Designation: E478 – 08 (Reapproved 2017)

Standard Test Methods for Chemical Analysis of Copper Alloys[1]

This standard is issued under the fixed designation E478; 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 the chemical analysis of copper alloys having chemical ranges within the following limits:[2]

Element	Composition, %
Aluminum	12.0 max
Antimony	1.0 max
Arsenic	1.0 max
Cadmium	1.5 max
Cobalt	1.0 max
Copper	40.0 min
Iron	6.0 max
Lead	27.0 max
Manganese	6.0 max
Nickel	50.0 max
Phosphorus	1.0 max
Silicon	5.0 max
Sulfur	0.1 max
Tin	20.0 max
Zinc	50.0 max

1.2 The test methods appear in the following order:

	Sections
Aluminum by the Carbamate Extraction-Ethylenedinitrilotetraacetate Titrimetric Test Method [2 % to 12 %]	71 – 78
Copper by the Combined Electrodeposition Gravimetric and Oxalyldihydrazide Spectrophotometric Test Method [50 %, minimum]	10 – 18
Iron by the 1,10-Phenanthroline Spectrophotometric Test Method [0.003 % to 1.25 %]	19 – 28
Lead by Atomic Absorption Spectrometry [0.002 % to 15 %]	90 – 100
Lead by the Ethylenedinitrilotetraacetic Acid (EDTA) Titrimetric Test Method [2.0 % to 30.0 %]	29 – 36
Nickel by the Dimethylglyoxime Extraction Sprectophotometric Test Method [0.03 % to 5.0 %]	37 – 46
Nickel by the Dimethylglyoxime Gravimetric Test Method [4 % to 50 %]	55 – 62
Silver in Silver-Bearing Copper by Atomic Absorption Spectrometry [0.01 % to 0.12 %]	101 – 112
Tin by the Iodotimetric Titration Test Method [0.5 % to 20 %]	63 – 70
Tin by the Phenylfluorone Spectrophotometric Test Method [0.01 % to 1.0 %]	113 – 123
Zinc by Atomic Absorption Spectrometry [0.2 % to 2 %]	79 – 89
Zinc by the Ethylenedinitrilotetraacetic Acid (EDTA) Titrimetric Test Method [2 % to 40 %]	47 – 54

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[4]

E255 Practice for Sampling Copper and Copper Alloys for the Determination of Chemical Composition

E1601 Practice for Conducting an Interlaboratory Study to

---

[1] These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.05 on Cu, Pb, Zn, Cd, Sn, Be, Precious Metals, their Alloys, and Related Metals.

Current edition approved Jan. 15, 2017. Published March 2017. Originally approved in 1973. Last previous edition approved in 2008 as E478 – 08. DOI: 10.1520/E0478-08R17.

[2] The actual limits of application of each test method are presented in 1.2.

[3] 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.

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

Evaluate the Performance of an Analytical Method

3. Terminology

3.1 For definitions of terms used in these test methods, refer to Terminology E135.

4. Significance and Use

4.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with composition 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.

5. Apparatus, Reagents, and Spectrophotometric Practice

5.1 Apparatus, standard solutions, and other reagents required for each determination are listed in separate sections preceding the procedure. Spectrophotometers shall conform to the requirements prescribed in Practice E60.

5.2 Spectrophotometric practice prescribed in these test methods shall conform to Practice E60.

6. Hazards

6.1 Specific hazard statements are given in 33.7, 51.13, and 107.1.

6.2 For other precautions to be observed in the use of certain reagents in these test methods, refer to Practices E50.

7. Sampling

7.1 For procedures for sampling the material, refer to Practice E255. However, this practice does not supersede any sampling requirements specified in a specific ASTM material specification.

8. Rounding Calculated Values

8.1 Calculated values shall be rounded to the desired number of places as directed in Practice E29.

9. Interlaboratory Studies

9.1 These test methods were evaluated in accordance with Practice E173 unless otherwise noted in the precision section. Practice E173 has been replaced by Practice E1601. The Reproducibility R_2 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability R_1 of Practice E173 corresponds to the Repeatability Index r of Practice E1601.

COPPER BY THE COMBINED ELECTRODEPOSITION GRAVIMETRIC AND OXALYLDIHYDRAZIDE SPECTROPHOTOMETRIC TEST METHOD

10. Scope

10.1 This test method covers the determination of copper in compositions greater than 50 %.

10.2 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

11. Summary of Test Method

11.1 After dissolution of the sample in HNO_3 and HF, the oxides of nitrogen are reduced with hydrogen peroxide, and the copper deposited electrolytically. Loss of platinum from the anode is minimized by the addition of lead. The copper oxalyldihydrazide complex is formed with the copper remaining in the electrolyte. Photometric measurement is made at approximately 540 nm.

12. Interferences

12.1 The elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

13. Apparatus

13.1 *Polytetrafluoroethylene or Polypropylene Beakers,* 250-mL capacity.

13.2 *Polytetrafluoroethylene or Polypropylene Split Covers.*

13.3 *Electrodes for Electroanalysis*—Recommended stationary type platinum electrodes are described in 13.3.1 and 13.3.2. The surface of the platinum electrode 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 electrode by sandblasting is not recommended.

13.3.1 *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 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 cm^2 exclusive of the stem.

13.3.2 *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 compositions 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 with an overall height of approximately 130 mm. A spiral anode of these dimensions will have a surface area of 9 cm^2. When both cathode and anode plates are to be determined, the anode should be made of the same material and design as the electrode described in 13.3.1. 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 cm^2 exclusive of the stem.

13.3.3 Gauze cathodes are recommended where rapid electrolysis is used.

14. Reagents

14.1 *Ammonium Chloride Solution* (0.02 g/L)—Dissolve 0.02 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L.

14.2 *Hydrogen Peroxide* (3 %)—Dilute 100 mL of 30 % hydrogen peroxide to 1 L.

14.3 *Lead Nitrate Solution* (10 g/L) —Dissolve 10.0 g of lead nitrate ($Pb(NO_3)_2$) in water and dilute to 1 L.

15. Procedure

15.1 Transfer a 2.000-g sample, weighed to the nearest 0.1 mg, to a 250-mL polytetrafluoroethylene or polypropylene beaker, add 2 mL of HF, and 30 mL of HNO_3 (1 + 1). Cover with a cover glass and allow to stand for a few minutes until the reaction has nearly ceased. Warm but do not heat over 80 °C. When dissolution is complete, add 25 mL of 3 % H_2O_2 and 3 mL of $Pb(NO_3)_2$ solution. Rinse the cover glass and dilute to approximately 150 mL with NH_4Cl solution.

15.2 With the electrolyzing current off, position the anode and the accurately weighed cathode in the solution so that the gauze is completely immersed. Cover the beaker with a split plastic cover.

15.3 Start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1.0 A/dm^2 and electrolyze overnight. Alternatively electrolyze at a current density of 4 A/dm^2 for 1.5 h. (The more rapid procedure requires the use of gauze electrodes).

15.4 Slowly withdraw the electrodes (or lower the beaker) with the current still flowing, and rinse with a stream of water from a wash bottle. Quickly remove the cathode, rinse it in water, and then dip into two successive baths of ethanol or methanol. Dry in an oven at 110 °C for 3 min to 5 min.

15.5 Return the voltage to zero and turn off the switch. Reserve the electrolyte.

15.6 Allow the electrode to cool to room temperature and weigh.

16. Calculation

16.1 Calculate the percentage of copper as follows:

$$\text{Copper, \%} = [(A+B)/C] \times 100 \qquad (1)$$

where:

A = deposited copper, g,
B = copper in the electrolyte as calculated in 17.10, g, and
C = sample used, g.

17. Spectrophotometric Determination of the Residual Copper in the Electrolyte

17.1 *Interferences*—The elements ordinarily present do not interfere if their composition is under the maximum limits shown in 1.1.

17.2 *Concentration Range*—The recommended concentration is from 0.0025 mg to 0.07 mg of copper per 50 mL of solution, using a 2-cm cell.

NOTE 1—This procedure has been written for cells having a 2-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

17.3 *Stability of Color*—The color fully develops in 20 min and is stable for 1 h.

17.4 *Reagents:*

17.4.1 *Acetaldehyde Solution* (40 %)—Dilute 400 mL of acetaldehyde to 1 L with water.

17.4.2 *Boric Acid Solution (50 g/L)*—Dissolve 50 g of boric acid (H_3BO_3) in hot water, cool, and dilute to 1 L.

17.4.3 *Citric Acid Solution (200 g/L)*—Dissolve 200 g of citric acid in water and dilute to 1 L.

17.4.4 *Copper, Standard Solution A (1 mL = 1.0 mg Cu)*—Transfer a 1.000-g sample of electrolytic copper (purity: 99.9 % minimum) to a 250-mL beaker and add 10 mL of HNO_3 (1 + 1). Evaporate nearly to dryness. Add 5 mL of water to dissolve the residue. Transfer to a 1-L volumetric flask, dilute to volume, and mix.

17.4.5 *Copper, Standard Solution B (1 mL = 0.010 mg Cu)*—Using a pipet, transfer 10 mL of Copper Solution A (1 mL = 1.0 mg Cu) to a 1-L volumetric flask, dilute to volume, and mix.

17.4.6 *Oxalyldihydrazide Solution (2.5 g/L)*—Dissolve 2.5 g of oxalyldihydrazide in warm water and dilute to 1 L.

17.5 *Preparation of Calibration Curve:*

17.5.1 *Calibration Solutions:*

17.5.1.1 Transfer 25 mL of boric acid solution to a 250-mL volumetric flask and then add a solution containing 150 mL of water, 2 mL of HF, and 30 mL of HNO_3 (1 + 1). Dilute to volume and mix.

17.5.1.2 Transfer 10 mL of this solution to each of four 50-mL volumetric flasks. Using pipets, transfer (1, 3, 5, and 7) mL of Copper Solution B (1 mL = 0.010 mg Cu) to the flasks. Proceed as directed in 17.5.3.

17.5.2 *Reference Solution*—Add 10 mL of boric acid solution prepared as directed in 17.5.1.1 to a 50-mL volumetric flask and proceed as directed in 17.5.3.

17.5.3 *Color Development*—Add in order, and with mixing after each addition, 5 mL of citric acid solution, 6 mL of NH_4OH, 10 mL of acetaldehyde solution, and 10 mL of oxalyldihydrazide solution. Cool, dilute to volume, and mix. Allow to stand for 30 min and proceed as directed in 17.5.4.

17.5.4 *Spectrophotometry:*

17.5.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 2-cm light path and a light band centered at approximately 540 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.