



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 9.

2. Referenced Documents

2.1 ASTM Standards:²

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

E 53 Test Method for Determination of Copper in Unalloyed Copper by Gravimetry

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E 255 Practice for Sampling Copper and Copper Alloys for the Determination of Chemical Composition

E 478 Test Methods for Chemical Analysis of Copper Alloys

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—For definitions and terms used in this test method, refer to Terminology E 135.

4. Summary of Test Method

4.1 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.

5. Significance and Use

5.1 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.

5.2 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.

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

6. Interferences

6.1 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.

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

7. Apparatus

7.1 Electrodes for Electroanalysis

7.1.1 *Electrodes*—Recommended stationary type platinum electrodes are described in 7.1.2 and 7.1.3. The surface of the platinum electrodes should be smooth, clean, and bright to promote uniform deposition and good adherence. Deviations from the exact size and shape are allowable. In instances where it is desirable to decrease the time of deposition and agitation of the electrolyte is permissible, a generally-available rotating type of electrode may be employed. Cleaning of the electrolyte by sandblasting is not recommended..

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

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

7.1.2 Cathodes—Platinum cathodes may be either open or closed cylinders formed from sheets that are plain or perforated, or from gauze. Gauze cathodes are recommended; preferably from 50-mesh gauze woven from approximately 0.21 mm (0.0085 in.) diameter wire. The top and bottom of gauze cathodes should be reinforced by doubling the gauze about 3 mm onto itself, or by the use of platinum bands or rings. The cylinder should be approximately 30 mm in diameter and 50 mm in height. The stem should be made from a platinum alloy wire such as platinum-iridium, platinum-rhodium or platinum-ruthenium, having a diameter of approximately 1.3 mm. It should be flattened and welded the entire length of the gauze. The overall height of the cathode should be approximately 130 mm. A cathode of these dimensions will have a surface area of 135 cm² exclusive of the stem.

7.1.3 Anodes—Platinum anodes may be a spiral type when anodic deposits are not being determined, or if the deposits are small (as in the electrolytic determination of lead when it is present in concentrations below 0.2 %). Spiral anodes should be made from 1.0 mm or larger platinum wire formed into a spiral of seven turns having a height of approximately 50 mm and a diameter of 12 mm, the overall height of approximately 130 mm. A spiral anode of these dimensions will have a surface area of 9 cm². When both cathodic and anodic plates are to be determined, the anode should be of the same material and design as the electrode described in 7.1.2. The anode cylinder should be approximately 12 mm in diameter and 50 mm in height and the overall height of the anode should be approximately 130 mm. A gauze anode of these dimensions will have a surface area of 54 cm² exclusive of the stem.

8. Reagents

- 8.1 *Acetone*, (CH₃COCH₃).
- 8.2 *Ammonium Sulfate*, [(NH₄)₂SO₄].
- 8.3 *Bromine*, (Br₂).
- 8.4 *Ethanol*, (C₂H₅OH).
- 8.5 *Hydrobromic Acid*, (HBr), 48%.

9. Hazards

9.1 Bromine (Br₂)—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.

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

9.2 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.

10. Sampling

10.1 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.

11. Preparation of Electrodes

11.1 Cathode—Clean the cathode in hot nitric acid, {HNO₃}, (1 + 1), rinse with distilled water, 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.

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

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

12. Procedure

12.1 Transfer 5.0 g of sample, weighed to the nearest 0.1 mg, to a 600-mL tall form beaker (see Note 1).

NOTE 1—A beaker of lesser volume may be used, but greater care is required.

12.2 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.

12.3 After the reaction has subsided, slip the cover glass aside approximately 0.5 cm and evaporate to dryness (see Note 2).

NOTE 2—With low heat, the sample can be conveniently taken to dryness overnight. Exercise care that spattering does not occur due to excessive heat.

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

12.5 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.

12.6 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.

12.7 Remove from heat and dilute to 150 mL.

12.8 Should the solution be cloudy, reheat to help coagulate the precipitate and then filter through a 25-mm diameter, 0.45 µm porosity membrane filter, or equivalent, washing the beaker and wall of the filter holder carefully with distilled water.

12.9 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 12.14.

12.10 To the filtrate from 12.8, add 5 to 10 g of (NH₄)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.

12.11 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.

12.12 Electrolyze at a current density of about 0.6 A/dm². (See Note 3.) 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 3—When a current density of 0.6 A/dm² is used, the electrolysis requires about 16 h and is conveniently carried out overnight.

12.13 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.

12.14 To the residue from 12.9, 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 12.13.

12.15 Determine the residual copper in the solution from 12.14 by the atomic absorption method described in Test Methods E 53 or by photometric method described in Test Methods E 478.

13. Calculation

13.1 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 12.15, g, and
D = sample used, g.

14. Precision and Bias ³

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

14.2 *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.

TABLE 1 Statistical Information—Copper^A

Sample	Average Determination, %	Standard Deviation		<i>R</i>
		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.

15. Keywords

15.1 anode copper; blister copper; copper

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: E01-1016.

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