Designation: E 478 – 03

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

This standard is issued under the fixed designation E 478; 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 Department of Defense.

1. Scope

1.1 These test methods cover the chemical analysis of copper alloys having chemical compositions within the following limits:[2]

Element	Concentration, %
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-(Ethylenedinitrilo) Tetraacetate Titrimetric Test Method [2 to 12 %]	70-77
Copper by the Combined Electrodeposition Gravimetric and Oxalyldihydrazide Photometric Test Method [50 %, minimum]	9-17
Iron by the 1,10-Phenanthroline Photometric Test Method [0.003 to 1.25 %]	18-27
Lead by the Atomic Absorption Test Method [0.002 to 15 %]	89-99
Lead by the (Ethylenedinitrilo)tetraacetic Acid (EDTA) Titrimetric Test Method [2.0 to 30.0 %]	28-35
Nickel by the Dimethylglyoxime Extraction Photometric Test Method [0.03 to 5.0 %]	36-45
Nickel by the Dimethylglyoxime Gravimetric Test Method [4 to 50 %]	54-61
Silver in Silver-Bearing Copper by the Atomic Absorption Test Method [0.01 to 0.12 %]	100-111
Tin by the Iodatimetric Titration Test Method [0.5 to 20 %]	62-69
Tin by the Phenylfluorone Photometric Test Method [0.01 to 1.0 %]	112-122
Zinc by Atomic Spectrometry [0.2 to 2 %]	78-88
Zinc by the (Ethylenedinitrilo)tetraacetic Acid (EDTA) Titrimetric Test Method [2 to 40 %]	46-53

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[4]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[4]

E 255 Practice for Sampling Copper and Copper Alloys for Determination of Chemical Composition[4]

E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry[4]

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method[4]

3. Significance and Use

3.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with compositional 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.

4. Apparatus, Reagents, and Photometric Practice

4.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The

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

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

[3] *Annual Book of ASTM Standards,* Vol 14.02.

[4] *Annual Book of ASTM Standards,* Vol 03.05.

apparatus, standard solutions, and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50, except that photometers shall conform to the requirements prescribed in Practice E 60.

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

5. Hazards

5.1 Specific hazard statements are given in Section 5, Note 4, and Section 106.

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

6. Sampling

6.1 For procedures for sampling the material, refer to Practice E 255. However, this method does not supersede any sampling requirements specified in a specific ASTM material specification.

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places as directed in Practice E 29.

8. Interlaboratory Studies

8.1 These test methods were evaluated in accordance with Practice E 173 unless otherwise noted in the precision section. E 173 has been replaced by Practice E 1601. The Reproducibility Index R_2 corresponds to the Reproducibility Index R of Practice E 1601. Likewise the Repeatability Index R_1 of E 173 corresponds to Repeatablility Index r of Practice E 1601.

COPPER BY THE COMBINED ELECTRODEPOSITION GRAVIMETRIC AND OXALYLDIHYDRAZIDE PHOTOMETRIC TEST METHOD

9. Scope

9.1 This test method covers the determination of copper in concentrations greater than 50 %.

10. Summary of Test Method

10.1 After dissolution of the sample in nitric and hydrofluoric acids, 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.

11. Interferences

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

12. Apparatus

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

12.2 *Polytetrafluoroethylene or Polypropylene Split Covers*.

12.3 *Electrodes for Electroanalysis*—Platinum electrodes of the stationary type are recommended as described in 12.3.1 and 12.3.2, but strict adherence to the exact size and shape of the electrodes is not mandatory. When agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes, generally available, may be employed. The surface of the platinum electrodes should be smooth, clean and bright to promote uniform deposition and good adherence. Sandblasting is not recommended.

12.3.1 *Cathodes*—Platinum cathodes may be formed either from plain or perforated sheets or from wire gauze, and may be either open or closed cylinders. Gauze cathodes are recommended, and shall be made preferably from 50-mesh gauze woven from wire approximately 0.21 mm (0.0085 in.) in diameter. The cathode should be stiffened by doubling the gauze for about 3 mm at the top and the bottom of the cylinder or by reinforcing the gauze at the top and bottom with a platinum band or ring. 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 1.30 mm. It should be flattened and welded the entire length of the gauze. The over-all 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.

12.3.2 *Anodes*—Platinum anodes may be of the 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 amounts not over 0.2 %). When used in analyses where both cathodic and anodic plates are to be determined, the anodes should be of wire gauze. Spiral anodes should be made from 1.00-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, the over-all height being approximately 130 mm. A spiral anode of this description will have a surface area of 9 cm^2. Platinum gauze anodes should be made of the same material and of the same general design as platinum gauze cathodes. The anode cylinder should be approximately 12 mm in diameter and 50 mm in height and the over-all height of the anode should be approximately 130 mm. A gauze anode of these dimensions will have a surface area of 54 cm^2. Both areas are exclusive of the stem.

12.3.3 Gauze cathodes are recommended where rapid electrolysis is used.

13. Reagents

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

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

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

14. Procedure

14.1 Transfer a 2.000-g sample, weighed to the nearest 0.1 mg, to a 250-mL poly(tetrafluoroethylene) 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.

14.2 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.

14.3 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).

14.4 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 to 5 min.

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

14.6 Allow the electrode to cool to room temperature, and weigh.

15. Calculation

15.1 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 16.10, g, and
C = sample used, g.

16. Photometric Determination of the Residual Copper in the Electrolyte

16.1 *Interferences*—The elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

16.2 *Concentration Range*—The recommended concentration range is from 0.0025 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.

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

16.4 *Reagents*:

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

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

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

16.4.4 *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 till nearly to dryness. Add 5 mL of water to dissolve the residue. Transfer to a 1-L volumetric flask, dilute to volume, and mix.

16.4.5 *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.

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

16.5 *Preparation of Calibration Curve*:

16.5.1 *Calibration Solutions*:

16.5.1.1 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.

16.5.1.2 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 16.5.3.

16.5.2 *Reference Solution*—Add 10 mL of boric acid solution prepared as directed in 16.5.1.1 to a 50-mL volumetric flask and proceed as directed in 16.5.3.

16.5.3 *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 16.5.4.

16.5.4 *Photometry*:

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

16.5.4.2 *Single-Cell Photometer*—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 540 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

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

16.6 *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 (Note 2). Proceed as directed in 16.8.

NOTE 2—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 16.8.

16.7 *Reference Solution*—Proceed as directed in 16.5.2.

16.8 *Color Development*—Proceed as directed in 16.5.3.

16.9 *Photometry*—Take the photometric reading of the test solution as directed in 16.5.4.

16.10 *Calculation*—Convert the net photometric 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.

17. Precision and Bias

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

TABLE 1 Statistical Information

Test Specimen	Copper Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
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

17.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the standard 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 PHOTOMETRIC TEST METHOD

18. Scope

18.1 This test method covers the determination of iron in concentrations from 0.003 to 1.25 %.

19. Summary of Test Method

19.1 The sample is dissolved in hydrochloric acid 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. Photometric measurement is made at approximately 510 nm.

20. Concentration Range

20.1 The recommended concentration range is from 0.005 to 0.125 mg of iron per 50 mL of solution, using a 2-cm cell.

NOTE 3—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.

21. Stability of Color

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

22. Interferences

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

23. Reagents

23.1 *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.

23.2 *Iron, Standard Solution A (1 mL = 0.125 mg Fe)*—Transfer 0.125 g of iron (purity: 99.9 % min) 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.

23.3 *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.

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

23.5 *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. Preparation of Calibration Curve

24.1 *Calibration Solutions*:

24.1.1 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.

24.1.2 Add 20 mL of $NH_2OH{\cdot}HCl$ solution, mix, and allow to stand 1 min. Proceed as directed in 24.3.

24.2 *Reference Solution*—Transfer 20 mL of water to a 50-mL volumetric flask and proceed as directed in 24.1.2.

24.3 *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.

24.4 *Photometry*:

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

24.4.2 *Single-Cell Photometer*—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 photometric readings of the calibration solutions.

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

25. Procedure

25.1 *Test Solution*:

25.1.1 Select and weigh a sample in accordance with the following:

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 poly(tetrafluoroethylene) beaker if HF is to be used.

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

25.1.3 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.

25.1.4 Using a pipet, transfer an aliquot in accordance with 25.1.1 to a 125-mL conical separatory funnel. Add HCl (1 + 1), as required, to adjust the volume to 25 mL.

25.1.5 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 3 times with 3 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 $NH_2OH{\cdot}HCl$ solution. Transfer the aqueous phase to a 50-mL volumetric flask. Repeat the extraction with a second 10-mL portion of $NH_2OH{\cdot}HCl$ solution, and transfer the extract to the 50-mL flask.

25.2 *Reference Solution*—Use the reagent blank solution prepared as directed in 25.1.2.

25.3 *Color Development*—Proceed as directed in 24.3.

25.4 *Photometry*—Proceed as directed in 24.4.

26. Calculation

26.1 Convert the net photometric 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.

27. Precision and Bias

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

27.2 *Bias*—The accuracy of this method has been deemed satisfactory based upon the data for the standard 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.

TABLE 2 Statistical Information

Test Specimen	Iron Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
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

LEAD BY THE (ETHYLENEDINITRILO)TETRAACETIC ACID (EDTA) TITRIMETRIC TEST METHOD

28. Scope

28.1 This test method covers the determination of lead in concentrations from 2.0 to 30.0 %.

29. Summary of Test Method

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

30. Interferences

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

31. Apparatus

31.1 *Separatory Funnels*, 250-mL capacity.

31.2 *Magnetic Stirrer and Poly(tetrafluoroethylene)-Covered Magnetic Stirring Bar*.

32. Reagents

32.1 *Ascorbic Acid*.

32.2 *Chloroform* ($CHCl_3$).

32.3 *Disodium (Ethylenedinitrilo) tetraacetic 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 33.7. 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.

32.4 *Fluoboric Acid* (37 to 40 %).

32.5 *Hexamethylenetetramine*.

32.6 *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.

32.7 *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.

NOTE 4—**Caution:** 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 Section 6 of Practices E 50.

32.8 *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 has stood more than 24 h.

32.9 *Sodium Hydroxide Solution (250 g/L)*—Dissolve 250 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Store in a plastic bottle.

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

32.11 *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.

33. Procedure

33.1 Select a sample in accordance with the following:

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.

33.2 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.

33.3 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 (**Caution,** Note 4), mixing after each addition. Cool to room temperature.

33.4 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 33.5. 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.

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

33.6 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 to 3 mL. Wash the cover and walls of the beaker, dilute to 100 mL, and heat to dissolve salts.

33.7 Place the beaker on a magnetic stirrer and stir (Note 5). Add 10 to 20 mg of ascorbic acid and 3 or 4 drops of xylenol orange solution. Add enough hexamethylenetetramine to color the solution purple. Add 4 or 5 drops of NaCN solution (**Caution,** Note 4) and titrate with the EDTA solution. When a yellow color begins to appear, stop the titration and add 2 to 3 g of hexamethylenetetramine and a drop of xylenol orange solution. Titrate dropwise until the color changes from purplish-red to yellow.

NOTE 5—The titration may be performed in either a hot or cold solution.

34. Calculation

34.1 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.

35. Precision and Bias

35.1 *Precision*—Due to limited data, a precision statement conforming to the requirements of Practices E 173 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 %.

35.2 *Bias*—No information on the accuracy of this method is known, because at the time it was tested, no standard 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 PHOTOMETRIC TEST METHOD

36. Scope

36.1 This test method covers the determination of nickel in concentrations from 0.03 to 5.0 %.

37. Summary of Test Method

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

38. Concentration Range

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

NOTE 6—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.

39. Stability of Color

39.1 The color is stable for at least 2 h.

40. Interferences

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

41. Reagents

41.1 *Chloroform* ($CHCl_3$).