Designation: E62 – 89 (Reapproved 2004)

Standard Test Methods for Chemical Analysis of Copper and Copper Alloys (Photometric Methods)[1]

This standard is issued under the fixed designation E62; 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 photometric procedures for the chemical analysis of copper and copper alloys having chemical compositions within the following limits:

Copper, %	50 and over
Tin, %	0.0 to 20
Lead, %	0.0 to 27
Iron, %	0.0 to 4
Manganese, %	0.0 to 6
Silicon, %	0.0 to 5
Aluminum, %	0.0 to 12
Nickel, %	0.0 to 5
Sulfur, %	0.0 to 0.1
Phosphorus, %	0.0 to 1.0
Arsenic, %	0.0 to 1.0
Antimony, %	0.0 to 1.0
Zinc	remainder

1.2 The analytical procedures appear in the following order:

Antimony by the Iodoantimonite (Photometric) Test Method	70 to 79
Arsenic in Fire-Refined Copper by the Molybdate Test Method	60 to 69
Iron by the Thiocyanate Test Method	1a
Manganese by the Periodate Test Method	41 to 48
Nickel by the Dimethylglyoxime-Extraction Photometric Test Method	1a
Phosphorus by the Molybdivanadophosphoric Acid Method:	
Deoxidized Copper and Phosphorized Brasses	17 to 24
Copper-Base Alloys Containing 0.01 to 1.2 % Phosphorus	25 to 33
Tin by the Phenylfluorone Photometric Test Method	80 to 90
Silicon by the Molybdisilicic Acid Test Method	49 to 59

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.* For precautions to be observed in the use of certain reagents, refer to Practices E50.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition
E60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry
E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition
E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[3]

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

[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 E01.05 Cu, Pb, Zn, Cd, Sn, Be, their Alloys, and Related Metals on Cu, Pb, Zn, Cd, Sn, Be, their Alloys and Related Metals.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

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. Photometric Practice, Apparatus, and Reagents

4.1 *Photometers and Photometric Practice*—Photometers and photometric practice prescribed in these test methods shall conform to Practice E60.

4.2 Apparatus other than photometers, 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 E50.

5. Sampling

5.1 Wrought products shall be sampled in accordance with Practice E55. Cast products shall be sampled in accordance with Practice E88.

6. Rounding Calculated Values

6.1 Calculated values shall be rounded to the desired number of places in accordance with the rounding method given in 3.4 and 3.5 of Practice E29.

NICKEL BY THE DIMETHYLGLYOXIME-EXTRACTION PHOTOMETRIC TEST METHOD

(This test method, which consisted of Sections 7 through 16 of this standard, was discontinued in 1975.)

PHOSPHORUS BY THE MOLYBDIVANADOPHOSPHORIC ACID TEST METHOD

(Deoxidized Copper and Phosphorized Brasses)

17. Principle of Test Method

17.1 A yellow-colored complex is formed when an excess of molybdate solution is added to an acidified mixture of a vanadate and an ortho-phosphate. Photometric measurement is made at approximately 420 nm.

18. Concentration Range

18.1 The recommended concentration range is from 0.04 to 1.0 mg of phosphorus in 50 mL of solution, using a cell depth of 1 cm.

NOTE 1—This procedure has been written for a cell 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.

19. Stability of Color

19.1 The color of the phosphorus complex develops within 5 min and is stable for at least 1 h.

20. Interfering Elements

20.1 The elements ordinarily present in deoxidized copper and phosphorized brasses do not interfere, with the possible exception of tin.[4]

21. Reagents

21.1 *Ammonium Molybdate Solution* (95 g $(NH_4)_6Mo_7$-O_{24}/L)—Dissolve 100 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 600 mL of water at 50°C, and dilute to 1 L. Filter before using.

21.2 *Ammonium Vanadate Solution* (2.5 g NH_4VO_3/L)—Dissolve 2.50 g of NH_4VO_3 in 500 mL of hot water. When solution is complete, add 20 mL of HNO_3 (1+1) cool, and dilute to 1 L.

21.3 *Copper (low-phosphorus)*—Copper containing under 0.0002 % of phosphorus.

21.4 *Hydrogen Peroxide* (3 %)—Dilute 10 mL of H_2O_2(30 %) to 100 mL. Store in a dark bottle in a cool place.

21.5 *Potassium Permanganate Solution* (10 g $KMnO_4$/L).

21.6 *Standard Phosphorus Solution* (1 mL = 0.05 mg P)—Dissolve 0.2292 g of Na_2HPO_4 in about 200 mL of water. Add 100 mL of HNO_3 (1+5) and dilute to 1 L in a volumetric flask.

22. Preparation of Calibration Curve

22.1 Transfer a 1.000-g portion of low-phosphorus copper to each of six 150-mL beakers.

22.2 Add exactly 10 mL of HNO_3 (2 + 3) to each beaker. Cover and let stand on a steam bath until dissolution is complete.

22.3 Carry one portion through as a blank, and to the others add 1.0, 5.0, 10.0, 15.0, and 20.0-mL aliquots of phosphorus solution (1 mL = 0.05 mg P).

22.4 Boil the covered solutions, including the blank, for about 1 min to expel brown fumes. Avoid vigorous or prolonged boiling, since excessive loss of HNO_3 will affect subsequent color development. Add 2 mL of $KMnO_4$ (10 g/L) and heat just to boiling. Add 1 mL of H_2O_2 (3 %) and swirl the sample until excess $KMnO_4$ is destroyed and the solution clears. Add 2 mL of ammonium vanadate (2.5 g/L) and boil gently until the solution is a clear blue, which indicates that excess H_2O_2 has been destroyed. Cool to room temperature, transfer to a 50-mL volumetric flask, and add 2 mL of ammonium molybdate (95 g/L). Dilute to the mark, mix thoroughly, and allow to stand 5 min.

22.5 Transfer a suitable portion of the solution to an absorption cell and measure the transmittance or absorbance at approximately 420 nm. Compensate or correct for the blank.

22.6 Plot the values obtained against milligrams of phosphorus per 50 mL of solution.

[4] For the determination of phosphorus in the presence of tin, see Sections 25 to 32.

23. Procedure for Deoxidized Copper

23.1 Transfer 1.000 g of the sample (Note 2) to a 150-mL beaker. Transfer 1.000 g of low-phosphorus copper to a second beaker and carry through as a blank. Continue in accordance with 22.2, 22.4, and 22.5.

NOTE 2—If tin is present, the time of boiling and period of digestion should be controlled carefully to avoid appreciable reduction of fluoride content and resultant precipitation of tin.

23.2 Using the value obtained, read from the calibration curve the number of milligrams of phosphorus present in the sample.

23.3 *Calculation*—Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, } \% = A/(B \times 10)$$

where:
A = phosphorus, mg, and
B = sample used, g.

24. Procedure for Phosphorized Brasses

24.1 Transfer a portion of the sample containing 1.000 g of copper (Note 3) to a 150-mL beaker. Transfer 1.000 g of low-phosphorus copper to a second beaker and carry through as a blank. Continue as directed in Section 23, except that in dissolving, add an additional 0.7 mL of HNO_3 (2+3) for each 0.1 g of sample over 100 g.

NOTE 3—Since $Cu(NO_3)_2$ shows a slight absorption at 420 nm, it is desirable that the amount of copper present in the sample be approximately the same as that present in the solutions used for the preparation of the calibration curve, as well as that present in the blank.

PHOSPHORUS BY THE MOLYBDIVANADOPHOSPHORIC ACID TEST METHOD

(Copper Alloys containing 0.01 to 1.2 % of Phosphorus, with or without Tin)

25. Principle of Test Method

25.1 A yellow-colored complex is formed when an excess of molybdate solution is added to an acidified mixture of a vanadate and an ortho-phosphate. Photometric measurement is made at approximately 470 nm.

26. Concentration Range

26.1 The recommended concentration range for low phosphorus contents is from 0.1 to 2 mg of phosphorus in 50 mL of solution, and for high phosphorus contents is from 0.3 to 6 mg of phosphorus in 100 mL of solution, using a cell depth of 1 cm (see Note 1).

27. Stability of Color

27.1 The color of the phosphorus complex develops within 5 min and is stable for at least 1 h.

28. Interfering Elements

28.1 Iron causes a slight interference (Note 4). Silicon and arsenic do not interfere when present in amounts up to about 1 %, but higher amounts of silicon cause interference by the formation of a turbid solution (Note 5).

NOTE 4—The interference of iron may be avoided by using a portion of the sample for the blank and adding all reagents as prescribed in Section 32, with the exception of the molybdate solution. If electrolytic copper is used for the blank, a correction factor should be determined and applied.

NOTE 5—Silver, if present in amounts over approximately 0.03 % (about 10 oz/ton), may cause interference by the formation of a turbid solution.

29. Reagents

29.1 *Ammonium Molybdate Solution* (95 g $(NH_4)_6Mo_7O_{24}$/L)—Dissolve 100 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 600 mL of water at 50°C, and dilute to 1 L. Filter before using.

29.2 *Ammonium Vanadate Solution* (2.5 g NH_4VO_3/L)—Dissolve 2.50 g of NH_4VO_3 in 500 mL of hot water. When solution is complete, add 20 mL of HNO_3 (1+1), cool, and dilute to 1 L.

29.3 *Copper (low-phosphorus)*—Copper containing under 0.0002 % of phosphorus.

29.4 *Hydrogen Peroxide* (3 %)—Dilute 10 mL of H_2O_2(30 %) to 100 mL. Store in a dark bottle in a cool place.

29.5 *Mixed Acids*—Add 320 mL of HNO_3 and 120 mL of HCl to 500 mL of water. Cool, dilute to 1 L, and mix.

29.6 *Standard Phosphorus Solution* (1 mL = 0.05 mg P)—Dilute one volume of phosphorus solution (1 mL = 0.4 mg P) with seven volumes of water.

29.7 *Standard Phosphorus Solution* (1 mL = 0.2 mg P)—Dilute one volume of phosphorus solution (1 mL = 0.4 mg P) with one volume of water.

29.8 *Standard Phosphorus Solution* (1 mL = 0.4 mg P)—Dissolve 1.8312 g of Na_2HPO_4 in about 200 mL of water. Add 100 mL of HNO_3 (1 + 5) and dilute to 1 L in a volumetric flask.

30. Preparation of Calibration Curve for Alloys Containing 0.01 to 0.2 % of Phosphorus

30.1 Transfer 1.00 g of low-phosphorus copper to each of ten 150-mL beakers. Transfer 2.0, 4.0, 6.0, 8.0, and 10.0-mL aliquots of phosphorus solution (1 mL = 0.05 mg P) to five of the beakers and transfer 4.0, 6.0, 8.0, and 10.0-mL aliquots of phosphorus solution (1 mL = 0.2 mg P) to four of the beakers. Carry the tenth through as a blank.

30.2 Add 15.0 mL of the mixed acids (Note 6) and add a few glass beads. Cover and heat moderately until dissolution is complete.

NOTE 6—The mixed acids should be measured accurately, since the time required for full color development is dependent on the pH of the solution.

30.3 Add 1 mL of H_2O_2 (3 %) to the solution, and boil gently for 3 to 5 min, avoiding vigorous or prolonged boiling, since excessive loss of acid will affect the subsequent color development. Remove from heat, add 5 mL of ammonium vanadate (2.5 g/L), cool to room temperature, and transfer to a 50-mL volumetric flask. Add 5 mL of ammonium molybdate (95 g/L), dilute to 50 mL, and mix thoroughly. Allow to stand for 5 min.

30.4 Transfer a suitable portion of the solution to an absorption cell, and measure the transmittancy or absorbancy at approximately 470 nm. Compensate or correct for the blank.

30.5 Plot the values obtained against milligrams of phosphorus per 50 mL of solution.

31. Preparation of Calibration Curve for Alloys Containing 0.06 to 1.2 % of Phosphorus

31.1 Transfer 0.500 g of low-phosphorus copper to each of nine 150-mL beakers. Transfer 1.0, 2.0, 3.0, 5.0, and 10.0-mL aliquots of phosphorus solution (1 mL = 0.2 mg P) to five of the beakers and transfer 8.0, 10.0, and 15.0-mL aliquots of phosphorus solution (1 mL = 0.4 mg P) to three of the beakers. Carry the ninth through as a blank.

31.2 Add 20.0 mL of the mixed acids (Note 6) and a few grains of silicon carbide. Cover and heat moderately until dissolution is complete.

31.3 Add 1 mL of H_2O_2 (3 %) to the solution, and boil gently for 3 to 5 min, avoiding vigorous or prolonged boiling, since excessive loss of acid will affect the subsequent color development. Remove from heat, add 10 mL of ammonium vanadate (2.5 g/L), cool to room temperature, and transfer to a 100-mL volumetric flask. Add 10 mL of ammonium molybdate (95 g/L), dilute to 100 mL, and mix thoroughly. Allow to stand for 5 min.

31.4 Transfer a suitable portion of the solution to an absorption cell, and measure the transmittance or absorbance at approximately 470 nm. Compensate or correct for the blank.

31.5 Plot the values obtained against milligrams of phosphorus per 100 mL of solution.

32. Procedure

32.1 If the phosphorus content of the sample is from 0.01 to 0.2 %, transfer to a 150-mL beaker, 1.00 g of the sample in the form of fine drillings or sawings. To a second beaker transfer 1.00 g of low-phosphorus copper for a blank (see Note 4). Continue as directed in 30.2–30.4.

32.2 If the phosphorus content of the sample is from 0.06 to 1.2 %, transfer to a 150-mL beaker, 0.500 g of the sample in the form of fine drillings or sawings. To a second beaker transfer 0.500 g of low-phosphorus copper for a blank (see Note 4). Continue as directed in 31.2–31.4.

32.3 Using the value obtained, read from the proper calibration curve the number of milligrams of phosphorus present in the sample.

32.4 *Calculation*—Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, } \% = A/(B \times 10)$$

where:
A = phosphorus, mg, and
B = sample used, g.

33. Precision and Bias

33.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data is no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method is adequate for the contemplated use.

IRON BY THE THIOCYANATE TEST METHOD

(This test method, which consisted of Sections 34 through 40 of this standard, was discontinued in 1975.)

MANGANESE BY THE PERIODATE TEST METHOD (For Manganese Bronze)

41. Principle of Test Method

41.1 Manganese in an acid solution is oxidized to permanganate by means of potassium periodate. Photometric measurement is made at approximately 520 nm.

42. Concentration Range

42.1 The recommended concentration range is from 0.1 to 2 mg of manganese in 100 mL of solution, using a cell depth of 1 cm (see Note 1).

43. Stability of Color

43.1 The permanganate color is stable indefinitely if reducing agents are absent.

44. Interfering Elements

44.1 The elements ordinarily present in copper alloys do not interfere if their contents are under the maximum limits shown in 1.1, provided that the proper acid mixture is used for dissolving the sample.

45. Reagents

45.1 *Copper (manganese-free)*—Copper containing under 0.0001 % of manganese.

45.2 *Hydrofluoric-Boric Acid Mixture*—Add 200 mL of HF to 1800 mL of a saturated solution of H_3BO_3 and mix. This mixture can be stored in glass.

45.3 *Standard Manganese Solution* (1 mL = 0.10 mg Mn)—Dissolve 0.100 g of high-purity manganese in 10 mL of HNO_3

(1+1) and boil to expel brown fumes. Cool, dilute to 1 L in a volumetric flask, and mix. Alternatively, the solution may be prepared as follows: Dissolve 2.88 g of $KMnO_4$ in about 200 mL of water, add 20 mL of H_2SO_4 (1+1), and reduce the permanganate solution by additions of Na_2SO_3 or H_2O_2. Boil to remove excess SO_2 or H_2O_2, cool, dilute to 1 L in a volumetric flask, and mix. Dilute 100 mL of this solution to 1 L in a volumetric flask and mix.

46. Preparation of Calibration Curve

46.1 Transfer 0.500 g of manganese-free copper to each of seven 300-mL Erlenmeyer flasks and dissolve in accordance with 46.2 and 46.4 or 46.3 and 46.4.

46.2 For the analysis of samples containing 0.05 % and over of tin or 0.01 % and over of silicon, add 15 mL of HF - H_3BO_3 mixture, 15 mL of water, 15 mL of HNO_3, and 5 mL of H_3PO_4.

46.3 For the analysis of samples containing under 0.05 % of tin and under 0.01 % of silicon, add 30 mL of water, 15 mL of HNO_3, and 5 mL of H_3PO_4.

46.4 Allow dissolution to proceed without applying heat until reaction has nearly ceased. Heat at 80 to 90°C until dissolution is complete and brown fumes have been expelled.

46.5 Transfer to six of the flasks, 1.0, 3.0, 5.0, 10.0, 15.0, and 20.0-mL aliquots of manganese solution (1 mL = 0.10 mg), and carry the seventh through as a blank.

46.6 Add to each flask approximately 0.3 g of KIO_4. Heat to boiling and boil gently for 2 min, and then digest just below the boiling point for 20 min to develop full intensity of color (Note 7). Cool to room temperature, dilute to 100 mL in a volumetric flask, and mix.

NOTE 7—If tin is present, the time of boiling and period of digestion should be controlled carefully to avoid appreciable reduction of fluoride content and resultant precipitation of tin.

46.7 Transfer a suitable portion of the solution to an absorption cell and measure the transmittance or absorbance at approximately 520 nm. Compensate or correct for the blank.

46.8 Plot the values obtained against milligrams of manganese per 100 mL of solution.

47. Procedure

47.1 Transfer two 0.500-g portions of the sample, in the form of fine drillings or sawings, to 300-mL Erlenmeyer flasks. Depending on the tin and silicon content, dissolve in accordance with 46.2 and 46.4 or 46.3 and 46.4 (Note 8 and Note 9). Carry one portion of the sample through all steps of the procedure as a blank, except to omit the addition of KIO_4. Proceed in accordance with 46.6.

NOTE 8—If the manganese content exceeds 3 %, dilute the dissolved sample in a volumetric flask and take an aliquot, preferably containing under 1.5 mg of manganese. Dilute to approximately 30 mL and adjust the acid content to be equivalent to 10 mL of HNO_3 and 5 mL of H_3PO_4. Proceed in accordance with 46.6 and 46.7 and 47.3 and 47.4.

NOTE 9—It is essential that the procedure used for dissolving the sample be the same as that used for the standards.

47.2 Transfer an aliquot containing from 0.1 to 2 mg of manganese to a 100-mL volumetric flask, dilute to the mark, and mix. Proceed in accordance with 46.7.

47.3 Using the value obtained, read from the calibration curve the number of milligrams of manganese present in 100 mL of the final solution.

47.4 *Calculation*—Calculate the percentage of manganese as follows:

$$\text{Manganese, \%} = A/(B \times 10)$$

where:

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

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

48. Precision and Bias

48.1 This test method was originally approved for publication before the inclusion of precision and bias statements within standards was mandated. The original interlaboratory test data is no longer available. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this test method is adequate for the contemplated use.

SILICON BY THE MOLYBDISILICIC ACID TEST METHOD

49. Principle of Test Method

49.1 A slightly acidic (Note 10) solution of either silicic or fluosilicic acid, when treated with an excess of ammonium molybdate, forms yellow molybdisilicic acid. Photometric measurement is made at approximately 400 nm.

NOTE 10—There is considerable disagreement in the literature about the optimum pH for development of the molybdisilicic acid complex. It seems probable that the optimum value is influenced by the kinds of acid present and also by the kinds and concentration of salts in solution. A pH of 1.10 to 1.20 has been found to give full color development in less than 10 min under the conditions described in this test method.

50. Concentration Range

50.1 The recommended concentration range is from 0.04 to 1.00 mg of silicon in 100 mL of solution, using a cell depth of 2 cm (see Note 1).

51. Stability of Color

51.1 Full color develops in less than 10 min and gradually fades (Note 11). A uniform time for color development should be used for both calibration solutions and samples.

NOTE 11—Samples in contact with soft glass, such as absorption tubes, may dissolve silica slowly from the glass, even in the presence of excess H_3BO_3, giving an increase in color intensity. Borosilicate glass volumetric ware should be used and samples transferred to absorption tubes just prior to reading.

52. Interfering Elements

52.1 Phosphorus present in the final solution in excess of 0.05 mg will interfere unless the solution is treated with citric acid to selectively destroy molybdiphosphoric acid.

53. Apparatus

NOTE 12—All apparatus in contact with HF solutions must be of nonsilicate material.

53.1 *Platinum Crucibles*, fitted with covers. Crucibles of 40 to 50-mL capacity are desirable, although 20-mL crucibles may often be satisfactory.

NOTE 13—A small plastic beaker (approximately 5-oz capacity) and cover may be used here. In this case the boric acid is added directly to the sample solution in the beaker.

53.2 *Funnel*—A plastic or hard rubber funnel about 60 mm in diameter fitted with a 200-mm stem of stiff plastic tubing about 8 mm in diameter.

NOTE 14—Long-stem hard rubber or plastic funnels do not seem to be commercially available. Short-stem funnels of either type are readily available and a piece of plastic tubing may easily be cemented on to lengthen the stem.

53.3 *Bottle*—A wax, plastic, or hard rubber bottle of from 500 to 1000-mL capacity.

54. Reagents

54.1 *Ammonium Molybdate Solution* (95 g $(NH_4)_6Mo_7O_{24}$/L)—Dissolve 100 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water and dilute to 1 L.—

54.2 *Boric Acid Solution (saturated)*—Dissolve about 60 g of H_3BO_3 in 1 L of hot water. Cool to room temperature before use.

54.3 *Citric Acid Solution* (50 g/L)—Dissolve 5.0 g of citric acid in water and dilute to 100 mL. This solution shall be freshly prepared.

54.4 *Copper (low-silicon)*—Copper containing under 0.001 % of silicon.

54.5 *Standard Silicon Solution* (1 mL = 0.040 mg Si)—Fuse 0.0856 g of anhydrous SiO_2 with 1.0 g of anhydrous Na_2CO_3 in a platinum crucible. Cool the melt, dissolve completely in water, and dilute to 1 L in a volumetric flask. Transfer at once to a wax, plastic, or hard rubber bottle.

54.6 *Urea Solution* (100 g/L)—Dissolve 10 g of urea in water and dilute to 100 mL. This solution shall be freshly prepared.

55. Preparation of Calibration Curve for Alloys Containing 0.01 to 0.20 % of Silicon

55.1 *Calibration Solutions*—Transfer portions of low-silicon copper, approximately equivalent in weight to the copper present in 1.00 g of the alloy to be tested (Note 15), to each of four platinum crucibles. Add to each portion 6 to 8 drops (0.3 to 0.4 mL) of HF followed by 0.7 mL of HNO_3 (1+2) for each 100 mg of metal, plus 4.0 mL of HNO_3 (1+2) in excess (Note 16). Cover the crucibles and let stand for 5 min. If dissolution is not complete, the crucibles may be heated on a steam plate at 60 to 65°C. Transfer the cool solutions to 100-mL volumetric flasks through a long-stem plastic or hard rubber funnel dipping into 25 mL of H_3BO_3 solution previously added to the flasks. Dilute to the mark and mix. Using a dry pipet, transfer 50-mL aliquots to four additional 100-mL volumetric flasks, making eight 50-mL portions in all, and add 1.0, 2.0, 5.0, 10.0, 15.0, 20.0, and 25.0-mL portions of standard silicon solution to seven of the flasks. Continue in accordance with 55.3.

NOTE 15—Copper salts decrease the intensity of the color of the molybdisilicic acid complex. Therefore it is necessary to have the same amount of copper (plus or minus 100 mg) present in the final solutions of both calibration solutions and samples.

NOTE 16—This dissolving mixture is designed to convert the silicon in the sample quantitatively to fluosilicic acid. The use of HF is necessary to obtain solution of refractory silicides and also to prevent the formation of colloidal silicic acid which does not react with ammonium molybdate.

55.2 *Reference Solution*—Treat the aliquot (55.1) to which no silicon solution has been added as directed in 55.3, for use as a reference solution.

55.3 *Color Development*—Add 5 mL of urea solution and swirl the flask vigorously. Let stand 1 to 2 min to allow nitrogen to escape. Add 5.0 mL of ammonium molybdate solution. Dilute to the mark and mix. Let stand for 10 min.

55.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 400 nm. While maintaining this photometer adjustment, take the photometric readings of the calibration solutions.

55.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of silicon per 100 mL of solution.

56. Preparation of Calibration Curve for Alloys Containing 0.20 to 5.00 % of Silicon

56.1 *Calibration Solutions*—Transfer 0.500 g of low-silicon copper (see Note 15) to a platinum crucible. Add 6 to 8 drops (0.3 to 0.4 mL) of HF, followed by 8.0 mL of HNO_3 (1+2). Cover the crucible and let stand for 5 min. If dissolution is not complete, the crucible may be heated on a steam plate at 60 to 65°C. Transfer the cool solution to a 250-mL volumetric flask through a long-stem plastic or hard rubber funnel dipping into 25 mL of H_3BO_3 solution previously added to the flask. Dilute to the mark and mix. Transfer 10-mL aliquots to seven 100-mL volumetric flasks. Add 2.0 mL of HNO_3 (1+2) to each solution and dilute to about 50 mL. Add 1.0, 2.0, 5.0, 10.0, 15.0, 20.0, and 25.0-mL portions of silicon solution (1 mL = 0.040 mg Si), and proceed as described in 55.3.

56.2 *Reference Solution*—Transfer an additional 10-mL portion of the copper solution (56.1) to a 100-mL volumetric flask, add 2.0 mL of HNO_3 (1+2), and continue as described in 55.3.

56.3 *Photometry and Calibration Curve*—Continue as described in 55.4 and 55.5.