Designation: E581 – 10

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

This standard is issued under the fixed designation E581; 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 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 [0.003 % to 0.02 %]	11-20
Manganese by the (Ethylenedinitrilo) Tetraacetic Acid (EDTA)—Back-Titrimetric Method [28 % to 32 %]	21-27
Phosphorus by the Molybdivanadophosphoric Acid Extraction Photometric Method [0.002 % to 0.014 %]	28-38

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

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

E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

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E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[3]

E1601 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 E135.

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 E60.

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 E50.

[1] 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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[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.

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

TABLE 1 Statistical Information

Test Sample	Labs	Iron Found, %	Repeatability (r, Practice E1601)	Reproducibility (R, Practice E1601)
Manganese Copper	7	0.0137	0.0013	0.0028

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 Analytical Reagents of the American Chemical Society where such specifications are available.[4] 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 D1193.

7. Hazards

7.1 For precautions to be observed in this method, refer to Practices E50.

7.2 A warning statement is given in 24.7.

8. Sampling

8.1 For procedures for sampling the material, refer to Practices E55 and E88.

9. Rounding Calculated Values

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

10. Interlaboratory Studies

10.1 These test methods have been evaluated in accordance with Practice E173, unless otherwise noted in the precision section. The Reproducibility R_2 of Practice E173 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.

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 HCl 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 mg 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 ($NH_2OH \cdot HCl$) 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 CH_3COOH, and, while cooling, carefully add 265 mL of NH_4OH. 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 NH_4OH 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 $NH_2OH \cdot HCl$ 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.

[4] *Reagent Chemicals, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, http://www.usp.org.

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 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_2O_2 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 three times with 3-mL 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 $NH_2OH{\cdot}HCl$ solution. Transfer the aqueous phase to a 50-mL volumetric flask. Repeat the extraction with a second 10-mL portion of $NH_2OH{\cdot}HCl$ 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

20.1 *Precision*—Seven laboratories cooperated in testing this test method and obtained the precision data shown in Table 1, which were calculated in accordance with Practice E1601. 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 *Bias*—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 (ETHYLENEDINITRILO)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 HNO_3. 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_4Cl) to a 1-L beaker, dissolve in 500 mL of water, add 350 mL of NH_4OH, 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_3 (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 four drops to six drops of eriochrome black-T indicator solution and titrate with EDTA standard solution to the color