



# Standard Test Methods for Chemical Analysis of Manganese-Copper Alloys<sup>1</sup>

This standard is issued under the fixed designation E 581; 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.

## 1. Scope

1.1 These test methods cover the chemical analysis of manganese-copper alloys having chemical compositions within the following limits:

Element	Concentration Range, %
Copper	68.0 to 72.0
Manganese	28.0 to 32.0
Carbon	0.03 max
Iron	0.01 max
Phosphorus	0.01 max
Silicon	0.05 max
Sulfur	0.01 max

1.2 The test methods appear in the following order:

	Sections
Iron by the 1,10-Phenanthroline Photometric Method	11-20
Manganese by the (Ethylenedinitrilo) Tetraacetic Acid (EDTA)— Back-Titrimetric Method	21-27
Phosphorus by the Molybdivanadophosphoric Acid Extraction Photometric Method	28-38

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 precaution to be observed in the use of certain reagents, refer to Practices E 50. A specific precautionary statement is given in 24.7.

## 2. Referenced Documents

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

- D 1193 Specification for Reagent Water
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

<sup>1</sup> These 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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<sup>2</sup> 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.

- 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 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals<sup>3</sup>
- E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

## 3. Terminology

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

## 4. Significance and Use

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

## 5. Apparatus

5.1 Photometers shall conform to the requirements prescribed in Practice E 60.

## 6. Reagents and Materials

6.1 Reagents required for each determination are listed in separate sections of each test method. The standard solutions and certain other reagents used in more than one procedure shall conform to the requirements prescribed in Practices E 50.

6.2 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on

<sup>3</sup> Withdrawn.

Analytical Reagents of the American Chemical Society where such specifications are available<sup>4</sup>. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.3 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193.

## 7. Hazards

7.1 For precautions to be observed in this method, refer to Practice E 50.

7.2 A warning statement is given in 24.7.

## 8. Sampling

8.1 For procedures for sampling the material, refer to Practices E 55 and E 88.

## 9. Rounding Calculated Values

9.1 Calculated values shall be rounded to the desired number of places as directed in Practice E 29 Rounding Method.

## 10. Interlaboratory Studies

10.1 These test methods have been evaluated in accordance with Practice E 173, unless otherwise noted in the precision section. The Reproducibility  $R_2$  of Practice E 173 corresponds to the Reproducibility Index  $R$  of Practice E 1601. The Repeatability  $R_1$  of Practice E 173 corresponds to the Repeatability Index  $r$  of Practice E 1601.

# IRON BY THE 1,10-PHENANTHROLINE PHOTOMETRIC METHOD

## 11. Scope

11.1 This test method covers the determination of iron in concentrations from 0.003 to 0.02 %.

## 12. Summary of Test Method

12.1 The sample is dissolved in hydrochloric acid and hydrogen peroxide, and the excess oxidant removed by evaporation. The iron is extracted with methyl isobutyl ketone-benzene mixture. The iron is extracted from the organic phase into a hydroxylamine hydrochloride solution and the red-colored 1,10-phenanthroline complex is formed. Photometric measurement is made at approximately 510 nm.

## 13. Concentration Range

13.1 The recommended concentration range is from 0.005 to 0.125 mg of iron per 50 mL of solution using a 2-cm cell.

NOTE 1—This test method 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.

## 14. Stability of Color

14.1 The color develops within 5 min and is stable for at least 4 h.

## 15. Interferences

15.1 Elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1.

## 16. Reagents

16.1 *Hydroxylamine Hydrochloride Solution* (10 g/L)—Dissolve 5.0 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ) in 500 mL of water. Prepare fresh as needed.

16.2 *Iron, Standard Solution A* (1 mL = 0.125 mg Fe)—Transfer 0.1250 g of iron (purity: 99.9 % min) to a 100-mL beaker. Add 10 mL of HCl (1 + 1) and 1 mL of bromine water. Boil gently until the excess bromine is removed. Add 20 mL of HCl, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

16.3 *Iron, Standard Solution B* (1 mL = 0.00625 mg Fe)—Using a pipet, transfer 50 mL of iron solution A (1 mL = 0.125 mg Fe) to a 1-L volumetric flask, dilute to volume with HCl (1 + 49), and mix.

16.4 *Methyl Isobutyl Ketone-Benzene Mixture*—Mix 200 mL of methyl isobutyl ketone (MIBK) and 100 mL of benzene.

16.5 *1,10-Phenanthroline-Ammonium Acetate Buffer Solution*—Dissolve 1.0 g of 1,10-phenanthroline monohydrate in 5 mL of HCl in a 600-mL beaker. Add 215 mL of  $\text{CH}_3\text{COOH}$ , and, while cooling, carefully add 265 mL of  $\text{NH}_4\text{OH}$ . Cool to room temperature. Using a pH meter, check the pH; if it is not between 6.0 and 6.5, adjust it to that range by adding acetic acid or  $\text{NH}_4\text{OH}$  as required. Dilute to 500 mL.

## 17. Preparation of Calibration Curve

17.1 *Calibration Solutions:*

17.1.1 Using pipets, transfer 1, 2, 5, 10, 15, and 20 mL of iron solution B (1 mL = 0.00625 mg Fe) to 50-mL volumetric flasks. Dilute to 20 mL.

17.1.2 Add 20 mL of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  solution, mix, and allow to stand 1 min. Proceed as directed in 17.3.

17.2 *Reference Solution*—Transfer 20 mL of water to a 50-mL volumetric flask and proceed as directed in 17.1.2.

17.3 *Color Development*—Add 5 mL of 1,10-phenanthroline-ammonium acetate buffer solution, dilute to volume, and mix. Allow to stand at least 5 min but not more than 4 h.

17.4 *Photometry:*

17.4.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 2-cm light path and a light band centered at approximately 510 nm. Using the test cell, take the photometric readings of the calibration solutions.

17.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light

**TABLE 1 Statistical Information**

Test Sample	Labs	Iron Found, %	Repeatability ( $r$ , E 1601)	Reproducibility ( $R$ , E 1601)
Manganese Copper	7	0.0137	0.0013	0.0028

<sup>4</sup> *Reagent Chemical, American Chemical Society Specifications*, American Chemical Society, Washington, DC, www.chemistry.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc., (USPC), Rockville, MD, www.uspc.org.

path and adjust the photometer to the initial setting, using a light band centered at approximately 510 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

17.5 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of iron per 50 mL of solution.

## 18. Procedure

### 18.1 Test Solution:

18.1.1 Transfer a 2.0-g sample, weighed to the nearest 10 mg, to a 400-mL beaker.

18.1.2 Carry a reagent blank through the entire procedure, using the same amounts of all reagents but with the sample omitted.

18.1.3 Add 25 mL of HCl (7 + 3) and then H<sub>2</sub>O<sub>2</sub> as needed to dissolve the alloy completely. When dissolution is complete, add 20 mL of HCl and heat carefully to decompose excess peroxide. Cool to room temperature, transfer to a 125-mL conical separatory funnel. Add HCl (1 + 1), as required, to adjust the volume to 50 mL.

18.1.4 Add 20 mL of MIBK - benzene mixture to the separatory funnel and shake 1 min. Allow the phases to separate, discard the aqueous phase, wash the organic phase 3 times with 3 to 5-mL portions of HCl (1 + 1) to remove copper, and discard the washings. Extract the iron from the organic phase by shaking vigorously 30 s with 10 mL of NH<sub>2</sub>OH·HCl solution. Transfer the aqueous phase to a 50-mL volumetric flask. Repeat the extraction with a second 10-mL portion of NH<sub>2</sub>OH·HCl solution, and transfer the extract to the 50-mL flask. Dilute to 40 mL and proceed as directed in 18.3.

18.2 *Reference Solution*—Use the reagent blank solution prepared as directed in 18.1.2.

18.3 *Color Development*—Proceed as directed in 17.3.

18.4 *Photometry*—Proceed as directed in 17.4.

## 19. Calculation

19.1 Convert the net photometric reading of the test solution to milligrams of iron by means of the calibration curve. Calculate the percentage of iron as follows:

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

where:

*A* = milligrams of iron found in 50 mL of the final test solution, and

*B* = grams of sample represented in 50 mL of the final test solution.

## 20. Precision and Bias <sup>5</sup>

20.1 Seven laboratories cooperated in testing this test method and obtained the precision data shown in Table 1, which were calculated in accordance with Practice E 1601. Although samples covered by this test method with iron

concentrations near the lower limit of the scope were not available for testing, the precision data obtained should apply.

20.2 The accuracy of this test method could not be evaluated because adequate certified standard reference materials were unavailable at the time of testing. The user is encouraged to verify by the use of certified reference materials, if available, that the accuracy of this test method is adequate for the contemplated use.

## MANGANESE BY THE (ETHYLENEDINITRILLO)TETRAACETIC ACID (EDTA)—BACK-TITRIMETRIC METHOD

### 21. Scope

21.1 This test method covers the determination of manganese in concentrations from 28.0 to 32.0 %.

### 22. Summary of Test Method

22.1 The sample is dissolved in nitric acid. Manganese is chelated with disodium (ethylenedinitrilo) tetraacetate (EDTA), which is added in excess. The pH of the solution is adjusted to 10 and sodium cyanide is added to complex copper. The manganese is then determined by back-titration with standard manganese solution.

### 23. Interferences

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

### 24. Reagents

24.1 *Buffer Solution* (pH 10)—Transfer 54 g of ammonium chloride (NH<sub>4</sub>Cl) to a 1-L beaker, dissolve in 500 mL of water, add 350 mL of NH<sub>4</sub>OH, dilute to 1 L, and mix. Store in a polyethylene bottle.

24.2 *Copper Solution* (25 g/L)—Transfer 2.50 g of copper (purity: 99.9 % min) to a 250-mL beaker. Add 20 mL of HNO<sub>3</sub>(1 + 1). When dissolution is complete, boil to expel oxides of nitrogen. Cool, dilute to 100 mL, and mix.

24.3 *Disodium (Ethylenedinitrilo)tetraacetic Acid Dihydrate (EDTA), Standard Solution* (0.05 M)—Dissolve 18.6127 g of disodium (ethylenedinitrilo) tetraacetate dihydrate in water, transfer to a 1-L volumetric flask, dilute to volume, and mix. The solution is stable for several months when stored in plastic or borosilicate glass bottles.

24.3.1 Standardize the solution as follows: Using a pipet, transfer 25 mL of zinc solution (0.050 M) to a 400-mL beaker. Add 25 mL of buffer solution and dilute to about 250 mL. Add 4 to 6 drops of eriochrome black-T indicator solution and titrate with EDTA standard solution to the color change from magenta to blue. Calculate the molarity of the EDTA solution as follows:

$$\text{Molarity of EDTA solution, } A = \frac{1.25}{B} \quad (2)$$

where:

*A* = molarity of EDTA solution, and

*B* = millilitres of EDTA solution required to titrate 25 mL of zinc standard solution (0.050 M).

<sup>5</sup> Supporting data are available from ASTM International Headquarters. Request RR: E03-1006.