

Designation: E 1771 – 95

Standard Test Method for Determination of Copper in Anode and Blister Copper¹

This standard is issued under the fixed designation E 1771; 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 This test method describes the electrolytic determination of copper in commercial anode (99.0 to 99.8%) and blister copper (92.0 to 98.0 %).

1.2 *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.* Specific hazards statements are given in Section 8.

2. Referenced Documents

2.1 ASTM Standards:

- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specific Limiting Values²
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals³
- E 53 Test Methods for Chemical Analysis of Copper³
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals³
- E 255 Practice for Sampling Copper and Copper Alloys for Determination of Chemical Composition³
- E 478 Methods for Chemical Analysis of Copper Alloys⁴
- E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method²

3. Summary of Test Method

3.1 After dissolution of the sample, the solution is evaporated to dryness and fumes expelled by heat. The salt is dissolved in nitric acid, the solution is filtered, the acidity is adjusted, and the copper is electrolytically plated and weighed as the metal.

4. Significance and Use

4.1 This test method for the determination of copper in anode (99.0 to 99.8 %) and blister copper (92.0 to 98.0 %) is primarily intended as a referee method, to test such materials for compliance with compositional specifications. It is assumed

that users of this test method 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.

4.2 This test method is intended to determine the copper content of commercial anode and blister copper. Those elements that interfere are removed by precipitation or volatilization, or both. Copper is electrodeposited as the metal and weighed.

4.3 This method will also be found useful for the electrolytic determination of copper in some copper alloys and scrap.

5. Interferences

5.1 Commonly present elements, which co-deposit or partially co-deposit with copper are precipitated, (for example, silver as the chloride), or volatilized, (for example, antimony, arsenic, selenium), as metal bromides. Molybdenum also will co-deposit with copper to produce a dark plate. When less than 6 mg is present, the addition of 1 mg of sodium chloride will prevent deposition.

5.2 This test method does not address interferences caused by tungsten and bismuth.

6. Apparatus

6.1 *Electrodes for Electrolysis*—Apparatus No. 9 in Practices E 50.

7. Reagents

- 7.1 *Acetone*, (CH_3COCH_3).
- 7.2 *Ammonium Sulfate*, $[(\text{NH}_4)_2\text{SO}_4]$.
- 7.3 *Bromine*, (Br_2).
- 7.4 *Ethanol*, ($\text{C}_2\text{H}_5\text{OH}$).
- 7.5 *Hydrobromic Acid*, (HBr), 48%.

8. Hazards

8.1 *Bromine* (Br_2)—Liquid bromine vaporizes at room temperature. Fumes attack organic material and are highly irritating to eyes and lungs. The liquid will cause serious burns and blisters if allowed to contact skin or other soft tissues. Inhalation of vapors may cause pulmonary edema and death. Ingestion may cause severe gastroenteritis and death.

NOTE 1—Warning: Work only in an efficient exhaust hood with proper protective equipment. Familiarity with proper first-aid procedure is essential before beginning work.

¹ This test method is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.07 on Cu and Cu Alloys.

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² *Annual Book of ASTM Standards*, Vol 14.02.

³ *Annual Book of ASTM Standards*, Vol 03.05.

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

8.2 *Hydrobromic Acid* (HBr)—Liquid hydrobromic acid and its fumes are highly irritating to eyes, skin, mucous membranes, and the respiratory system. HBr is a strong acid, with properties similar to hydrochloric acid.

8.3 For precautions to be observed in the use of certain reagents and equipment in this test method, refer to Practices E 50.

9. Sampling

9.1 For procedures in sampling, refer to Practice E 255. However, this practice does not supersede any sampling requirement in a specific ASTM material specification nor preclude a procedure agreed upon by the producer, supplier, or purchaser.

10. Preparation of Electrodes

10.1 *Cathode*—Clean the cathode in hot nitric acid, {HNO₃}, (1 + 1), rinse in two separate baths of ethanol or acetone. Dry at a low temperature, (110°C for 3 to 5 min), and cool to room temperature in a desiccator.

10.2 *Anode*—Clean in hydrochloric acid, {HCl}, (1 + 1), rinse with distilled water.

10.3 Weigh the cathode to the nearest 0.1 mg and record the weight. The anode does not have to be weighed.

11. Procedure

11.1 Transfer 5.0 g of sample, weighed to the nearest 0.1 mg, to a 600-mL tall form beaker (see Note 2).

NOTE 2—A beaker of lesser volume may be used, but greater care is required.

11.2 Place a cover glass on top of the beaker and with the cover glass slightly slipped aside, carefully add 15 mL of HBr, 10 mL of Br₂, and 20 mL of ethanol. Reposition the cover glass over the beaker.

11.3 After the reaction has subsided, slip the cover glass aside approximately 0.5 cm and evaporate to dryness (see Note 3).

NOTE 3—With low heat, the sample can be conveniently taken to dryness overnight. Exercise care that spattering does not occur due to excessive heat.

11.4 When the sample appears dry, slowly increase the hot plate temperature to maximum and bake the sample until all fumes are expelled.

11.5 Reduce the temperature of the hot plate before removing the beaker. The beaker cooling rate shall not be faster than the cooling rate of the salt; otherwise, the beaker may crack.

11.6 After the sample has reached ambient temperature, add 50 mL of distilled water, 30 mL of HNO₃ and 2 drops of HCl, (1 + 9). Heat to boiling and boil until the volume has been reduced to approximately 25 mL.

11.7 Remove from heat and dilute to 150 mL.

11.8 Should the solution be cloudy, reheat to help coagulate the precipitate and then filter through a 25-mm diameter, 0.45

µm porosity membrane filter⁵, or equivalent, washing the beaker and wall of the filter holder carefully with distilled water.

11.9 Transfer the residue from the filtering apparatus into a 250-mL beaker. Wash off the membrane with distilled water, being careful to control total to 50-mL maximum. Reserve for 11.14.

11.10 To the filtrate from 11.8, add 5 to 10 g of (HN₄)₂SO₄, 10 mL of sulfuric acid {H₂SO₄}, (1 + 1), and agitate with a stirring rod until all salts are in solution. Wash down the stirring rod as it is withdrawn, and dilute the solution to approximately 200 mL.

11.11 With the electrolyzing current off, position the tared cathode and anode in the solution, and if necessary, add water until the cathode is completely immersed. Cover the beaker with a split cover glass.

11.12 Electrolyze at a current density of about 0.6 A/dm². (See Note 4.) When the solution becomes colorless, wash down the cover glass, electrode stems, and side of beaker. Continue the electrolysis until deposition is essentially complete, as indicated by failure to plate on a new surface on the cathode stem when the solution level is raised by adding water.

NOTE 4—When a current density of 0.6 A/dm² is used, the electrolysis requires about 16 h and is conveniently carried out overnight.

11.13 With the current still flowing, slowly and carefully withdraw the electrodes or lower the beaker. Wash the cathode with a stream of water as it is being removed from the spent solution. Turn off the current source. Immediately wash the cathode successively in two baths of water and in two baths of ethanol or acetone. Reserve the spent electrolyte. Dry the cathode at 110°C for 3 to 5 min. Cool to ambient temperature in a desiccator, and weigh to the nearest 0.1 mg. Record the weight.

11.14 To the residue from 11.9, add 2 mL H₂SO₄(1 + 1), and heat to boiling. After boiling for 1 to 2 min. remove from the hot plate and filter through a medium-textured 9-cm paper, collecting the filtrate. Wash the paper 3 to 4 times and add the filtrate and washings to the spent electrolyte from 11.13.

11.15 Determine the residual copper in the solution from 11.14 by the atomic absorption method described in Test Methods E 53 or by photometric method described in Methods E 478.

12. Calculation

12.1 Calculate the percentage copper as follows:

$$\text{Copper, \%} = \frac{[(A - B) + C] \times 100}{D} \quad (1)$$

where:

A = weight of cathode plus deposited copper, g,

B = weight of cathode, g,

C = copper found in 11.15, g, and

D = sample used, g.

⁵ Metricel Membrane Filter GA-6, available from Gelman Instrument Co., 600 S. Wagner Rd., Ann Arbor, MI 48103-9019 and Filtration Apparatus No. 120750, available from Radnoti Glass Technology, Inc., 227 W. Maple Ave., Monrovia, CA 91016 have been found satisfactory.

13. Precision and Bias ⁶

13.1 *Precision*—Six laboratories cooperated in testing this method and obtained the precision data summarized in Table 1.

13.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this method may be judged by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

14. Keywords

14.1 anode copper; blister copper; copper

TABLE 1 Statistical Information—Copper^A

Sample	Average Determination, %	Standard Deviation		R
		Within-Laboratory	Between-Laboratories	
Anode Copper:				
Sample A	99.36	0.133	0.206	0.58
Sample C	99.62	0.029	0.086	0.24
Blister Copper:				
Sample B	97.00	0.125	0.270	0.76
Sample D	96.99	0.060	0.280	0.78
Pooled standard deviation ^B		0.089	0.216	0.60

^A Calculations based on Practice E 691-87.

^B Root mean square of individual standard deviations.

⁶ Supporting data are available from ASTM Headquarters. Request RR: E01-1016.

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