Designation: E 581 – 76 (Reapproved 1996)

An American National Standard

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

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 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	8-17
Manganese by the (Ethylenedinitrilo) Tetraacetic Acid (EDTA)—Back-Titrimetric Method	18-24
Phosphorus by the Molybdivanadophosphoric Acid Extraction Photometric Method	25-35

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 Note 2.

2. Referenced Documents

2.1 *ASTM Standards:*

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[2]

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals[3]

E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[3]

E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition[3]

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[3]

3. Significance and Use

3.1 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.

4. Apparatus, Reagents, and Photometric Practice

4.1 Apparatus and reagents required for each determination are listed in separate sections of each test method. The apparatus, standard solutions, and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50, except that photometers shall conform to the requirements prescribed in Practice E 60.

5. Sampling

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

6. Rounding Calculated Values

6.1 Calculated values shall be rounded to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

7. Interlaboratory Studies

7.1 These test methods have been evaluated in accordance with Practice E 173, unless otherwise noted in the precision section.

IRON BY THE 1,10-PHENANTHROLINE PHOTOMETRIC METHOD

8. Scope

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

[1] These methods are under the jurisdiction of ASTM Committee E-1 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] *Annual Book of ASTM Standards*, Vol 14.02.

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

9. Summary of Test Method

9.1 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.

10. Concentration Range

10.1 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.

11. Stability of Color

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

12. Interferences

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

13. Reagents

13.1 *Hydroxylamine Hydrochloride Solution* (10 g/L)—Prepare a solution as directed for Reagent No. 131, but dilute to 500 mL.

13.2 *Iron, Standard Solution A* (1 mL = 0.125 mg Fe)—Prepare a solution as directed for Reagent No. 4, but use 0.1250 g instead of the specified weight.

13.3 *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.

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

13.5 *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.

14. Preparation of Calibration Curve

14.1 *Calibration Solutions*:

14.1.1 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.

14.1.2 Add 20 mL of $NH_2OH{\cdot}HCl$ solution, mix, and allow to stand 1 min. Proceed as directed in 14.3.

14.2 *Reference Solution*—Transfer 20 mL of water to a 50-mL volumetric flask and proceed as directed in 14.1.2.

14.3 *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.

14.4 *Photometry*:

14.4.1 *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.

14.4.2 *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.

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

15. Procedure

15.1 *Test Solution*:

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

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

15.1.3 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.

15.1.4 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 $NH_2OH{\cdot}HCl$ 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 15.3.

15.2 *Reference Solution*—Use the reagent blank solution prepared as directed in 15.1.2.

15.3 *Color Development*—Proceed as directed in 14.3.

15.4 *Photometry*—Proceed as directed in 14.4.

16. Calculation

16.1 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.

17. Precision and Bias [4]

17.1 Seven laboratories cooperated in testing this test method and obtained the data shown in Table 1. 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. The reproducibility (R_1) and repeatability (R_2) are not tabulated because the required number of data were not obtained paired.

17.2 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 cautioned 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

18. Scope

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

19. Summary of Test Method

19.1 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.

20. Interferences

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

21. Reagents

21.1 *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.

21.2 *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.

21.3 *Disodium (Ethylenedinitrilo)tetraacetic Acid Dihydrate (EDTA), Standard Solution* (0.05 *M*)—Prepare a solution as directed for Reagent No. 22, but use 18.6127 g instead of the specified weight. Standardize the solution as follows: Using a pipet, transfer 25 mL of zinc solution (0.0500 *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:

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

where:

A = molarity of EDTA solution, and
B = millilitres of EDTA solution required to titrate 25 mL of zinc standard solution (0.05 M).

21.4 *Eriochrome Black-T Indicator Solution* (8 g/L)—Reagent No. 44.

21.5 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Reagent No. 131.

21.6 *Manganese, Standard Solution* (0.05 *M*)—Prepare a solution as directed for Reagent No. 24, Method A, but use 2.7470 g instead of the specified weight. Standardize as follows: Using a pipet, transfer 25 mL of the manganese solution to a 400-mL beaker. Add 10 mL of copper solution. Proceed as directed in 22.2. Calculate the EDTA equivalent of the solution as follows:

$$EDTA \text{ equivalent, mL } EDTA/\text{mL } Mn = 30.00/(25.00 \times C) \quad (3)$$

where:

C = millilitres of manganese solution required for titration of excess EDTA solution.

21.7 *Sodium Cyanide Solution* (200 g/L)—Dissolve 200 g of sodium cyanide (NaCN) in water, and dilute to 1 L. Store in a plastic bottle.

NOTE 2—**Caution:** The preparation, storage, and use of NaCN solutions require care and attention. Avoid inhalation of fumes and exposure of the skin to the chemical or its solutions. Work in a well-ventilated hood. Refer to Section 6 of Practices E 50.

21.8 *Sodium Tartrate Solution* (250 g/L)—Dissolve 250 g of sodium tartrate in water, and dilute to 1 L. Store in a plastic bottle.

21.9 *Zinc, Standard Solution* (0.050 *M*)—Transfer 3.2690 g of zinc (purity: 99.9 % min) to a 400-mL beaker, and cover. Add 25 mL of HNO_3 (1 + 1) and warm gently until the zinc is dissolved. Boil to expel oxides of nitrogen. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

22. Procedure

22.1 Transfer a 5.0-g sample, weighed to the nearest 1 mg, to a 400-mL beaker, and cover. Cautiously, add 40 mL of HNO_3 (1 + 1) and warm gently until dissolution is complete.

[4] Supporting data are available from ASTM Headquarters. Request RR: E03-1006.

TABLE 1 Tabulation of Interlaboratory Data of Iron by the 1, 10-Phenanthroline Photometric Method

Laboratory	Iron, %	
	1st Day	2nd Day
1	0.0136	0.0134
2	0.0140	0.0124
3	0.0144	0.0142
4	0.0144	0.0144
5	0.0120	0.0120
6	0.0133	0.0138
7	0.0149	0.0149
	$\bar{X}i$ = 0.01380	$\bar{Y}i$ = 0.01359

Boil to expel oxides of nitrogen. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix. Using a pipet, transfer 25 mL of the test solution to a 400-mL beaker.

22.2 Add 10 mL of $NH_2OH·HCl$ solution. Using a pipet, add 30 mL of EDTA solution, and mix. Add 5 mL of sodium tartrate solution, 25 mL of buffer solution, and 10 mL of NaCN solution, mixing after each addition. Adjust the volume to about 200 mL. Add 4 to 6 drops of eriochrome black-T indicator solution. Using a 10-mL buret, titrate the excess EDTA with manganese standard solution to the first permanent pink end point, and record the buret reading to the nearest 0.01 mL.

23. Calculation

23.1 Calculate the percentage of manganese as follows:

$$\text{Manganese, \%} = [30.00 - (D \times E)] \times F \times 21.98 \quad (4)$$

where:

- D = millilitres of manganese standard solution required for back-titration of the test solution,
- E = millilitres of EDTA standard solution equivalent to 1 millilitre of manganese standard solution (refer to 21.6), and
- F = molarity of EDTA standard solution (refer to 21.3).

24. Precision and Bias [4]

24.1 Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 2.

24.2 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 cautioned to verify by the use of certified reference materials, if available, that the accuracy of this test method is adequate for the contemplated use.

PHOSPHORUS BY THE MOLYBDIVANADOPHOSPHORIC ACID—EXTRACTION PHOTOMETRIC METHOD

25. Scope

25.1 This test method covers the determination of phosphorus in concentrations from 0.002 to 0.014 %.

26. Summary of Test Method

26.1 The sample is dissolved in nitric and hydrochloric acids. The quinquevalent phosphorus reacts with an excess of molybdate solution in the presence of vanadate to form the yellow molybdivanadophosphoric acid complex which is extracted into methyl isobutyl ketone. Photometric measurement is made at approximately 400 nm.

TABLE 2 Statistical Information

Test Specimen	Manganese Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1. Manganese copper	30.44	0.20	0.32

27. Concentration Range

27.1 The recommended concentration range is from 0.0035 to 0.07 mg of phosphorus per 15 mL of solution, using a 2-cm cell.

NOTE 3—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.

28. Stability of Color

28.1 Full color develops in the aqueous solution within 7 min. The extracted color is stable for at least 1 h.

29. Interferences

29.1 Elements ordinarily present in manganese copper alloys do not interfere if their concentrations are under the maximum limits shown in 1.1.

30. Apparatus

30.1 Glassware must be phosphorus- and arsenic-free. Boil the glassware with hydrochloric acid and rinse with water before use. It is recommended that the glassware used for this determination be reserved for this use only. Many detergents contain phosphorus and must not be used for cleaning purposes.

31. Reagents

31.1 *Ammonium Molybdate Solution* (100 g/L)—Dissolve 100 g of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}·4H_2O$) in 600 mL of hot water, and dilute the solution to about 950 mL. Cool and dilute to 1 L. Store in a polyethylene bottle.

31.2 *Ammonium Vanadate Solution* (2.4 g/L)—Dissolve 2.4 g of ammonium vanadate (NH_4VO_3) in 500 mL of hot water. When dissolution is complete, add 20 mL of HNO_3(1 + 1), cool, and dilute to 1 L. Store in a polyethylene bottle.

31.3 *Citric Acid Solution* (500 g/L)—Dissolve 500 g of citric acid monohydrate in 800 mL of water and dilute to 1 L. Store in a polyethylene bottle.

31.4 *Methyl Isobutyl Ketone (MIBK).*

31.5 *Phosphorus, Standard Solution A* (1 mL = 0.5 mg P)—Dissolve 0.9285 g of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) in 200 mL of water in a 500-mL volumetric flask, dilute to volume, and mix.

31.6 *Phosphorus, Standard Solution B* (1 mL = 0.01 mg P)—Using a pipet, transfer 10 mL of phosphorus Solution A (1 mL = 0.5 mg P) to a 500-mL volumetric flask, dilute to volume, and mix.

32. Preparation of Calibration Curve

32.1 *Calibration Solutions*:

32.1.1 Using pipets, transfer 1, 2, 4, and 6 mL of Solution B (1 mL = 0.01 mg P) to 150-mL beakers.

32.1.2 Add 50 mL of water and 10 mL of $HClO_4$. Cool. Proceed as directed in 32.3.

32.2 *Reference Solution*—Transfer 50 mL of water and 10 mL of $HClO_4$ to a 150-mL beaker. Cool. Proceed as directed in 32.3.

32.3 *Color Development*:

32.3.1 Add 10 mL of NH_4VO_3 solution and mix. Add 15 mL of ammonium molybdate solution, mix, and transfer into a 125-mL conical separatory funnel (Note 3). Drain the beaker well but do not rinse. Let stand for 7 min. Add 10 mL of citric acid solution, stopper the funnel, and shake for 5 s.

32.3.2 Using a pipet, transfer 15 mL of MIBK to the solution and shake again, vigorously, for 30 s. Allow the phases to separate. Drain and discard the aqueous phase. Rinse the stem of the separatory funnel with about 1 mL of the MIBK phase. Filter, using a dry, triple-folded, 9-cm, hardened paper, into a dry absorption cell.

32.4 *Photometry*:

32.4.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 2-cm light path and a light band centered at approximately 400 nm. Using the test cell, take the photometric readings of the calibration solutions.

32.4.2 *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 400 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

32.5 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of phosphorus per 15 mL of MIBK.

33. Procedure

33.1 *Test Solution*:

33.1.1 Transfer a 0.50-g sample, weighed to the nearest 5 mg, to a 150-mL beaker (Note 3).

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

33.1.3 Add a mixture of 5 mL of HNO_3 and 5 mL of HCl and warm gently. When dissolution is complete, heat to boiling and evaporate from 6 to 7 mL. Add 50 mL of water and 10 mL of $HClO_4$. Cool. Proceed as directed in 33.3.

33.2 *Reference Solution*—Use the reagent blank solution prepared as directed in 33.1.2.

33.3 *Color Development*—Proceed as directed in 32.3.

33.4 *Photometry*—Proceed as directed in 32.4.

34. Calculation

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

$$\text{Phosphorus, \%} = A/(B \times 10) \quad (5)$$

where:

A = milligrams of phosphorus found in 15 mL of the final test solution, and

B = grams of sample represented in 15 mL of the final test solution.

35. Precision and Bias [4]

35.1 Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 3. Although samples covered by this test method with phosphorus concentrations near the lower and upper limits of the scope were not available for testing, the precision data obtained should apply.

35.2 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 cautioned to verify by the use of certified reference materials, if available, that the accuracy of this test method is adequate for the contemplated use.

TABLE 3 Statistical Information

Test Specimen	Phosphorus Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1. Manganese copper	0.0021	0.0005	0.0015