



# Standard Test Methods for Chemical Analysis of Copper and Copper Alloys (Photometric Methods)<sup>1</sup>

This standard is issued under the fixed designation E 62; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover 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	<sup>1a</sup>
Manganese by the Periodate Test Method	41 to 48
Nickel by the Dimethylglyoxime-Extraction Photometric Test Method	<sup>1a</sup>
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 E 50.

<sup>1</sup> 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. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals
- E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals
- E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals

## 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. Photometric Practice, Apparatus, and Reagents

4.1 *Photometers and Photometric Practice*—Photometers and photometric practice prescribed in these test methods shall conform to Practice E 60.

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 E 50.

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

## 5. Sampling

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

## 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 E 29.

### 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.<sup>3</sup>

## 21. Reagents

21.1 *Ammonium Molybdate Solution* (95 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ /L)—Dissolve 100 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 600 mL of water at 50°C, and dilute to 1 L. Filter before using.

21.2 *Ammonium Vanadate Solution* (2.5 g  $\text{NH}_4\text{VO}_3$ /L)—Dissolve 2.50 g of  $\text{NH}_4\text{VO}_3$  in 500 mL of hot water. When solution is complete, add 20 mL of  $\text{HNO}_3$  (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  $\text{H}_2\text{O}_2$ (30 %) to 100 mL. Store in a dark bottle in a cool place.

21.5 *Potassium Permanganate Solution* (10 g  $\text{KMnO}_4$ /L).

21.6 *Standard Phosphorus Solution* (1 mL = 0.05 mg P)—Dissolve 0.2292 g of  $\text{Na}_2\text{HPO}_4$  in about 200 mL of water. Add 100 mL of  $\text{HNO}_3$  (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  $\text{HNO}_3$  (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  $\text{HNO}_3$  will affect subsequent color development. Add 2 mL of  $\text{KMnO}_4$  (10 g/L) and heat just to boiling. Add 1 mL of  $\text{H}_2\text{O}_2$  (3 %) and swirl the sample until excess  $\text{KMnO}_4$  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  $\text{H}_2\text{O}_2$  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.

## 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:

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

<sup>3</sup> For the determination of phosphorus in the presence of tin, see Sections 25 to 32.

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<sub>3</sub> (2+3) for each 0.1 g of sample over 100 g.

NOTE 3—Since Cu(NO<sub>3</sub>)<sub>2</sub> 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<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>/L)—Dissolve 100 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O 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<sub>4</sub>VO<sub>3</sub>/L)—Dissolve 2.50 g of NH<sub>4</sub>VO<sub>3</sub> in 500 mL of hot water. When solution is complete, add 20 mL of HNO<sub>3</sub> (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<sub>2</sub>O<sub>2</sub>(30 %) to 100 mL. Store in a dark bottle in a cool place.

29.5 *Mixed Acids*—Add 320 mL of HNO<sub>3</sub> 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<sub>2</sub>HPO<sub>4</sub> in about 200 mL of water. Add 100 mL of HNO<sub>3</sub> (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<sub>2</sub>O<sub>2</sub> (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<sub>2</sub>O<sub>2</sub> (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<sub>3</sub>BO<sub>3</sub> 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<sub>3</sub> (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<sub>4</sub> in about 200 mL of water, add 20 mL of H<sub>2</sub>SO<sub>4</sub> (1+1), and reduce the permanganate solution by additions of Na<sub>2</sub>SO<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>. Boil to remove excess SO<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>, 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<sub>3</sub>BO<sub>3</sub> mixture, 15 mL of water, 15 mL of HNO<sub>3</sub>, and 5 mL of H<sub>3</sub>PO<sub>4</sub>.

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  $\text{HNO}_3$ , and 5 mL of  $\text{H}_3\text{PO}_4$ .

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  $\text{KIO}_4$ . 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  $\text{KIO}_4$ . 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  $\text{HNO}_3$  and 5 mL of  $\text{H}_3\text{PO}_4$ . 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  $\text{H}_3\text{BO}_3$ , 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  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ /L)—Dissolve 100 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in water and dilute to 1 L.—

54.2 *Boric Acid Solution (saturated)*—Dissolve about 60 g of  $\text{H}_3\text{BO}_3$  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  $\text{SiO}_2$  with 1.0 g of anhydrous  $\text{Na}_2\text{CO}_3$  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  $\text{HNO}_3$  (1+2) for each 100 mg of metal, plus 4.0 mL of  $\text{HNO}_3$  (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  $\text{H}_3\text{BO}_3$  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  $\text{HNO}_3$  (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  $\text{H}_3\text{BO}_3$  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  $\text{HNO}_3$  (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  $\text{HNO}_3$  (1+2), and continue as described in 55.3.

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

## 57. Procedure for Alloys Containing 0.01 to 0.20 % of Silicon and Not Over 0.05 % of Phosphorus

57.1 *Sample Solution*—Transfer 1.00 g of the sample (Note 17) to a platinum crucible and add 6 to 8 drops (0.3 to 0.4 mL) of HF, followed by 11.0 mL of  $\text{HNO}_3$  (1+2) (see Note 16). 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 100-mL volumetric flask through a long-stem plastic or hard rubber funnel dipping into 25 mL of  $\text{H}_3\text{BO}_3$  solution previously added to the flask. Dilute to the mark and mix. Using a dry pipet, transfer a 50-mL aliquot to a second 100-mL volumetric flask. Reserve one portion to be used in measuring the background color, and treat the other portion in accordance with 57.3.

NOTE 17—Fine particles of metal and light feathery drillings should be avoided as they react too vigorously with the dissolving mixture. Heavy

chunks of metal should also be avoided as they dissolve too slowly.

**57.2 Reference Solution**—Add 6 to 8 drops (0.3 to 0.4 mL) of HF and 4.0 mL of HNO<sub>3</sub> (1+2) to a platinum crucible. Transfer the solution to a 100-mL volumetric flask through a long-stem plastic or hard rubber funnel dipping into 25 mL of H<sub>3</sub>BO<sub>3</sub> solution previously added to the flask. Dilute to the mark and mix. Using a dry pipet, transfer a 50-mL aliquot to a second 100-mL volumetric flask. Reserve one portion to be used as reference solution in measuring the background color and treat the other portion in accordance with 57.3.

**57.3 Color Development**—If less than 0.05 mg of phosphorus is present in the aliquot taken for analysis, develop the color as described in 55.3. If more than 0.05 mg, but not more than 0.25 mg, of phosphorus is present in the aliquot taken for analysis, develop the color as directed in 55.3 through the addition of the ammonium molybdate solution; then dilute to about 90 mL, mix, and let stand for 10 min. Add 5.0 mL of citric acid solution, dilute to the mark, and mix. Take the photometric reading without delay.

**57.4 Photometry**—Take the photometric reading of the sample solution as described in 55.4.

**57.5 Background Color**—Treat the solutions reserved in 57.1 and 57.2 as directed in 57.3 except to omit the addition of the ammonium molybdate solution. Take the photometric reading of the background color as described in 55.4.

**57.6 Calculations**—Convert the photometric readings of the sample and the background color solutions to milligrams of silicon by means of the appropriate calibration curve. Calculate the percentage of silicon as follows:

$$\text{Silicon, \%} = (A - B)/C \times 10 \quad (1)$$

where:

- A = silicon found in the aliquot used, mg,
- B = background color correction, mg of silicon, and
- C = sample represented in the aliquot used, g.

## 58. Procedure for Alloys Containing 0.20 to 5.00 % of Silicon

**58.1 Sample Solution**—Transfer 0.500 g of sample (see Note 17) to a platinum crucible and add 6 to 8 drops (0.3 to 0.4 mL) of HF followed by 8.0 mL of HNO<sub>3</sub> (1+2) (see Note 16). Cover the crucible and let stand for 5 min. If dissolution is not complete, the crucible may be heated on a steam bath 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<sub>3</sub>BO<sub>3</sub> solution previously added to the flask. Dilute to the mark and mix. Transfer equal aliquots, containing less than 1.00 mg of silicon and less than 50 mg of copper, to two 100-mL volumetric flasks. Add 2.0 mL of HNO<sub>3</sub> (1+2) to each portion and dilute to about 50 mL. Reserve one portion to be used in measuring the background color, and treat the other portion as described in 57.3.

**58.2 Reference Solution**—Add 6 to 8 drops (0.3 to 0.4 mL) of HF and 4.0 mL of HNO<sub>3</sub> (1+2) to a platinum crucible. Transfer the solution to a 250-mL volumetric flask through a long-stem plastic or hard rubber funnel dipping into 25 mL of H<sub>3</sub>BO<sub>3</sub> solution previously added to the flask. Dilute to the

mark and mix. Transfer aliquots, equal in size to those taken in 58.1, to two 100-mL volumetric flasks. Add 2.0 mL of HNO<sub>3</sub> (1+2) to each portion and dilute to about 50 mL. Reserve one portion to be used as a reference solution in measuring the background color, and treat the other portion as described in 57.3.

**58.3 Photometry, Background Color, and Calculations**—Complete the determination as directed in 57.4–57.6.

## 59. Precision and Bias

59.1 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.

## ARSENIC IN FIRE-REFINED COPPER BY THE MOLYBDATE TEST METHOD

### 60. Scope

60.1 This test method covers the determination of arsenic in fire-refined copper.

60.2 It is likely that the method may be applied to other materials low in phosphorus and silicon, with suitable modification in sample size.

### 61. Summary of Test Method

61.1 In a moderately acidic solution, pentavalent arsenic reacts with ammonium molybdate to form a complex that may be extracted with *n*-butanol and measured photometrically.

61.2 A 5-g sample is dissolved in nitric acid, ammonium persulfate is added, and the solution is boiled to oxidize the arsenic. Ammonium molybdate is added and any phosphomolybdic acid formed is removed by a preliminary extraction with a chloroform-*n*-butanol mixture. Arseno-molybdic acid is then separated by extraction with *n*-butanol and the arsenic is determined by measuring the butanol extract photometrically at approximately 400 nm.

### 62. Concentration Range

62.1 The recommended concentration range is from 0.025 to 0.60 mg of arsenic per 25 mL of *n*-butanol, using a cell depth of 2 cm (see Note 1).

### 63. Interferences

63.1 Phosphorus or silicon in amounts greater than 0.05 mg may interfere; however, these elements are not likely to be found in sufficiently high concentration in fire-refined copper to cause difficulty.

## 64. Apparatus

64.1 *Separatory Funnels*, conical 125-mL capacity. Funnels with TFE-fluorocarbon valves, which need no lubrication, are desirable.

## 65. Reagents

65.1 *Ammonium Molybdate - Nitric Acid Solution*—Dissolve 15 g of ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) in 400 mL of water in a polyethylene bottle. Add 100 mL of  $\text{HNO}_3$  and mix.

65.2 *Ammonium Persulfate Solution (50 g/L)*—Dissolve 2.5 g of ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) in 50 mL of water. Prepare freshly each day as needed.

65.3 *Arsenic, Standard Solution (1 mL = 0.05 mg As)*—Transfer 0.0661 g of arsenious oxide ( $\text{As}_2\text{O}_3$ ) to a polyethylene beaker, add 1 pellet of sodium hydroxide (NaOH) plus 10 mL of water, and swirl to dissolve. Add about 90 mL of water and then pour into a chemical-resistant glass beaker containing 5 mL of  $\text{HNO}_3$  (1+1). Heat to boiling and add  $\text{KMnO}_4$  solution until a precipitate persists. Then add  $\text{H}_2\text{O}_2$  solution until the precipitate dissolves and the solution becomes colorless. Boil for 1 or 2 min; then cool to room temperature and transfer to a 1-L volumetric flask. Dilute to the mark and mix. Store in a polyethylene bottle.

65.4 *n-Butanol*.

65.5 *n-Butanol (water-saturated)*—Add 50 mL of water to 200 mL of *n*-butanol in a 500-mL separatory funnel and shake vigorously for 30 s. Allow the layers to separate, discard the aqueous layer, and store the *n*-butanol in a glass-stoppered bottle.

65.6 *Chloroform-Butanol Mixture (3+1)*—Mix 150 mL of chloroform with 50 mL of *n*-butanol in a glass-stoppered bottle.

65.7 *Hydrogen Peroxide Solution (3 %)* (Note 18)—Dilute 5 mL of hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 %) with 45 mL of water.

NOTE 18—These reagents are used only for the preparation of the standard arsenic solution (65.3).

65.8 *Potassium Permanganate Solution (10 g/L)* (see Note 18)—Dissolve 1 g of potassium permanganate ( $\text{KMnO}_4$ ) in 100 mL of water.

## 66. Preparation of Calibration Curve

66.1 *Calibration Solutions*—Transfer 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0-mL portions of arsenic solution (1 mL = 0.05 mg As) to 125-mL separatory funnels and dilute to 50 mL. Proceed as directed in 66.3.1 and 66.3.2.

66.2 *Reference Solution*—Transfer 50 mL of water to a separatory funnel and proceed as directed in 66.3.1 and 66.3.2.

66.3 *Color Development:*

66.3.1 Working individually, add 25 mL of ammonium molybdate - nitric acid solution to each funnel and mix. Then add 20 mL of *n*-butanol, stopper, and shake vigorously for 30 s. Allow the layers to separate; drain off the aqueous layer and discard.

66.3.2 Dry the interior of the separatory funnel stem with a roll of filter paper. Transfer the *n*-butanol extract to a dry 25-mL volumetric flask. Rinse out the separatory funnel with two small portions of *n*-butanol (water-saturated) and add the washings to the extract in the 25 mL volumetric flask. Dilute to the mark with *n*-butanol (water-saturated) and mix.

66.4 *Photometry*—Filter a sufficient amount of the reference solution through a 9-cm, rapid filter paper into an absorption cell and adjust the photometer to the initial setting with this solution, using a light band centered at approximately 400 nm. While maintaining this photometer adjustment, take the photometric readings of the calibration solutions, after similar filtration, carrying through the color development, extraction, and photometry of the solutions one at a time and avoiding delays.

66.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of arsenic per 25 mL of solution.

## 67. Procedure

67.1 *Test Solution*—Transfer a 5.00 g portion of the sample to a 250-mL beaker, add 30 mL  $\text{HNO}_3$  (1+1), and cover. When the rapid reaction subsides, warm on a hot plate to complete dissolution. Then boil just long enough to remove oxides of nitrogen. Cool slightly, and add 1 mL of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution. Boil for 2 or 3 min, and then cool to room temperature. Transfer to a 125-mL separatory funnel and dilute to 50 mL. Proceed as directed in 67.3.1 and 67.3.2.

67.2 *Reagent Blank*—Add 5 mL of  $\text{HNO}_3$  (1+1) and 25 mL of water to a 250-mL beaker and carry through all subsequent steps of the procedure for use as a reagent blank.

67.3 *Color Development:*

67.3.1 Add 25 mL of ammonium molybdate - nitric acid solution and mix. Add 10 mL of chloroform - butanol mixture, stopper, and shake vigorously for 30 s. Allow the layers to separate and discard the lower layer. Add a second 10-mL portion of chloroform - butanol mixture and extract as before, discarding the lower layer.

67.3.2 Add 15 mL of *n*-butanol to the solution in the separatory funnel and proceed with the extraction as directed in 66.3.1 and 66.3.2.

67.4 *Photometry*—Take the photometric readings of the test solution and the reagent blank as directed in 66.4, using *n*-butanol as a reference solution.

## 68. Calculation

68.1 Convert the photometric readings of the test and blank solutions to milligrams of arsenic by means of the calibration curve. Calculate the percentage of arsenic as follows:

$$\text{Arsenic, \%} = (A - B)/(C \times 10)$$

where:

- A* = arsenic in the test solution, mg,
- B* = arsenic in the reagent blank, mg, and
- C* = sample used, g.



## 69. Precision and Bias

69.1 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.

## ANTIMONY BY THE IODOANTIMONITE (PHOTOMETRIC) TEST METHOD

### 70. Summary of Test Method

70.1 After dissolution of the sample in nitric acid and dilution with water, the hydrated oxides of tin and antimony are separated by centrifuging, dissolved in sulfuric acid, diluted with water, and treated with a potassium iodide - sodium hypophosphite solution. Photometric measurement of the yellow iodo-antimonite complex is made at approximately 420 nm.

### 71. Concentration Range

71.1 The recommended concentration range is from 0.04 to 0.80 mg of antimony in 50 mL of solution, using a cell depth of 2 cm (see Note 1).

### 72. Stability of Color

72.1 The photometric reading should be made a minimum of 10 min after transferring the solution to the absorption cell. Mixing must be avoided during this period, as air oxidation could liberate iodine and cause high results.

NOTE 19—Difficulties due to air oxidation and iodine liberation can be minimized by adding approximately 25 mg of ascorbic acid (powder) to the volumetric flask before mixing (77.1.3). In this case the 10-min wait before photometry can be eliminated.

### 73. Interferences

73.1 Bismuth interferes; however, it is rarely encountered in copper-base alloys.

### 74. Apparatus

74.1 *Centrifuge*—Any conventional centrifuge, motor or hand operated, is satisfactory.

74.2 *Centrifuge Tubes*—Conical bottom, 50-mL capacity.

### 75. Reagents

75.1 *Potassium Iodide - Sodium Hypophosphite Solution*—Dissolve 100 g of potassium iodide (KI) and 20 g of sodium

hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ) in 100 mL of water. Allow to stand 1 day before using.

### 76. Preparation of Calibration Curve

76.1 *Calibration Solutions*—Carry weighed portions of appropriate standard samples through the procedure (77.1) to provide calibration solutions containing known amounts of antimony.

76.2 *Reference Solution*—Add 3 mL of  $\text{H}_2\text{SO}_4$  to 20 mL of water in a 50-mL volumetric flask and cool to room temperature. Add 10 mL of KI- $\text{NaH}_2\text{PO}_2$  solution, dilute to the mark, and mix.

76.3 *Photometry*—Transfer a suitable portion of the reference solution and of the calibration solutions to absorption cells and allow to stand 10 min (see Note 19). With the reference solution in place, adjust the photometer to the initial setting using a light path centered at approximately 420 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

76.4 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of antimony per 50 mL of solution.

### 77. Procedure

77.1 *Test Solution*:

77.1.1 Transfer a portion of the sample, weighed to the nearest 1 mg, and containing 0.04 to 0.80 mg of antimony (Note 20) to a 50-mL centrifuge tube. Add 10 mL of  $\text{HNO}_3$  (1+1), heat to dissolve, and boil gently to expel all oxides of nitrogen. Dilute to approximately 40 mL with hot water, mix, and centrifuge until the separation of the precipitate is complete. Decant and discard the solution.

NOTE 20—If the ratio of tin to antimony in the alloy is less than 10 to 1 a small amount of pure tin (0.01 g) should be added.

77.1.2 Add 3 mL of  $\text{H}_2\text{SO}_4$  and heat until the precipitate is completely dissolved. Take to  $\text{SO}_3$  fumes, but do not fume strongly. Cool somewhat, cautiously add 20 mL of cold water, mix, and cool to room temperature.

77.1.3 Transfer the clear solution to a 50-mL volumetric flask, add 10.0 mL of KI- $\text{NaH}_2\text{PO}_2$  solution, dilute to volume with water, and mix.

77.2 *Reference Solution*—Prepare a reference solution as described in 76.2.

77.3 *Photometry*—Take the photometric reading of the last solution as described in 76.3.

### 78. Calculation

78.1 Convert the photometric reading of the test solution to milligrams of antimony by means of the calibration curve. Calculate the percentage of antimony as follows:

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

where:

A = antimony found, mg, and

*B* = sample used, g.

## **79. Precision and Bias**

79.1 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.

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