissolve 1.000 g of tin (purity: 99.9 % minimum) in a mixture of 25 mL of HNO_3, 25 mL of HCl, and 25 mL of HBF_4. When dissolution is complete, boil gently to expel oxides of nitrogen, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Store in a polyethylene bottle.

119.12 *Tin, Standard Solution B (1 mL = 0.005 mg Sn)*—Using a pipet, transfer 5 mL of Tin Solution A (mL = 1.0 mg of Sn) to a 1-L volumetric flask, add 25 mL of HBF_4 (1 + 9), dilute to volume, and mix. Do not use a solution that is more than one week old.

119.13 *Tin, Standard Solution C (1 mL = 0.010 mg Sn)*—Using a pipet, transfer 10 mL of Tin Solution A (1 mL = 1.0 mg Sn) to a 1-L volumetric flask, add 25 mL of HBF_4 (1 + 9), dilute to volume, and mix. Do not use a solution that is more than one week old.

120. Preparation of Calibration Curve

120.1 *Calibration Solutions*—Using pipets, transfer (5, 10, and 15) mL of Tin Solution B (1 mL = 0.005 mg Sn), and (10 and 15) mL of Tin Solution C (1 mL = 0.010 mg Sn) to 150-mL beakers. Proceed as directed in 120.3.

120.2 *Reference Solution*—Transfer 15 mL of water to a 150-mL beaker. Proceed as directed in 120.3.

120.3 *Color Development*—Adjust the volume to 15 mL with water and add 15 mL of sodium citrate solution. Using a pH meter, adjust the pH to 12 ± 0.25 with NaOH solution. Using a pipet, add 10 mL of $HClO_4$ (9 + 31) and, while stirring, add $KMnO_4$ solution until a pink color persists. Add 25 mL of H_3BO_3 solution and 5 mL of gelatin solution, 25 mg to 50 mg of ascorbic acid, and 10 mL of phenylfluorone solution. Transfer the solution to a 100-mL volumetric flask, dilute to volume, and mix. Allow to stand 75 min ± 10 min.

120.4 *Spectrophotometry:*

120.4.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 1-cm path and a light band

[8] Eastman No. 6346 has been found satisfactory for this purpose.

TABLE 11 Statistical Information

Test Specimen	Tin Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Copper-zinc-nickel (NIST 157a 0.021 Sn)	0.023	0.002	0.004
2. Tin-copper alloy (Kennecott 1784)	0.201	0.013	0.031
3. High tensile brass (BCS 179/1 0.54 Sn)	0.528	0.016	0.085
4. Silicon bronze (NIST 158a 0.96 Sn)	0.962	0.024	0.120
5. Anaconda brass (AABC 681)	0.952	0.042	0.114

centered at approximately 510 nm. Using the test cell, take spectrophotometric readings of the calibration solutions. Test absorption cells must be cleaned after each reading in a solution of dilute HNO_3 (1 + 4) to remove the colored complex that may adhere to the windows.

120.4.2 *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 510 nm. While maintaining this adjustment, take spectrophotometric readings of the calibration solutions.

120.5 *Calibration Curve*—Plot the net spectrophotometric readings of the calibration solutions against milligrams of tin per 100 mL of solution.

121. Procedure

121.1 *Test Solution:*

121.1.1 Select and weigh a sample as follows:

Tin, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.01 to 0.035	2.00	1.0	100	15
0.03 to 0.10	1.00	1.0	100	15
0.09 to 0.16	1.00	1.0	100	10
0.15 to 0.32	0.50	0.5	100	10
0.30 to 0.64	0.25	0.25	100	10
0.60 to 1.00	0.25	0.25	100	5

Transfer it to a 100-mL borosilicate volumetric flask.

121.1.2 Add 10 mL of HBF_4 (1 + 9) and 10 mL of HNO_3 (1 + 1). When dissolution is complete, heat the solution to boiling and continue to boil until oxides of nitrogen are removed. Cool, dilute to volume, and mix.

121.1.3 Using a pipet, transfer 5 mL to 15 mL portions, as specified in 121.1.1, to 150-mL beakers. Proceed as directed in 121.3.

121.2 *Reference Solution*—Transfer a weight of copper taken in 121.1.1 to a 100-mL borosilicate volumetric flask. Treat an aliquot the same size as that of the test solution as directed in 121.1.2. Proceed as directed in 121.3.

121.3 *Color Development*—Proceed as directed in 120.3.

121.4 *Spectrophotometry*—Proceed as directed in 120.4.

122. Calculation

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

$$\text{Tin, \%} = \frac{A}{B \times 10} \quad (25)$$

where:

A = tin found in 100 mL of the final test solution, mg, and

B = sample represented in 100 mL of the final test solution, g.

123. Precision and Bias

123.1 *Precision*—Eight laboratories cooperated in testing this test method with one laboratory reporting a second pair of values. The data are summarized in Table 11.

123.2 *Bias*—The accuracy of this method has been deemed satisfactory based on the data for the certified reference materials in Table 11. Users are encouraged to use these or similar reference materials to verify that the method is performing accurately in their laboratories.

124. Keywords

124.1 atomic absorption spectrometry; copper; spectrophotometric; titrimetric