Designation: E478 – 08 (Reappproved 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

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]

[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.

E255 Practice for Sampling Copper and Copper Alloys for the Determination of Chemical Composition
E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definitions of terms used in 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:

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

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:

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

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