



Designation: B 170 – 99

## Standard Specification for Oxygen-Free Electrolytic Copper—Refinery Shapes<sup>1</sup>

This standard is issued under the fixed designation B 170; 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 approval. A superscript epsilon ( $\epsilon$ ) 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 This specification establishes the requirements for two grades of oxygen-free electrolytic copper wire bars, billets, and cakes produced without the use of metallic or metaloidal deoxidizers.

1.2 Oxygen-free copper, as described herein, is defined as copper containing oxygen not in excess of 0.0010 % (10 ppm).

1.2.1 Grade 1 copper (UNS C10100) corresponds to the designation OFE in Classification B 224.

1.2.2 Grade 2 copper (UNS C10200) corresponds to the designation OF in Classification B 224.

1.2.3 Grade 2 copper may be used to produce OFS designation coppers corresponding to UNS C10400, C10500, and C10700.

1.3 Although this specification includes certain UNS designations as described in Practice E 527, these designations are for cross reference only and are not specification requirements. In case of conflict, Specification B 170 shall govern.

1.4 The values stated in inch-pound units are to be regarded as the standard. The values given in parentheses are for information only, except for analytical measurements where SI units are the norm.

1.5 The following hazard caveat pertains only to Section 13 and Annex A1, of this specification. *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:

B 5 Specification for High Conductivity Tough-Pitch Copper Refinery Shapes<sup>2</sup>

B 193 Test Method for Resistivity of Electrical Conductor Materials<sup>3</sup>

B 224 Classification of Copper<sup>2</sup>

B 577 Test Methods for Hydrogen Embrittlement of Copper<sup>2</sup>

B 846 Terminology for Copper and Copper Alloys<sup>2</sup>

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>4</sup>

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals<sup>5</sup>

E 53 Methods for Chemical Analysis of Copper<sup>5</sup>

E 76 Methods for Chemical Analysis of Nickel-Copper Alloys<sup>5</sup>

E 255 Practice for Sampling Copper and Copper Alloys for Determination of Chemical Composition<sup>5</sup>

E 527 Practice for Numbering Metals and Alloys (UNS)<sup>6</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 Definition of terms used shall be that found in Classification B 224 and Terminology B 846.

### 4. Ordering Information

4.1 Orders for material shall include the following information:

4.1.1 ASTM designation and year of issue,

4.1.2 Grade,

4.1.2.1 Grade 1 copper, (UNS C10100), corresponds to the designation OFE in Classification B 224,

4.1.2.2 Grade 2 copper (UNS C10200), corresponds to the designation OF in Classification B 224,

4.1.3 Shape and size, and

4.1.4 Quantity.

4.2 The following options are available and should be specified at time of order when required:

4.2.1 Certification,

4.2.2 Test reports,

4.2.3 Piece identification,

4.2.4 The amount of silver required in troy oz/short ton for silver bearing (OFS) coppers,

<sup>1</sup> This specification is under the jurisdiction of ASTM Committee B-5 on Copper and Copper Alloys and is the direct responsibility of Subcommittee B05.07 on Refined Copper.

Current edition approved April 10, 1999. Published July 1999. Originally published as B 170 – 42 T. Last previous edition B 170 – 93.

<sup>2</sup> Annual Book of ASTM Standards, Vol 02.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 02.03.

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>5</sup> Annual Book of ASTM Standards, Vol 03.05.

<sup>6</sup> Annual Book of ASTM Standards, Vol 01.01.

4.2.4.1 The addition of silver up to an average of 30 troy oz/short ton (0.102 %) will be considered within the specification, with no individual silver analysis to exceed 35 troy oz/short ton (0.12 %), and

4.2.4.2 Copper with added silver corresponds to the designation OFS as shown in Classification B 224 and to coppers UNS C10400, C10500, and C10700 as defined by the agreed silver content.

## 5. Chemical Composition

5.1 The composition of each grade shall be in accordance with the requirements of Table 1.

5.2 By agreement between purchaser and supplier, analysis may be required and limits established for elements not specified in Table 1.

## 6. Physical Properties

### 6.1 Electrical Resistivity:

6.1.1 The maximum mass resistivity for Grade 1 is 0.15176  $\Omega$  g/m<sup>2</sup> (conductivity 101 %, minimum, International Annealed Copper Standards, (IACS).

6.1.2 The maximum mass resistivity for Grade 2 is 0.15328  $\Omega$  g/m<sup>2</sup> (conductivity 100 %, minimum, IACS).

### 6.2 Embrittlement Test:

6.2.1 Grade 1 shall withstand ten *reverse* bends without breaking, in accordance with Test Method D of Test Methods B 577.

6.2.2 Grade 2 shall withstand eight *reverse* bends without breaking in accordance with Test Method D of Test Methods B 577.

## 7. Dimensions, Mass, and Permissible Variations

7.1 *Standard Shapes and Sizes*—The copper shall be supplied in the form of wire bars, cakes, and billets (Note 1).

NOTE 1—For available shapes and sizes consult the manufacturer's published list.

7.1.1 Wire bars covered by this specification do not conform in dimension to Specification B 5.

**TABLE 1 Chemical Composition<sup>A</sup>**

Element	Grade 1	Grade 2
Copper, min %	99.99 <sup>B</sup>	...
Copper (including silver), min %	...	99.95
	ppm, max	ppm, max
Antimony	4	...
Arsenic	5	...
Bismuth	1	...
Cadmium	1	...
Iron	10	...
Lead	5	...
Manganese	0.5	...
Nickel	10	...
Oxygen	5	10
Phosphorus <sup>C</sup>	3	...
Selenium	3	...
Silver	25	...
Sulfur	15	...
Tellurium	2	...
Tin	2	...
Zinc	1	...

<sup>A</sup> Analytical uncertainty is not incorporated into the specified limits.

<sup>B</sup> Copper is determined by the difference of impurity total from 100.

<sup>C</sup> Refer to Section 13.

## 7.2 Wire Bars:

7.2.1 A variation of 5 % in weight, or

7.2.2 A variation of ¼ in. (6.4 mm) in height, or width, or both, or

7.2.3 A variation of 1 % in length from the purchaser's specification shall be considered good delivery.

## 7.3 Cakes:

7.3.1 A variation of 5 % in weight, or

7.3.2 A variation of ¼ in. (6.4 mm) in height or width, or both, from the purchaser's specification shall be considered good delivery.

7.3.3 Cakes may vary by 3 % from any listed or specified dimension greater than 8 in. (203 mm).

## 7.4 Billets:

7.4.1 For billets up to 6 in. (152.4 mm) in diameter, a variation of 5 % in weight and  $\pm 1/16$  in. (1.6 mm) in diameter from the purchaser's specification shall be considered good delivery.

7.4.2 For billets 6 in. (152.4 mm) and over in diameter, the diameter tolerance shall be  $+1/16, -1/8$  in. (+1.6 mm, -3.2 mm) for good delivery.

7.4.3 By agreement between the manufacturer and the purchaser a diameter tolerance of +0 in.,  $-3/16$  in. (+0 mm, -4.8 mm) may be specified for billets 6 in. and over in diameter.

7.4.4 Billets varying in length by  $\pm 2$  % from the listed or specified length shall be considered good delivery.

7.4.5 Billets shall be straight within ¼ in. (6.4 mm) in 4 ft (1.22 m) as measured at the center of the billet.

7.4.6 Billets shall not be cupped except by specific agreement at time of purchase.

## 8. Workmanship, Finish and Appearance

8.1 *Wire Bars, Billets, and Cakes*—Shall be substantially free of shrink holes, porosity, cracks, cold sets, pits, inclusions, and similar defects.

## 9. Sampling

9.1 For routine sampling, the method of sampling shall be at the discretion of the sampler.

9.2 In the case of special requirements specified in the purchase order or contract, the method of sampling shall be as agreed upon between the producer, or supplier, and the purchaser.

9.3 In case of dispute, a sampling lot shall consist of all pieces in a shipment manufactured during a single production period as defined and recorded by the manufacturer.

9.4 *Chemical Composition*—In case of dispute concerning chemical composition, each party shall select two pieces from the lot to be investigated.

9.4.1 Each of the four selected pieces shall be sampled in the presence of both parties by drilling five holes, approximately ½ in. (12.7 mm) in diameter, at points equally spaced between the ends of the pieces.

9.4.2 For wire bars or billets, these holes shall be along an approximate center line, and with cakes, along an approximate diagonal line between opposite corners.

9.4.3 The drilling shall be completely through each piece. Surface drillings shall be rejected.

9.4.3.1 The drill bit used shall be thoroughly cleaned prior to use. The bit shall be made from a noncontaminating material.

9.4.3.2 No lubricant shall be used, and the drill shall not be forced sufficiently to cause oxidation of the drillings.

9.4.4 In case of a section more than 5 in. (125 mm) in thickness, drillings may be made from opposite sides for a depth of not less than 2 in. (51 mm) in each direction instead of completely through each piece, but, in other respects, the drillings shall be conducted as previously described.

9.4.5 The drillings from each of the four pieces are individually mixed and divided into three approximately equal portions.

9.4.5.1 Each portion shall be placed in a sealed, noncontaminating, package, and

9.4.5.2 The twelve portions shall be individually identified, and

9.4.5.3 Divided into three groups of four portion each, one portion from each of the original four pieces; one group each for the manufacturer, the purchaser, and the umpire, if necessary.

9.4.6 Sampling of individual pieces weighing over 1000 lb (453 kg) shall be by agreement between manufacturer and the purchaser.

9.5 *Oxygen*—In case of dispute concerning oxygen content, each party shall select two pieces from the lot to be investigated.

9.5.1 Each of the four selected pieces shall be sampled in the presence of both parties. A single piece of adequate size shall be cut from each of the four pieces by mutually agreeable means.

9.5.2 Each piece shall be cut into three approximately equal portions. The twelve portions thus obtained shall be individually identified.

9.5.3 The twelve portions shall be divided into three groups of four portions each, one from each of the original four pieces; one group each for the manufacturer, the purchaser, and the umpire, if necessary.

9.6 *Resistivity*— In case of dispute concerning mass resistivity, each party shall select two pieces from the lot.

9.6.1 In the presence of both parties, and by mutually agreeable means, a single sample of adequate size shall be cut from each of the four pieces and fabricated into a wire.

9.6.2 Each coil shall be cut into three portions of approximately equal length, and the twelve portions thus obtained shall be individually identified.

9.6.3 The twelve wires shall be divided into three groups of four wires each, one from each of the four original selected pieces; one group each for the manufacturer, the purchaser, and the umpire, if necessary.

9.7 *Embrittlement*— In case of dispute concerning freedom from embrittlement, sampling shall be described in 9.6.

9.8 *Variation in Weights or Dimensions*—In case of dispute concerning weights or dimensions, the representative of the manufacturer and purchaser shall inspect all pieces where physical defects or variations in weights are claimed. If such

inspection is not practical, or if agreement is not reached, the question of fact shall be submitted to a mutually agreeable umpire.

## 10. Number of Tests and Retests

### 10.1 *Number of Tests:*

10.1.1 The chemical composition, except for oxygen, shall be determined as the mean of the observations from three replicate analyses of each of the four portions.

10.1.2 The oxygen content shall be determined as the mean of the results from the four test specimens.

10.1.3 The mass resistivity shall be determined as the mean of the results from the four test specimens.

10.1.4 The freedom from embrittlement shall be determined as the mean of the results from the four test specimens.

### 10.2 *Retest:*

10.2.1 In case of dispute one retest may be made by the manufacturer or the purchaser or both, under the conditions of 10.1.

### 10.3 *Umpire Test:*

10.3.1 In the case where the retest does not settle the dispute, a second retest may be made by a third qualified laboratory agreeable to the manufacturer and the purchaser. The second retest shall be made on the samples set aside for this purpose.

10.3.2 The umpire provision does not preclude other arrangements, by agreement or contract.

## 11. Specimen Preparation

### 11.1 *Oxygen:*

11.1.1 The test specimen shall originate as a single piece of appropriate size cut from a bar, cake, or billet from which a 0.25-in. (6.4-mm) test cube specimen is fabricated by means agreeable to the manufacturer and the purchaser.

11.1.2 The test specimen shall be etched with a solution of nitric acid (1+1) for a time sufficient to produce a visible reaction.

11.1.3 The test specimen is removed from the acid with stainless steel, or platinum tipped, tongs, or forceps, and rinsed four times with distilled or deionized water.

11.1.4 The test specimen is covered with concentrated hydrochloric acid for 5 min, rinsed four times with water, blotted dry, dipped in acetone, and allowed to air dry.

11.1.5 The test specimen is weighed to the nearest 0.1 mg and analyzed in a properly calibrated oxygen analyzer.

### 11.2 *Resistivity:*

11.2.1 Each test specimen shall originate as a single piece of appropriate size cut from a bar, cake, or billet. The specimen shall be forged or hot rolled.

11.2.2 The external oxide shall be removed and the specimen cold drawn into a wire approximately 0.080 in. (2.03 mm) in diameter.

11.2.3 The wire shall be annealed in an inert atmosphere at approximately 500°C (932°F) for 30 min and cooled to ambient temperature in the same inert atmosphere.

### 11.3 *Embrittlement (Bend):*

11.3.1 Each specimen shall originate as a single piece of appropriate size cut from a selected bar, cake, or billet. The specimen shall be forged or hot rolled.

11.3.2 The external oxide shall be removed and the specimen cold drawn into a wire approximately 0.080 in. (2.03 mm) in diameter.

11.3.3 The wire shall be annealed in an atmosphere containing not less than 10 % hydrogen for 30 min at  $850^{\circ}\text{C} \pm 25^{\circ}$  ( $1517$  to  $1607^{\circ}\text{F}$ ) and cooled to ambient temperature in the same atmosphere.

## 12. Test Methods

12.1 For routine analysis, the analytical test method shall be at the discretion of the analyst.

12.2 In the case of special requirements specified in the purchase order or contract, the methods of analysis used shall be as agreed upon between the producer, or the supplier, and the purchaser.

12.3 In case of dispute concerning the chemical composition of Grade 1, except for phosphorus, oxygen, and sulfur, the method of analysis shall be by electrothermal atomization atomic absorption spectrometer with background correction capability as described in the annex.

12.4 In case of dispute concerning the copper content of Grade 1, copper shall be determined by difference of “impurity total” from 100 %.

12.4.1 *impurity total*— defined as the sum of antimony, arsenic, bismuth, cadmium, iron, lead, manganese, nickel, oxygen, phosphorus, silver, selenium, sulfur, tellurium, tin, and zinc.

12.5 Phosphorous is normally determined by the optical emission spectroscopy technique. Therefore, in case of dispute concerning the phosphorous content, reference material for instrument calibration shall be by agreement between the producer, or the supplier, and the purchaser in the absence of suitable standard reference materials from the National Institute of Standards and Technology.

12.6 In case of dispute concerning the oxygen content of Grade 1 or Grade 2, the method of analysis shall be by the conductometric method, the vacuum fusion method, or the inert gas fusion technique, described in the annex.

12.7 In case of dispute concerning the sulfur content of Grade 1, the method of analysis shall be by induction furnace combustion and infrared detection instrumentation in accordance with the test method described in the annex, or by agreement between the manufacturer or supplier and the purchaser, or by the direct combustion method described in Methods E.

12.8 In case of dispute concerning copper content of Grade 2, the method of analysis shall be the electrolytic determination of copper method in Methods E.

12.9 *Resistivity*— In case of dispute concerning the electrical resistivity, the test method shall be in accordance with Test Method B 193.

12.10 *Embrittlement*— As required in 6.2, freedom from embrittlement shall be determined by lightly clamping each of the four test specimens, individually, between jaws having a radius of 0.200 in. (5.1 mm).

12.10.1 The specimen shall then be bent by hand over one edge through an angle of  $90^{\circ}$  and returned to its original position, this constitutes one bend.

12.10.2 The specimen shall then be bent in the reverse direction through  $90^{\circ}$  and returned to its original position, this constitutes a second bend.

12.10.3 Each successive bend shall be made in the opposite direction of the previous bend until the test is completed.

## 13. Significance of Numerical Limits

13.1 For purposes of determining conformance with this specification, an observed value obtained from analysis shall be rounded to the nearest unit in the last right-hand place of figures used in expressing the limiting value in accordance with Practice E 29.

## 14. Inspection

14.1 The manufacturer shall inspect and make tests necessary to verify that the product furnished, conforms to the specified requirements.

14.2 The manufacturer and the purchaser, by mutual agreement, may accomplish the final inspection simultaneously.

## 15. Rejection and Rehearing

### 15.1 *Rejection*:

15.1.1 Product that fails to conform to the specification requirements when tested by the purchaser or purchaser’s agent may be rejected.

15.1.2 Rejection shall be considered as follows:

15.1.2.1 Chemical composition, embrittlement, or resistivity by lot,

15.1.2.2 Variation in weight, dimensions, and workmanship by individual pieces,

15.1.3 Rejection shall be reported to the manufacturer or supplier promptly, and in writing, and

15.1.4 In case of dissatisfaction with results of the test upon which rejection is based, the manufacturer or supplier may make claim for a rehearing.

15.2 *Rehearing*—As a result of product rejection, the manufacturer or supplier may make claim for a retest to be conducted by the manufacturer or supplier and the purchaser. Samples of the rejected product shall be taken in accordance with the product specification and subjected to test by both parties using the test method(s) specified therein, or alternatively, upon agreement by both parties, an independent laboratory may be selected for the test(s) using the test methods specified in the specification.

## 16. Certification

16.1 When specified in the purchase order or contract, the purchaser shall be furnished certification that samples representing each lot have been either tested or inspected as directed in this specification and the requirements have been met.

16.2 When specified in the purchase order the certificate of compliance shall include the statement, “The material furnished on this purchase order does not contain functional mercury in any form.”

## 17. Test Report

17.1 When specified in the contract or purchase order, a report of test results shall be furnished.

## 18. Product Marking

18.1 Each wire bar, billet, and cake shall be stamped with the manufacturer's brand and with an identifying number.

## 19. Packaging and Package Marking

19.1 The manufacturer shall arrange rail car loads, truck loads, or other shipping units so that, as far as possible, each shipping unit shall contain pieces bearing a single identifying lot number.

19.2 In case of dispute, a lot shall consist of all pieces of the same shape and size bearing the same identifying number.

## 20. Keywords

20.1 billets; cakes; oxygen free; refinery shapes; silver containing; wire bars

## ANNEX

### (Mandatory Information)

#### A1. TEST METHODS FOR DETERMINATION OF COMPLIANCE WITH CHEMICAL COMPOSITION REQUIREMENTS OF SPECIFICATION B 170 FOR OXYGEN-FREE ELECTROLYTIC COPPER-REFINERY SHAPES

##### A1.1 Scope

A1.1.1 These test methods cover the chemical analysis of oxygen-free electrolytic copper for the elements with the specified limiting value stated in Table 1 of Specification B 170.

A1.1.2 *These test methods may involve hazardous materials, operations, and equipment. These test methods do not purport to address all of the safety concerns associated with their use. It is the responsibility of the user of these test methods to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to their use.* Special hazard statements are given in A1.11, A1.24, and A1.36.

A1.1.3 These test methods are arranged as follows:

Antimony, Arsenic, Bismuth, Cadmium, Iron Lead, Manganese, Mercury, Nickel, Selenium, Silver, Tellurium, Tin, and Zinc by Electrothermal Atomization	Sections A1.7-A1.17
Atomic Absorption Spectrometry	
Oxygen by Inert Gas Fusion Principle and Thermal Conductivity or Infrared Detector	A1.18-A1.30
Sulfur by Combustion and Infrared Detector	A1.31-A1.42

##### A1.2 Significance and Use

A1.2.1 These test methods are primarily intended to test oxygen-free copper for compliance with chemical composition

requirements of Specification B 170. It is assumed that all who use these test 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.

##### A1.3 Apparatus

A1.3.1 Apparatus required for each determination are listed in separate sections preceding the procedure.

##### A1.4 Reagents and Material

A1.4.1 Reagents and materials required for each test method are listed in a separate section in the test method.

##### A1.5 Sampling

A1.5.1 In the absence of specific specification requirements, sampling shall be in accordance with Practice E 255.

##### A1.6 Rounding Calculated Values

A1.6.1 Calculated values shall be rounded to the desired number of places as directed in Practice E 29.

#### TEST METHOD FOR ANTIMONY, ARSENIC, BISMUTH, CADMIUM, IRON, LEAD, MANGANESE, NICKEL, SELENIUM, SILVER, TELLURIUM, TIN, AND ZINC BY ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROSCOPY

##### A1.7 Scope

A1.7.1 This test method covers the determination of antimony, arsenic, bismuth, cadmium, iron, lead, manganese, nickel, selenium, silver, tellurium, tin, and zinc in oxygen-free electrolytic copper.

##### A1.8 Summary of Test Method

A1.8.1 The test sample is dissolved in nitric acid and the solution diluted to a known volume. An aliquot is introduced

into an electrothermal atomic absorption spectrometer with background correction capability. The absorption of the resonance line energy from the spectrum of the element is measured and compared with that of calibration solutions of the same element in a matched matrix.

##### A1.9 Significance and Use

A1.9.1 This test method is intended to test oxygen-free electrolytic copper for compliance with antimony, arsenic,

bismuth, cadmium, iron, lead, manganese, nickel, selenium, silver, tellurium, tin, and zinc requirements of this specification.

### A1.10 Interferences

A1.10.1 Elements normally present in oxygen-free electrolytic copper do not interfere.

### A1.11 Hazards

#### A1.11.1 Warning:

A1.11.1.1 The ultraviolet radiation must be shielded at all times to prevent eye damage.

A1.11.1.2 Arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) is a hazardous reagent and may be fatal if swallowed. Avoid inhalation and prolonged or repeated skin contact.

A1.11.1.3 Cadmium and cadmium compounds are potentially hazardous reagents. Avoid ingestion or inhalation.

A1.11.1.4 Tellurium and tellurium compounds are hazardous reagents and may be fatal if ingested. Avoid inhalation and prolonged or repeated skin contact.

A1.11.1.5 Selenium and selenium compounds are potentially hazardous reagents. Avoid ingestion, inhalation, or prolonged and repeated skin contact.

A1.11.1.6 For other specific hazards refer to Practices E 50

#### A1.11.2 Technical Hazards: **Caution:**

A1.11.2.1 It is essential that acids and water be carefully checked for purity to avoid contamination from this source.

A1.11.2.2 Laboratory glassware should be thoroughly cleaned, soaked in HNO<sub>3</sub> (1 + 10) for several hours, and rinsed, prior to use. Avoid previously etched glassware.

A1.11.2.3 Effects of nonspecific absorption and light scattering must be compensated by matrix matching of calibration solutions and background correction.

A1.11.2.4 Matrix modifiers: The copper matrix reduces loss for most elements during the char step. Modifiers such as magnesium nitrate may be found useful to further stabilize elements like cadmium, nickel, and tin and ammonium hydroxide for manganese.

A1.11.2.5 Should lack of homogeneity be suspect in the test material, a 10 g sample, weighed to the nearest 1 mg should be taken and diluted to 1 L with the appropriate amount of acid.

A1.11.2.6 The lower limit of elemental determination is affected by the residual level of the element in the copper.

A1.11.2.7 Optimum settings for operating parameters vary instrument to instrument, and must be experimentally established for a particular instrument.

### A1.12 Apparatus

A1.12.1 *Atomic Absorption Spectrometer and Electrothermal Atomizer*—The instrument shall be equipped with a background corrector and high-speed read-out electronics, or a high-speed recorder, or both. The instrument should be capable of using single-element hollow cathode lamps or electrodeless discharge lamps. Follow the manufacturer's manual for installation and system operation.

A1.12.2 *Graphite Tubes*—Pyrolytically coated graphite tubes and T'vov platforms for use in the electrothermal atomizer.

A1.12.3 *Micropipets*—5 to 250 μL.

A1.12.3.1 The analytical lines are:

Element	Wavelength, nm
Antimony	217.6
Arsenic	193.9
Bismuth	223.0
Cadmium	228.8
Iron	248.3
Lead	283.3
Manganese	279.5
	232.0
Selenium	196.0
Silver	321.8
Tellurium	214.3
Tin	224.6
Zinc	213.8

A1.12.4 *Operating Parameters*—Determine the sample size and optimum electrothermal atomizer parameters for the type of atomizer used as recommended by the instrument manufacturer.

### A1.13 Reagents and Materials

A1.13.1 *Reagents:*

A1.13.1.1 *Acids*—acids, hydrochloric and nitric, should be carefully checked for purity to ensure they do not contaminate the analysis.

A1.13.1.2 *Water*—The quality of the water should be carefully checked for purity to ensure it does not contaminate the analysis.

A1.13.1.3 *Argon*—purity: 99.98 %, minimum.

A1.13.1.4 *Copper Solution (1 mL = 50 mL Cu)*—Transfer 10 g of certified high purity copper (National Institute of Standards and Technology, Standard Reference Material, (NIST SRM) 393 or equivalent) into a 250-mL beaker. Add 25 mL water and 25 mL HNO<sub>3</sub> in 5-mL increments. After the last increment addition, heat gently to dissolve the copper and expel the brown fumes. Cool, transfer to a 200-mL volumetric flask, dilute to volume with HNO<sub>3</sub>(1+1) and mix.

A1.13.1.5 Standard solutions for calibration purposes shall be made in accordance with Table A1.1.

### A1.14 Calibration

A1.14.1 *Calibration Solutions*—Using micropipets, transfer to individual 100-mL volumetric flasks the volume of each standard solution as indicated as follows:

Flask No.	μL	ppm: arsenic, antimony, bismuth, cadmium, iron, lead, manganese, nickel, silver, selenium, tellurium, and zinc
1	5	0.5
2	10	1.0
3	25	2.5
4	50	5.0
5	100	10.0
6	250	25.0

and with the following:

**TABLE A1.1 Calibrated Solutions**

Standard Solution <sup>A</sup>	Reagent	Purity	Weight, g	Dissolution Reagent	mL
Antimony <sup>B</sup>	Potassium Antimony Tartrate, (KSbC <sub>4</sub> H <sub>4</sub> O <sub>7</sub> · ½H <sub>2</sub> O)	99.9	0.2740		250
Arsenic <sup>C</sup>	Arsenic Trioxide, (As <sub>2</sub> O <sub>3</sub> )	99.9	0.1320	Water	50
	Potassium Hydroxide, (KOH)			1 or 2 Pellets	
Bismuth <sup>C</sup>	Bismuth Metal	99.9	0.050	HNO <sub>3</sub> (1+3)	10
Cadmium <sup>C</sup>	Cadmium Metal	99.9	0.050	HNO <sub>3</sub>	10
Iron <sup>C</sup>	Iron Metal	99.9	0.050	HNO <sub>3</sub>	10
Lead <sup>C</sup>	Lead Metal	99.9	0.050	HNO <sub>3</sub>	10
Manganese <sup>C</sup>	Manganese Metal	99.9	0.050	HNO <sub>3</sub>	10
Nickel <sup>C</sup>	Nickel Metal	99.9	0.050	HNO <sub>3</sub> (1+1)	20
Selenium <sup>D</sup>	Selenium Dioxide, (SeO <sub>2</sub> )	99.9	0.0703	Water	50
Silver <sup>C</sup>	Silver Metal	99.9	0.050	HNO <sub>3</sub> (1+1)	20
Tellurium <sup>C</sup>	Tellurium Metal	99.9	0.050	HNO <sub>3</sub>	10
Tin <sup>E</sup>	Tin Metal	99.9	0.050	HCl (1+2)	75
Zinc <sup>C</sup>	Zinc Metal	99.9	0.050	HNO <sub>3</sub>	10

<sup>A</sup> 1 mL of Standard Solution = 0.1 mg of element.

<sup>B</sup> After dissolution of salt, transfer to a 500-mL volumetric flask, dilute to volume, and mix.

<sup>C</sup> Heat gently to dissolve the salt or metal and expel fumes, if any. Cool, transfer to a 500-mL volumetric flask. Add 50 mL HNO<sub>3</sub>, dilute to volume, and mix.

<sup>D</sup> After dissolution of the salt, transfer to a 500-mL volumetric flask. Add 50 mL HNO<sub>3</sub>, dilute to volume, and mix.

<sup>E</sup> Heat gently to dissolve the metal. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix.

Flask No.	µL	ppm: As, Sb, Bi, Cd, Fe, Pb, Mn, Ni, Se, Sn, Te, and Zn
7	5	0.5
8	10	1.0
9	25	2.5
10	50	5.0
11	100	10.0
12	250	25.0

A1.14.1.1 Add 20 mL of the copper standard solution to each flask in both sections, dilute to volume, and mix. Known impurities in the copper standard solution must be considered when determining final specific element ppm concentration in both sections.

#### A1.14.2 Calibration:

A1.14.2.1 Instrument parameters: (a) Set the required instrument parameters and align the electrothermal atomizer according to the manufacturer's recommendation and (b) Determine the optimum electrothermal atomizer parameters for the particular type atomizer and sample size as recommended by the instrument manufacturer.

#### A1.14.2.2 Spectrometry:

(1) Zero the instrument, or set the base line on the recorder, or both.

(2) Check the zero stability and lack of spectral interference within the atomization system by running the preset heating program for blank firing of the electrothermal atomizer. Repeat to ensure baseline stability.

(3) Inject and atomize the calibration solutions in the order of increasing concentrations. Inject each solution three times and record the readings. Should good replication not be achieved, repeat the process.

(4) Check for memory effects by running the blank firing program and reset the zero, or baseline, if necessary.

(5) Plot the average reading from each calibration versus concentration of the analyte in the calibration solution.

(6) For systems with direct instrument calibration, a sufficient number of each calibration solutions should be injected and atomized to determine the proper calibration has been achieved.

#### A1.15 Procedure

A1.15.1 Dissolve a 1 g sample, weighed to the nearest 1 mg, in a 100-mL beaker with 20 mL HNO<sub>3</sub> (1+1). Heat gently to dissolve the copper and expel the brown fumes. Transfer to a 100-mL volumetric flask. Cool, dilute to volume and mix.

A1.15.2 Ensure that the test solution is within 1°C of the calibration solutions. Inject and atomize the test solution for three readings and record the observations.

#### A1.16 Calculation

A1.16.1 Calculate the concentration of each element to be determined using the analytical curves prepared in (5) in the Calibration Section.

A1.16.2 Systems with direct reading capability will provide results in the calibration concentration units.

#### A1.17 Precision and Bias

A1.17.1 *Precision*—The precision of this test method is dependent upon sample preparation care and preciseness of calibration.

A1.17.2 *Bias*—The accuracy of this test method is dependent to a large extent upon the care with which the calibration solutions are prepared as well as the purity of the reagents used.

## TEST METHOD FOR OXYGEN BY INERT GAS FUSION PRINCIPLE AND THERMAL CONDUCTIVITY OR INFRARED DETECTOR

### A1.18 Scope

A1.18.1 This test method covers the determination of oxygen in electrolytic grade coppers.

### A1.19 Summary of Test Method

A1.19.1 This test method is for use with automated, commercially available analyzers that are based on the inert gas fusion principle and use a variety of gas conditions and measuring techniques. All use calibration methods traceable to primary standard reference materials (SRM).

A1.19.2 The sample is contained in a small, single-use graphite crucible, is fused under a flowing inert gas stream at a temperature sufficient to release oxygen. The oxygen combines with carbon from the crucible to form carbon monoxide (CO) and is carried by the inert gas stream to thermal conductivity or infrared detectors. The detector output is compared to that obtained from the SRM and is displayed as oxygen content of the copper.

### A1.20 Significance and Use

A1.20.1 This test method is primarily intended to test electrolyte grade copper products for compliance with compositional specification.

### A1.21 Interferences

A1.21.1 The elements normally present in electrolytic grade copper do not interfere.

### A1.22 Apparatus

A1.22.1 *Apparatus*—These instrument systems are commercially available and their general features are readily available from the manufacturer.

### A1.23 Reagents and Materials

A1.23.1 *Reagents*:

A1.23.1.1 *Acetone*—Residue after evaporation must be less than 0.0005 %.

A1.23.2 *Ascarite II (sodium hydroxide on clay)*—Used in some instruments to absorb CO<sub>2</sub>.

A1.23.3 *Inert gas*—Use the purity specified by the manufacturer; helium or argon.

A1.23.3.1 *Magnesium Perchlorate*—Used in most instruments as a moisture trap. Use the purity specified by the manufacturer.

A1.23.4 *Material*:

A1.23.4.1 The graphite crucibles must be made from high quality graphite and recommended by the instrument manufacturer or its equivalent.

### A1.24 Hazards

A1.24.1 For precautions to be observed in the use of certain reagents in this test method refer to Practices E 50.

A1.24.2 Use care when handling hot crucibles and operating furnaces to avoid either burns or electrical shock.

### A1.25 Sample Preparation

A1.25.1 Use only solid samples to minimize the potential for errors due to surface oxidation. Samples must be of the proper size to permit free introduction into the sample loading device, if required, and to fit into the graphite crucible.

A1.25.2 Cut the sample to an appropriate size using a silicon carbide, water-cooled, cut-off wheel, or by other means that will prevent overheating. Avoid oxide cutting or oxide abrading materials. When appropriate, flat samples may be stamped using a punch and die.

A1.25.3 Etch the specimen with HNO<sub>3</sub> (1+1) for a time sufficient for the reaction to become clearly visible. Remove with stainless steel, or platinum tipped, tongs or forceps, and thoroughly rinse away the HNO<sub>3</sub>. Cover the specimen with HCl for 5 min, rinse four times with water, blot dry, dip in acetone air dry, and weigh.

A1.25.4 **Precaution:** Do not touch the specimen with fingers during or following the final stages of cleaning. Store the prepared specimen in a desiccator and analyze within 4 h of preparation.

A1.25.5 The careful adherence to the specimen preparation procedure is critical to obtaining accurate and precise results. The use of small and irregularly shaped pieces requires a diligent effort to ensure that all surface contamination is removed.

A1.25.6 The sample preparation described herein does not supersede specific compositional specification requirements.

### A1.26 Preparation of Apparatus

A1.26.1 Assemble the apparatus according to the manufacturer's instructions. Make the necessary power, gas, and water connections. Turn on the instrument and allow sufficient warm-up time to stabilize the system.

A1.26.2 Change the chemical traps and filters as required. Test the furnace and the analyzer to ensure the absence of leaks. Condition the system according to the manufacturer's instructions before attempting to calibrate or to determine the value of the blank.

### A1.27 Calibration

A1.27.1 *Calibration standards*—When possible, select three calibration standards which approximate the low, middle, and high of the expected range of oxygen in the product to be tested. Designate them as Standards A, B, and C respectively.<sup>7</sup>

A1.27.2 *Gas dosing*—Automated and manual gas dosing can be used to set up the instrument, but the instrument response must be confirmed as described using the standards from A1.27.1.

A1.27.3 *Adjustment of response of measurement system*—Using Standard B as the specimen, proceed as directed in A1.28.2-A1.28.5. Repeat A1.28.2-A1.28.5 until the absence of

<sup>7</sup> Reference materials are available from LECO Corporation, St. Joseph, MI 49085-2396 and Alpha Resources, Inc., Stevensville, MI.



drift is indicated. Continue running a series of specimens until the last four readings are within the maximum acceptable range, making appropriate adjustments according to the manufacturer's instructions.

A1.27.4 Using Standard A as the specimen, proceed as directed in A1.28.2-A1.28.5. Repeat a sufficient number of times to establish that a low average and consistent individual blank values are obtained.

A1.27.4.1 Blank values are equal to the total result of the crucible and Standard A minus the value of Standard A. Record the average value of four successive blank determinations that meet the requirements for maximum and consistent values. If the blank values are too high or inconsistent, determine the cause, correct it, and repeat steps as directed in A1.28.2-A1.28.5.

A1.27.4.2 Enter the average blank value in the appropriate mechanism of the analyzer and refer to the manufacturer's instructions. Should the unit not have this function, the blank value must be subtracted from the total result prior to any other calculations.

A1.27.5 *System calibration*—In accordance with the manufacturer's instruction, weigh an appropriate specimen of Standard C to the nearest 1 mg, and place it in the instrument sample loading device. Follow the calibration procedure recommended by the manufacturer using Standard C as the primary standard.

A1.27.5.1 Run specimen of standard C until the results of four successive specimens are within the maximum acceptable range. Treat each as directed in A1.28.2-A1.28.5 before proceeding to the next one.

A1.27.5.2 Confirm the calibration by analyzing an additional Standard C specimen after calibration procedure is completed. The value should be within the allowable limits of the standard's value. If not, repeat the calibration procedure.

A1.27.5.3 Next, weigh at least two appropriate sized specimens of Standard B to the nearest 1 mg, and transfer to the instrument sample loading device. Treat each specimen as directed in A1.28.3 and A1.28.5 before proceeding to the next specimen. Record the results and compare them to the oxygen

value of Standard B. Should the results not be within the allowable limits refer to the manufacturer's instructions for checking linearity of the system (Note A1.1).

NOTE A1.1—Repeat the calibration when: (a) a different lot of crucibles is used, (b) the system has not been used in 1 h, or (c) the carrier gas has been changed.

### A1.28 Procedure

A1.28.1 Assemble the apparatus, calibrate, set the blank, and test the performance as directed in A1.10 and A1.11.

A1.28.2 Transfer an appropriate-sized specimen, weighed to the nearest 1 mg, to the instrument's sample loading device.

A1.28.3 Place a crucible on the furnace pedestal and raise the pedestal into position.

A1.28.4 Start the crucible degassing cycle (Note A1.2). Refer to the manufacturer's recommended procedure regarding entry of sample weight.

NOTE A1.2—For some instruments this procedure precedes the analysis cycle.

A1.28.5 Transfer the specimen to the crucible and start the analysis cycle.

### A1.29 Calculation

A1.29.1 Follow the manufacturer's direction to ensure that all essential variables in the calculations of analytical results have been considered.

A1.29.2 Since the output of most modern instruments is given directly in percent concentration, post-analysis calculations may not be required.

### A1.30 Precision and Bias

A1.30.1 *Precision*—The precision of this test method is dependent upon sample preparation care and preciseness of calibration.

A1.30.2 *Bias*—The accuracy of this test method is dependent to a large extent upon the accuracy of the methods used to determine the oxygen concentration in the calibration standards as well as their homogeneity.

## SULFUR BY COMBUSTION AND INFRARED DETECTOR

### A1.31 Scope

A1.31.1 This test method covers the determination of sulfur in oxygen-free electrolytic copper.

### A1.32 Summary of Test Method

A1.32.1 The sulfur is converted to sulfur dioxide (SO<sub>2</sub>) by combustion in a stream of oxygen and the SO<sub>2</sub> is measured by infrared absorption.

A1.32.2 This test method is written for use with commercial analyzers, equipped to carry out the operations automatically.

### A1.33 Interferences

A1.33.1 The elements ordinarily present do not interfere.

### A1.34 Apparatus

A1.34.1 *Combustion and Analyzing Instrumentation*, capable of making the required measurements.

### A1.35 Reagents and Material

A1.35.1 *Reagents*:

A1.35.1.1 *Accelerator*—Use the accelerator recommended by the instrument manufacturer which, for copper, should be sulfur and tin free.

A1.35.1.2 *Oxygen*—ultra high purity (purity: 99.95 % minimum). Other grades of oxygen may be used if sulfur free, or the oxygen may be purified as described in Practice E 50.

A1.35.2 *Materials*:

A1.35.2.1 *Crucibles*—Use crucibles recommended by the manufacturer, or equivalent.

A1.35.2.2 *Crucible Tongs*, capable of handling recommended crucibles.

### A1.36 Hazards

A1.36.1 For precautions to be observed in the use of certain reagents in this test method refer to Practice E 50.

A1.36.2 Use care when handling hot crucibles and operating the furnace to avoid burns and electrical shock.

### A1.37 Preparation of Apparatus

A1.37.1 Assemble the apparatus and test the apparatus as recommended by the manufacturer.

### A1.38 Sample Preparation

A1.38.1 The sample should be uniform in size but not finer than 40 mesh.

### A1.39 Calibration

A1.39.1 *Calibration Reference Materials*—Select a minimum of two reference materials with sulfur content near the mid-point and high limit.

A1.39.2 *Instrument Calibration*—Calibrate according to the manufacturer's instructions.

### A1.40 Procedure

A1.40.1 Stabilize the furnace and analyzer according to the manufacturer's instruction.

A1.40.2 Transfer the weight of sample recommended by the manufacturer into a crucible and add the same amount of accelerator used in the calibration. Proceed as directed by the manufacturer's instructions.

### A1.41 Calculation

A1.41.1 Since most commercially available instruments calculate percent concentrations directly, including corrections for blank and sample weight, calculations by the analyst are not required.

A1.41.2 If the analyzer does not compensate for blank and sample weight values, then use the following equation:

$$\text{Sulfur, \%} = \frac{(A - B) \times C}{D}$$

where:

*A* = Digital Voltmeter, (DVM) reading for specimen,

*B* = DVM reading for blank,

*C* = weight compensator setting, and

*D* = specimen weight in grams.

### A1.42 Precision and Bias

A1.42.1 *Precision*—The precision of this test method is dependent upon sample preparation care and preciseness of calibration.

A1.42.2 *Bias*—The accuracy of this test method is dependent to a large extent upon the accuracy of the methods used to determine the sulfur concentration in the calibration standards as well as their homogeneity.

## SUMMARY OF CHANGES

Committee B-5 has identified the location of selected changes to this standard since the last issue (B 170 – 98) that may impact the use of this standard.

(1) The scope and Sections 3, 4, 5, 6, 12.7, 15, 16, and 17 were revised to correct errors or to satisfy Blue Book requirements.

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