



Designation: E354 – 14

Standard Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys¹

This standard is issued under the fixed designation E354; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover the chemical analysis of high-temperature, electrical, magnetic, and other similar iron, nickel, and cobalt alloys having chemical compositions within the following limits:

Element	Composition Range, %
Aluminum	0.005 to 18.00
Beryllium	0.001 to 0.05
Boron	0.001 to 1.00
Calcium	0.002 to 0.05
Carbon	0.001 to 1.10
Chromium	0.10 to 33.00
Cobalt	0.10 to 75.00
Columbium (Niobium)	0.01 to 6.0
Copper	0.01 to 10.00
Iron	0.01 to 85.00
Magnesium	0.001 to 0.05
Manganese	0.01 to 3.0
Molybdenum	0.01 to 30.0
Nickel	0.10 to 84.0
Nitrogen	0.001 to 0.20
Phosphorus	0.002 to 0.08
Silicon	0.01 to 5.00
Sulfur	0.002 to 0.10
Tantalum	0.005 to 10.0
Titanium	0.01 to 5.00
Tungsten	0.01 to 18.00
Vanadium	0.01 to 3.25
Zirconium	0.01 to 2.50

1.2 The test methods in this standard are contained in the sections indicated below:

	Sections
Aluminum, Total, by the 8-Quinolinol Gravimetric Method (0.20 % to 7.00 %)	100
Carbon, Total, by the Combustion-Thermal Conductivity Method	Discontinued
Carbon, Total, by the Combustion Gravimetric Method (0.05 % to 1.10 %)	Discontinued
Chromium by the Atomic Absorption Method (0.006 % to 1.00 %)	165

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 E01.01 on Iron, Steel, and Ferroalloys.

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Chromium by the Peroxydisulfate Oxidation—Titration Method (0.10 % to 33.00 %)	175
Chromium by the Peroxydisulfate-Oxidation Titrimetric Method	Discontinued
Cobalt by the Ion-Exchange-Potentiometric Titration Method (2 % to 75 %)	53
Cobalt by the Nitroso-R-Salt Spectrophotometric Method (0.10 % to 5.0 %)	61
Copper by Neocuproine Spectrophotometric Method (0.01 % to 10.00 %)	90
Copper by the Sulfide Precipitation-Electrodeposition Gravimetric Method (0.01 % to 10.00 %)	71
Iron by the Silver Reduction Titrimetric Method (1.0 % to 50.0 %)	192
Manganese by the Periodate Spectrophotometric Method (0.05 % to 2.00 %)	9
Molybdenum by the Ion Exchange—8-Hydroxyquinoline Gravimetric Method (1.5 % to 30 %)	184
Molybdenum by the Spectrophotometric Method (0.01 % to 1.50 %)	153
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 % to 84.0 %)	135
Phosphorus by the Molybdenum Blue Spectrophotometric Method (0.002 % to 0.08 %)	19
Silicon by the Gravimetric Method (0.05 % to 5.00 %)	46
Sulfur by the Gravimetric Method	Discontinued
Sulfur by the Combustion-Iodate Titration Method (0.005 % to 0.1 %)	Discontinued
Sulfur by the Chromatographic Gravimetric Method	
Tin by the Solvent Extraction—Atomic Absorption Method (0.002 % to 0.10 %)	143

1.3 Methods for the determination of carbon and sulfur not included in this standard can be found in Test Methods E1019.

1.4 Some of the composition ranges given in 1.1 are too broad to be covered by a single method and therefore this standard contains multiple methods for some elements. The user must select the proper method by matching the information given in the Scope and Interference sections of each method with the composition of the alloy to be analyzed.

1.5 The values stated in SI units are to be regarded as standard.

1.6 *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 6 and in special “Warning” paragraphs throughout these test methods.*

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

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)³

E350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron

E351 Test Methods for Chemical Analysis of Cast Iron—All Types

E352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels

E353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition

2.2 Other Document:

ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests⁴

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 compositional specifications, particularly those under the jurisdiction of the ASTM Committee on Steel, Stainless Steel and Related Alloys. 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 under appropriate quality control practices such as those described in Guide **E882**.

5. Apparatus, Reagents, and Instrumental Practice

5.1 *Apparatus*—Specialized apparatus requirements are listed in the “Apparatus” Section in each method.

5.2 Reagents:

5.2.1 *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. 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.

5.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as conforming to Type I or Type II of Specification **D1193**. Type III or IV may be used if they effect no measurable change in the blank or sample.

5.3 *Spectrophotometric Practice*—Spectrophotometric practice prescribed in these test methods shall conform to Practice **E60**.

6. Hazards

6.1 For precautions to be observed in the use of certain reagents and equipment in these methods, refer to Practices **E50**.

7. Sampling

7.1 For procedures for sampling the material, reference shall be made to Practice **E1806**.

8. Interlaboratory Studies and Rounding Calculated Values

8.1 These test methods have been evaluated in accordance with Practice **E173** (withdrawn 1997) or ISO 5725. The Reproducibility R2 of Practice **E173** corresponds to the Reproducibility Index R of Practice **E1601**. The Repeatability R1 of Practice **E173** corresponds to the Repeatability Index r of Practice **E1601**.

8.2 Calculated values shall be rounded to the desired number of places in accordance with the Rounding Method of Practice **E29**.

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

9.1 This method covers the determination of manganese in compositions from 0.05 % to 2.00 %.

10. Summary of Method

10.1 Manganous ions are oxidized to permanganate ions by treatment with periodate. Tungsten when present at compositions greater than 0.5 % is kept in solution with H₃PO₄.

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.

⁴ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

Solutions of the samples are fumed with HClO_4 so that the effect of periodate is limited to the oxidation of manganese. Spectrophotometric measurements are made at approximately 545 nm.

11. Concentration Range

11.1 The recommended concentration range is 0.15 mg to 0.8 mg of manganese per 50 mL of solution, using a 1-cm cell (Note 1) and a spectrophotometer with a band width of 10 nm or less.

NOTE 1—This method has been written for cells having a 1-cm light path and a “narrow-band” instrument. The concentration range depends upon band width and spectral region used as well as cell optical path length. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

12. Stability of Color

12.1 The color is stable for at least 24 h.

13. Interferences

13.1 HClO_4 acid treatment, which is used in the procedure, yields solutions which can be highly colored due to the presence of Cr (VI) ions. Although these ions and other colored ions in the sample solution undergo no further change in color quality upon treatment with metaperiodate ion, the following precautions must be observed when filter spectrophotometers are used: Select a filter with maximum transmittance between 545 nm and 565 nm. The filter must transmit not more than 5 % of its maximum at a wavelength shorter than 530 nm. The band width of the filter should be less than 30 nm when measured at 50 % of its maximum transmittance. Similar restrictions apply with respect to the wavelength region employed when other “wide-band” instruments are used.

13.2 The spectral transmittance curve of permanganate ions exhibits two useful minima, one at approximately 526 nm, and the other at 545 nm. The latter is recommended when a “narrow-band” spectrophotometer is used.

13.3 Tungsten, when present in amounts of more than 0.5 % interferes by producing a turbidity in the final solution. A special procedure is provided for use with samples containing more than 0.5 % tungsten which eliminates the problem by preventing the precipitation of the tungsten.

14. Reagents

14.1 *Manganese, Standard Solution* (1 mL = 0.032 mg Mn)—Transfer the equivalent of 0.4000 g of assayed, high-purity manganese (purity: 99.99 % minimum), to a 500-mL volumetric flask and dissolve in 20 mL of HNO_3 by heating. Cool, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 500-mL volumetric flask, dilute to volume, and mix.

14.2 *Nitric-Phosphoric Acid Mixture*—Cautiously, while stirring, add 100 mL of HNO_3 and 400 mL of H_3PO_4 to 400 mL of water. Cool, dilute to 1 L, and mix. Prepare fresh as needed.

14.3 *Potassium Metaperiodate Solution* (7.5 g/L)—Dissolve 7.5 g of potassium metaperiodate (KIO_4) in 200 mL of hot HNO_3 (1 + 1), add 400 mL of H_3PO_4 , cool, dilute to 1 L, and mix.

14.4 *Water, Pretreated with Metaperiodate*—Add 20 mL of KIO_4 solution to 1 L of water, mix, heat at not less than 90°C for 20 min to 30 min, and cool. Use this water to dilute solutions to volume that have been treated with KIO_4 solution to oxidize manganese, and thus avoid reduction of permanganate ions by any reducing agents in the untreated water. **Caution**—Avoid the use of this water for other purposes.

15. Preparation of Calibration Curve

15.1 *Calibration Solutions*—Using pipets, transfer 5 mL, 10 mL, 15 mL, 20 mL, and 25 mL of manganese standard solution (1 mL = 0.032 mg Mn) to 50-mL borosilicate glass volumetric flasks, and, if necessary, dilute to approximately 25 mL. Proceed as directed in 15.3.

15.2 *Reference Solution*—Transfer approximately 25 mL of water to a 50-mL borosilicate glass volumetric flask. Proceed as directed in 15.3.

15.3 *Color Development*—Add 10 mL of KIO_4 solution, and heat the solutions at not less than 90°C for 20 min to 30 min (Note 2). Cool, dilute to volume with pretreated water, and mix.

NOTE 2—Immersing the flasks in a boiling water bath is a preferred means of heating them for the specified period to ensure complete color development.

15.4 Spectrophotometry:

15.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using the Reference Solution (15.2) in absorption cells with a 1-cm light path and using a light band centered at approximately 545 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions versus the Reference Solution (15.2)

15.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the Reference Solution (15.2) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 545 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

15.5 *Calibration Curve*—Follow the instrument manufacturer’s instructions for generating the calibration curve.

16. Procedure

16.1 *Test Solutions*—Select and weigh a sample in accordance with the following:

Manganese, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL
0.01 to 0.5	0.80	0.5	100
0.45 to 1.0	0.35	0.3	100
0.85 to 2.0	0.80	0.5	500

16.1.1 *For Samples Containing Not More Than 0.5 % Tungsten:*

16.1.1.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO_3 as needed to hasten dissolution, and then add 3 mL to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of HClO_4 ; evaporate to fumes to oxidize chromium, if present, and to expel HCl . Continue fuming until salts begin to separate. Cool,

add 50 mL of water, and digest if necessary to dissolve the salts. Cool and transfer the solution to a 100-mL volumetric flask. Proceed to 16.1.3.

16.1.1.2 For samples whose dissolution is hastened by HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO₃ and a few drops of HF as needed to hasten dissolution, and then add 3 mL to 4 mL of HNO₃. When dissolution is complete, cool, then add 10 mL of HClO₄, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to either a 100-mL or 500-mL volumetric flask as indicated in 16.1. Proceed to 16.1.3.

16.1.2 For Samples Containing More Than 0.5 % Tungsten:

16.1.2.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 mL to 6 mL of H₂SO₄, and 3 mL to 4 mL of HNO₃. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 min to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO₃. Cool, add 50 mL of water, and digest, if necessary, to dissolve the salts. Transfer the solution to either a 100-mL or 500-mL volumetric flask as directed in 16.1. Proceed to 16.1.3.

16.1.2.2 For samples whose dissolution is hastened by HF: Add 8 mL to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 mL to 6 mL of H₂SO₄, 3 mL to 4 mL of HNO₃, and a few drops of HF. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 min to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO₃. Cool, add 50 mL of water, digest, if necessary, to dissolve the salts, cool, and transfer the solution to a 100-mL or 500-mL volumetric flask as directed in 16.1. Proceed to 16.1.3.

16.1.2.3 Cool the solution, dilute to volume, and mix. Allow insoluble matter to settle, or dry-filter through a coarse paper and discard the first 15 mL to 20 mL of the filtrate, before taking aliquots.

16.1.3 Using a pipet, transfer 20-mL aliquots to two 50-mL borosilicate glass volumetric flasks; treat one as directed in 16.3 and the other as directed in 16.4.1.

16.2 *Reagent Blank Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with the sample omitted.

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

16.4 Reference Solutions:

16.4.1 *Background Color Solution*—To one of the sample aliquots in a 50-mL volumetric flask, add 10 mL of HNO₃-H₃PO₄ mixture, and heat the solution at not less than 90 °C for 20 min to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

16.4.2 *Reagent Blank Reference Solution*—Transfer the reagent blank solution (16.2) to the same size volumetric flask as used for the test solutions and transfer the same size aliquots as used for the test solutions to two 50-mL volumetric flasks. Treat one portion as directed in 16.3 and use as reference solution for test samples. Treat the other as directed in 16.4.1 and use as reference solution for Background Color Solutions.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Spectrophotometric Method

Test Specimen	Manganese Found, %	Repeatability (R ₁ , E173)	Reproducibility (R ₂ , E173)
1. Nickel alloy, 77Ni-20Cr (NIST 169, 0.073 Mn)	0.074	0.002	0.008
2. High-temperature alloy 68Ni-14Cr-7Al-6Mo (NIST 1205, 0.29 Mn)	0.289	0.007	0.026
3. Cobalt alloy 41Co-20Ni-20Cr-4Mo-4W (NIST 168, 1.50 Mn)	1.49	0.03	0.08
4. Stainless steel 18Cr-9Ni (NIST 101e, 1.77 Mn)	1.79	0.03	0.07

16.5 *Spectrophotometry*—Establish the cell corrections with the Reagent Blank Reference solution to be used as a reference solution for Background Color solutions. Take the spectrophotometric readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference Solutions as directed in 15.4.

17. Calculation

17.1 Convert the net spectrophotometric reading of the test solution and of the background color solution to milligrams of manganese by means of the calibration curve. Calculate the percentage of manganese as follows:

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

where:

- A = manganese, mg, found in 50 mL of the final test solution,
- B = apparent manganese, mg, found in 50 mL of the final background color solution, and
- C = sample weight, g, represented in 50 mL of the final test solution.

18. Precision and Bias

18.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 1.

18.2 *Bias*—No information on the accuracy of this 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.

PHOSPHORUS BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD

19. Scope

19.1 This method covers the determination of phosphorus in compositions from 0.002 % to 0.08 %.

20. Summary of Method

20.1 The sample is dissolved in mixed acids and the solution is fumed with HClO₄. Ammonium molybdate is added to react with the phosphorus to form the heteropoly phosphomolybdate. This species is then reduced with hydrazine sulfate