



Designation: E350 – 18

Standard Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron¹

This standard is issued under the fixed designation E350; 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 carbon steels, low-alloy steels, silicon electrical steels, ingot iron, and wrought iron having chemical compositions within the following limits:

Element	Composition Range, %
Aluminum	0.001 to 1.50
Antimony	0.002 to 0.03
Arsenic	0.0005 to 0.10
Bismuth	0.005 to 0.50
Boron	0.0005 to 0.02
Calcium	0.0005 to 0.01
Cerium	0.005 to 0.50
Chromium	0.005 to 3.99
Cobalt	0.01 to 0.30
Columbium (Niobium)	0.002 to 0.20
Copper	0.005 to 1.50
Lanthanum	0.001 to 0.30
Lead	0.001 to 0.50
Manganese	0.01 to 2.50
Molybdenum	0.002 to 1.50
Nickel	0.005 to 5.00
Nitrogen	0.0005 to 0.04
Oxygen	0.0001 to 0.03
Phosphorus	0.001 to 0.25
Selenium	0.001 to 0.50
Silicon	0.001 to 5.00
Sulfur	0.001 to 0.60
Tin	0.002 to 0.10
Titanium	0.002 to 0.60
Tungsten	0.005 to 0.10
Vanadium	0.005 to 0.50
Zirconium	0.005 to 0.15

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

Aluminum, Total, by the 8-Quinolinol Gravimetric Method (0.20 % to 1.5 %)

Sections

124–131

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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Aluminum, Total, by the 8-Quinolinol Spectrophotometric Method (0.003 % to 0.20 %)	76–86
Aluminum, Total or Acid-Soluble, by the Atomic Absorption Spectrometry Method (0.005 % to 0.20 %)	308–317
Antimony by the Brilliant Green Spectrophotometric Method (0.0002 % to 0.030 %)	142–151
Bismuth by the Atomic Absorption Spectrometry Method (0.02 % to 0.25 %)	298–307
Boron by the Distillation-Curcumin Spectrophotometric Method (0.0003 % to 0.006 %)	208–219
Calcium by the Direct-Current Plasma Atomic Emission Spectrometry Method (0.0005 % to 0.010 %)	289–297
Carbon, Total, by the Combustion Gravimetric Method (0.05 % to 1.80 %)— <i>Discontinued 1995</i>	
Cerium and Lanthanum by the Direct Current Plasma Atomic Emission Spectrometry Method (0.003 % to 0.50 % Cerium, 0.001 % to 0.30 % Lanthanum)	249–257
Chromium by the Atomic Absorption Spectrometry Method (0.006 % to 1.00 %)	220–229
Chromium by the Peroxydisulfate Oxidation-Titration Method (0.05 % to 3.99 %)	230–238
Cobalt by the Nitroso-R Salt Spectrophotometric Method (0.01 % to 0.30 %)	53–62
Copper by the Sulfide Precipitation-Iodometric Titration Method (<i>Discontinued 1989</i>)	87–94
Copper by the Atomic Absorption Spectrometry Method (0.004 % to 0.5 %)	279–288
Copper by the Neocuproine Spectrophotometric Method (0.005 % to 1.50 %)	114–123
Lead by the Ion-Exchange—Atomic Absorption Spectrometry Method (0.001 % to 0.50 %)	132–141
Manganese by the Atomic Absorption Spectrometry Method (0.005 % to 2.0 %)	269–278
Manganese by the Metaperiodate Spectrophotometric Method (0.01 % to 2.5 %)	9–18
Manganese by the Peroxydisulfate-Arsenite Titrimetric Method (0.10 % to 2.50 %)	164–171
Molybdenum by the Thiocyanate Spectrophotometric Method (0.01 % to 1.50 %)	152–163
Nickel by the Atomic Absorption Spectrometry Method (0.003 % to 0.5 %)	318–327
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 % to 5.00 %)	180–187

	Sections
Nickel by the Ion-Exchange-Atomic-Absorption Spectrometry Method (0.005 % to 1.00 %)	188–197
Nitrogen by the Distillation-Spectrophotometric Method (<i>Discontinued 1988</i>)	63–75
Phosphorus by the Alkalimetric Method (0.02 % to 0.25 %)	172–179
Phosphorus by the Molybdenum Blue Spectrophotometric Method (0.003 % to 0.09 %)	19–30
Silicon by the Molybdenum Blue Spectrophotometric Method (0.01 % to 0.06 %)	103–113
Silicon by the Gravimetric Titration Method (0.05 % to 3.5 %)	46–52
Sulfur by the Gravimetric Method (<i>Discontinued 1988</i>)	31–36
Sulfur by the Combustion-Iodate Titration Method (0.005 % to 0.3 %) (<i>Discontinued 2017</i>)	37–45
Tin by the Sulfide Precipitation-Iodometric Titration Method (0.01 % to 0.1 %)	95–102
Tin by the Solvent Extraction-Atomic Absorption Spectrometry Method (0.002 % to 0.10 %)	198–207
Titanium by the Diantiprylmethane Spectrophotometric Method (0.025 % to 0.30 %)	258–268
Vanadium by the Atomic Absorption Spectrometry Method (0.006 % to 0.15 %)	239–248

1.3 Test methods for the determination of several elements 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 test method and therefore this standard contains multiple test methods for some elements. The user must select the proper test method by matching the information given in the Scope and Interference sections of each test method with the composition of the alloy to be analyzed.

1.5 The values stated in SI units are to be regarded as standard. In some cases, exceptions allowed in [IEEE/ASTM SI 10](#) are also used.

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, health, and environmental 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.

1.7 *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:²

[D1193 Specification for Reagent Water](#)

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.

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
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
E354 Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt 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
E1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry (Withdrawn 2004)³
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
IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System
2.2 <i>ISO Standard:</i> ⁴
ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests

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 ASTM Committees A01 on Steel, Stainless Steel, and Related Alloys and A04 on Iron Castings. 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

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>.

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 Practices

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

5.1.1 In the methods specifying spectrophotometric testing, the cells utilized to contain the reference material solutions and the sample solutions in spectrophotometers are referred to as “absorption cells.” Please note that the radiant energy passed through the cells can be measured as absorbance or transmittance. These methods refer to absorbance measurements. Refer to Practice E60 for details.

5.2 Reagents:

5.2.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the reagent grade specifications of the American Chemical Society.⁵ Other chemicals may be used, provided it is first ascertained that they are of sufficiently high purity to permit their use without adversely affecting the expected performance of the determination, as indicated in the Precision and Bias section.

5.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall 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.

6. Hazards

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

7. Sampling

7.1 For procedures to sample the material, refer to Practice E1806.

8. Interlaboratory Studies and Rounding Calculated Values

8.1 These test methods have been evaluated using Practice E173 or ISO 5725.

8.1.1 Practice E173 has been replaced by Practice E1601. 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.

8.2 Rounding of test results obtained using these test methods shall be performed as directed in Practice E29, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

⁵ *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>.

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

9.1 This test method covers the determination of manganese from 0.01 % to 2.5 %.

10. Summary of Test Method

10.1 Manganous ions are oxidized to permanganate ions by reaction with metaperiodate ions. Solutions of the samples are fumed with HClO_4 so that the effect of metaperiodate ion is limited to the oxidation of manganese. Spectrophotometric absorbance measurement is made at 545 nm.

11. Concentration Range

11.1 The recommended concentration range is from 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 test 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 The elements ordinarily present do not interfere. HClO_4 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.

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, 10, 15, 20, 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 545 nm. Using the test cell, take the spectrophotometric absorbance 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 545 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

15.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of manganese per 50 mL of solution.

16. Procedure

16.1 Test Solution:

16.1.1 Select and weigh a sample as follows:

Manganese, %	Sample Mass, g	Tolerance in Sample Mass, mg	Dilution, mL	Aliquot Volume, mL
0.01 to 0.5	0.80	0.5	100	20
0.45 to 1.0	0.35	0.3	100	20
0.85 to 2.0	0.80	0.5	500	20
1.95 to 2.5	0.80	0.5	500	10

Transfer the sample to a 100-mL or 500-mL borosilicate glass volumetric flask as directed in the above table or to a 300-mL Erlenmeyer flask if HF is to be used in sample dissolution.

16.1.2 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 either a 100-mL or 500-mL volumetric flask as indicated in 16.1.1. Proceed to 16.1.4.

16.1.3 For samples whose dissolution is hastened by HF, treat them in a 300-mL Erlenmeyer flask by adding 8 mL to 10 mL of HCl (1 + 1), and heating. Add HNO_3 and a few drops of HF as needed to hasten dissolution, and then add 3 mL to 4 mL of HNO_3 . 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, 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 16.1.1.

16.1.4 Cool the solution to room temperature, 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.

16.1.5 Using a pipet, transfer 10 mL to 20 mL aliquots, as directed in 16.1.1, to two 50-mL borosilicate glass volumetric flasks. Treat one portion as directed in 16.3. Treat the other portion 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 nitric-phosphoric acid mixture, and heat the solution at not less than 90 °C for 20 min to 30 min (Note 2 in 15.3). 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.

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 absorbance 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 absorbance reading of the test solution and of the background color solution to milligrams of manganese by means of the calibration curve. Calculate the percent of manganese as follows:

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

where:

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

18. Precision and Bias

18.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in **Table 1**. Although a sample covered by this test method with manganese composition of approximately 2.5 % was not available, the precision data for this composition should be similar to those obtained for Material 7.

18.2 *Bias*—The accuracy of this test method has been deemed satisfactory based upon the data for the certified reference materials in **Table 1**. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

PHOSPHORUS BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD

19. Scope

19.1 This test method covers the determination of phosphorus from 0.003 % to 0.09 %.

19.2 The upper limit of the scope has been set at 0.09 % because sufficient numbers of test materials containing higher phosphorus contents were unavailable for testing as directed in Practice **E173**. However, recognizing that the chemical principles used in this test method are capable of handling higher compositions, the test method includes a calibration procedure up to 0.25 %. Users of this test method are cautioned that its use above 0.09 % is not supported by interlaboratory testing.

20. Summary of Test 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 to form the molybdenum blue complex. Spectrophotometric

absorbance measurement is made at 650 nm or 825 nm, depending upon the concentration.

21. Concentration Range

21.1 The recommended concentration range is from 0.005 mg to 0.05 mg of phosphorus per 100 mL of solution when measured at 825 nm and from 0.05 mg to 0.3 mg of phosphorus per 100 mL of solution when measured at 650 nm, using a 1-cm cell.

NOTE 3—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

22. Stability of Color

22.1 The molybdenum blue complex is stable for at least 2 h.

23. Interferences

23.1 None of the elements usually present interfere except arsenic, which is removed by volatilization as the bromide.

24. Apparatus

24.1 Glassware must be phosphorus and arsenic-free. Boil the glassware with HCl 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.

25. Reagents

25.1 *Ammonium Molybdate Solution* (20 g/L)—Cautiously, while stirring and cooling, add 300 mL of H₂SO₄ to 500 mL of water and cool. Add 20 g of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O), cautiously dilute to 1 L, and mix.

25.2 *Ammonium Molybdate-Hydrazine Sulfate Solution*—Dilute 250 mL of the ammonium molybdate solution to 600 mL, add 100 mL of the hydrazine sulfate solution, dilute to 1 L, and mix. Do not use a solution that has stood for more than 1 h.

25.3 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ((NH₂)₂·H₂SO₄) in water, dilute to 1 L, and mix. Discard any unused solution after 24 h.

25.4 *Phosphorus Standard Solution A* (1 mL = 1.0 mg P)—Transfer 2.292 g of anhydrous disodium hydrogen phosphate (Na₂HPO₄), previously dried to constant mass at 105 °C, to a 500-mL volumetric flask; dissolve in about 100 mL of water, dilute to volume, and mix.

TABLE 1 Statistical Information—Manganese—Metaperiodate Spectrophotometric Method

Test Material	Manganese Found, %	Repeatability (R ₁ , E173)	Reproducibility (R ₂ , E173)
1. Alloy steel (BCS 252, 0.016 Mn)	0.022	0.004	0.006
2. Alloy steel (BCS 255/1 0.16 Mn)	0.161	0.004	0.010
3. Low-alloy steel (NIST 72f, 0.545 Mn)	0.551	0.010	0.020
4. Low-alloy steel (NIST 139a, 0.780 Mn)	0.780	0.009	0.030
5. Alloy steel (NIST, 159, 0.807 Mn)	0.819	0.010	0.034
6. Carbon steel (NIST 13f, 0.889 Mn)	0.892	0.015	0.027
7. Low-alloy steel (NIST 100b, 1.89 Mn)	1.91	0.02	0.04

25.5 *Phosphorus Standard Solution B* (1 mL = 0.01 mg P)—Using a pipet, transfer 10 mL of Solution A (1 mL = 1.0 mg P) to a 1-L volumetric flask, add 50 mL of HClO₄ (1 + 5), dilute to volume, and mix.

25.6 *Phosphorus Standard Solution C* (1 mL = 0.10 mg P)—Using a pipet, transfer 50 mL of Solution A (1 mL = 1.0 mg P) to a 500-mL volumetric flask, add 50 mL of HClO₄ (1 + 5), dilute to volume, and mix.

25.7 *Sodium Sulfite Solution* (100 g/L)—Dissolve 100 g of sodium sulfite (Na₂SO₃) in water, dilute to 1 L, and mix.

26. Preparation of Calibration Curve for Concentrations from 0.005 mg/100 mL to 0.05 mg/100 mL

26.1 *Calibration Solutions*—Using pipets, transfer (5, 10, 15, 25, and 50) mL of Phosphorus Standard Solution B (1 mL = 0.01 mg P) to 100-mL volumetric flasks. Add 20 mL of HClO₄, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 100-mL borosilicate glass volumetric flask. Proceed as directed in 26.3.

26.2 *Reagent Blank*—Transfer 12 mL of HClO₄ (1 + 5) to a 100-mL borosilicate glass volumetric flask.

26.3 Color Development:

26.3.1 Add 15 mL of Na₂SO₃ solution, boil gently for 30 s, and add 50 mL of ammonium molybdate-hydrazine sulfate solution that has been prepared within the hour.

26.3.2 Heat the solutions at not less than 90 °C for 20 min, quickly cool, dilute to volume, and mix.

NOTE 4—Immersing the flasks in a boiling water bath is the preferred means of heating them for complete color development.

26.4 *Reference Solution*—Water.

26.5 Spectrophotometry:

26.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) versus the reference solution (26.4) using absorption cells with a 1-cm light path and using a light band centered at 825 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions versus the reference solution.

26.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (26.4) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting using a light band centered at 825 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the reagent blank solution and of the calibration solutions.

26.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of phosphorus per 100 mL of solution.

27. Preparation of Calibration Curve for Concentrations from 0.05 mg/100 mL to 0.30 mg/100 mL

27.1 *Calibration Solutions*—Using pipets, transfer (5, 10, 15, 20, 25, and 30) mL of Phosphorus Standard Solution C (1 mL = 0.10 mg P) to 100-mL volumetric flasks. Add 20 mL of

HClO₄, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 100-mL borosilicate glass volumetric flask.

27.2 *Reagent Blank*—Proceed as directed in 26.2.

27.3 *Color Development*—Proceed as directed in 26.3.

27.4 *Reference Solution*—Water.

27.5 Spectrophotometry:

27.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) versus the reference solution (27.4) using absorption cells with a 1-cm light path and a light band centered at 650 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions versus the reference solution.

27.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (27.4) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting using a light band (no change) centered at 650 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the reagent blank solution and of the calibration solutions.

27.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of phosphorus per 100 mL of solution.

28. Procedure

28.1 Test Solution:

28.1.1 Transfer a 1.0-g sample, weighed to the nearest 0.5 mg, to a 250-mL Erlenmeyer flask.

28.1.2 Add 15 mL of a freshly prepared mixture of 1 volume of HNO₃ and 3 volumes of HCl, slowly and in small portions. When the reaction has ceased, add 10 mL of HClO₄ and evaporate to fumes. Remove the flask immediately to avoid undue loss of HClO₄, cool, and add 20 mL of HBr (1 + 4). Evaporate the solution to copious white fumes and then, without delay, fume strongly enough to cause the white fumes to clear the neck of the flask, and continue at this rate for 1 min.

28.1.3 Cool the solution, add 60 mL of HClO₄ (1 + 5), and swirl to dissolve the salts. Transfer to a 100-mL volumetric flask, cool, dilute to volume, and mix. Allow insoluble matter to settle or dry filter the solution. Using a pipet, transfer 10-mL portions to two 100-mL borosilicate glass volumetric flasks; treat one as directed in 28.3 and the other as directed in 28.4.2.

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

28.3 *Color Development*—Proceed with one of the 10-mL portions obtained in 28.1.3, as directed in 26.3.

28.4 Reference Solutions:

28.4.1 *Water*—Use this as the reference solution for the reagent blank solution.

28.4.2 *Background Color Reference Solution*—Add 15 mL of Na₂SO₃ solution to the second 10-mL portion obtained in

28.1.3. Boil gently for 30 s, add 50 mL of H₂SO₄ (3 + 37), cool, dilute to volume, and mix. Use this as the reference solution for the test solution.

28.5 Spectrophotometry—Take the spectrophotometric absorbance readings of the reagent blank solution and of the test solution (using the respective reference solutions) as directed in **26.5** or **27.5** depending upon the estimated level of phosphorus in the sample.

29. Calculation

29.1 Convert the net spectrophotometric absorbance reading of the test solution and of the reagent blank solution to milligrams of phosphorus by means of the appropriate calibration curve. Calculate the percent of phosphorus as follows:

$$\text{Phosphorus, \%} = (A - B)/(C \times 10) \quad (2)$$

where:

- A = phosphorus found in 100 mL of the final test solution, mg,
- B = phosphorus found in 100 mL of the final reagent blank solution, mg, and
- C = sample represented in 100 mL of the final test solution, g.

30. Precision and Bias

30.1 Precision—Nine laboratories cooperated in testing this test method and obtained the data summarized in **Table 2**.

30.2 Bias—The accuracy of this test method has been deemed satisfactory based upon the data for the certified reference materials in **Table 2**. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

SULFUR BY THE GRAVIMETRIC METHOD

(This test method, which consisted of Sections 31 through 36 of this standard, was discontinued in 1988.)

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

(This test method, which consisted of Sections 37 through 45 of this standard, was discontinued in 2017.)

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

46.1 This test method covers the determination of silicon from 0.05 % to 3.5 %.

46.2 The upper limit of the scope has been set at 3.5 % because test materials containing higher silicon contents were unavailable for testing as directed in **Practice E173**. However, recognizing that the chemical principles used in this test method are capable of handling higher compositions, the test method should be expandable to at least 5 %. Users of this test method are cautioned that its use above 3.5 % is not supported by interlaboratory testing.

47. Summary of Test Method

47.1 After dissolution of the sample, silicic acid is dehydrated by fuming with H₂SO₄ or HClO₄. The solution is filtered, and the impure silica is ignited and weighed. The silica is then volatilized with HF. The residue is ignited and weighed; the loss in mass represents silica.

48. Interferences

48.1 The elements normally present do not interfere if their compositions are under the maximum limits shown in **1.1**.

49. Reagents

49.1 The analyst should ensure, by analyzing blanks and other checks, that possible silicon contamination of reagents will not significantly bias the results.

49.2 HClO₄:

49.2.1 Select a lot of HClO₄ that contains not more than 0.0002 % silicon for the analysis of samples containing silicon in the range from 0.02 % to 0.10 % and not more than 0.0004 % silicon for samples containing more than 0.10 % by determining duplicate values for silicon as directed in **49.2.2 – 49.2.6**.

49.2.2 Transfer 15 mL of HClO₄ (**Note 5**) to each of two 400-mL beakers. To one of the beakers transfer an additional 50 mL of HClO₄. Using a pipet, transfer 20 mL of Na₂SiO₃ solution (1 mL = 1.00 mg Si) to each of the beakers. Evaporate the solutions to fumes and heat for 15 min to 20 min at such a rate that HClO₄ refluxes on the sides of the beakers. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C).

NOTE 5—The 15-mL addition of HClO₄ can be from the same lot as the one to be tested. Once a lot has been established as having less than 0.0002 % silicon, it should preferably be used for the 15-mL addition in all subsequent tests of other lots of acid.

49.2.3 Add paper pulp and filter immediately, using low-ash 11-cm medium-porosity filter papers. Transfer the precipitates to the papers, and scrub the beakers thoroughly with a rubber-tipped rod. Wash the papers and precipitates alternately with 3 mL to 5 mL portions of hot HCl (1 + 19) and hot water, for a total of 6 times. Finally wash the papers twice with H₂SO₄ (1 + 49). Transfer the papers to platinum crucibles.

TABLE 2 Statistical Information—Phosphorus—Molybdenum Blue Spectrophotometric Method

Test Material	Phosphorus Found, %	Repeatability (<i>R</i> ₁ , E173)	Reproducibility (<i>R</i> ₂ , E173)
1. Ingot iron (NIST 55e, 0.003 P)	0.002	0.001	0.002
2. Carbon steel (NIST 12g, 0.014 P)	0.014	0.002	0.003
3. Carbon steel (NIST 10g, 0.086 P)	0.084	0.006	0.009

49.2.4 Dry the papers and heat at 600 °C until the carbon is removed. Finally ignite at 1100 °C to 1150 °C to constant mass (at least 30 min). Cool in a desiccator and weigh.

49.2.5 Add enough H₂SO₄ (1 + 1) to moisten the SiO₂, and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H₂SO₄ is removed. Ignite for 15 min at 1100 °C to 1150 °C, cool in a desiccator, and weigh.

49.2.6 Calculate the percent of silicon as follows:

$$\text{Silicon, \%} = [(A - B) - (C - D)] \times 0.4674/E \times 100 \quad (3)$$

where:

A = initial mass of crucible plus impure SiO₂ when 65 mL of HClO₄ was taken, g,

B = final mass of crucible plus impurities when 65 mL of HClO₄ was taken, g,

C = initial mass of crucible plus impure SiO₂ when 15 mL of HClO₄ was taken, g,

D = final mass of crucible plus impurities when 15 mL of HClO₄ was taken, g, and

E = nominal mass (80 g) of 50 mL of HClO₄.

49.3 *Sodium Silicate Solution*—Transfer 11.0 g of sodium silicate (Na₂SiO₃·9H₂O) to a 400-mL beaker. Add 150 mL of water and dissolve the salt. Filter through a medium paper, collecting the filtrate in a 1-L volumetric flask, dilute to volume, and mix. Store in a polyethylene bottle. Use this solution to determine the suitability of the HClO₄.

49.4 *Tartaric Acid Solution* (20.6 g/L)—Dissolve 20.6 g of tartaric acid (C₄H₆O₆) in water, dilute to 1 L, and filter.

50. Procedure

50.1 Select and weigh a sample as follows:

Silicon, %	Sample mass, g	Tolerance in Sample mass, mg	Dehydrating Acid, mL	
			H ₂ SO ₄ (1 + 4)	HClO ₄
0.05 to 0.10	5.0	5	150	75
0.10 to 1.0	4.0	4	100	60
1.0 to 2.0	3.0	3	100	50
2.0 to 5.0	2.0	2	100	40

Transfer the sample to a 400-mL beaker or a 300-mL porcelain casserole. Proceed as directed in 50.2 or 50.3.

50.2 H₂SO₄ Dehydration:

50.2.1 Add amounts of HCl or HNO₃, or mixtures and dilutions of these acids, that are sufficient to dissolve the sample; and then add the H₂SO₄ (1 + 4) as specified in 50.1, and cover. Heat until dissolution is complete. Remove and rinse the cover glass; substitute a ribbed cover glass.

50.2.2 Evaporate until salts begin to separate; at this point evaporate the solution rapidly to the first appearance of fumes and fume strongly for 2 min to 3 min. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat, if necessary, but do not boil. Proceed immediately as directed in 50.4.

50.3 HClO₄ Dehydration:

50.3.1 Add amounts of HCl or HNO₃, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample, and cover. Heat until dissolution is complete. Add HNO₃ to provide a total of 35 mL to 40 mL, followed by HClO₄ as specified in the table in 50.1. Remove and rinse the cover glass; substitute a ribbed cover glass.

50.3.2 Evaporate the solution to fumes and heat for 15 min to 20 min at such a rate that the HClO₄ refluxes on the sides of the container. Cool sufficiently and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat to boiling. If the sample solution contains more than 100 mg of chromium, add, while stirring, 1 mL of tartaric acid solution for each 25 mg of chromium.

50.4 Add paper pulp and filter immediately, on a low-ash 11-cm medium-porosity filter paper. Collect the filtrate in a 600-mL beaker. Transfer the precipitate to the paper, and scrub the container thoroughly with a rubber-tipped rod. Wash the paper and precipitate alternately with 3 mL to 5 mL portions of hot HCl (1 + 19) and hot water until iron salts are removed but for not more than a total of ten washings. If 50.3 was followed, wash the paper twice more with H₂SO₄ (1 + 49), but do not collect these washings in the filtrate; discard the washings. Transfer the paper to a platinum crucible and reserve.

50.5 Add 15 mL of HNO₃ to the filtrate, stir, and evaporate as directed in either 50.2 or 50.3, depending upon the dehydrating acid used. Filter immediately, using a low-ash, 9-cm-100-porosity filter paper, and wash as directed in 50.4.

50.6 Transfer the paper and precipitate to the reserved platinum crucible. Dry the papers and then heat the crucible at 600 °C until the carbon is removed. Finally ignite at 1100 °C to 1150 °C to constant mass (at least 30 min). Cool in a desiccator and weigh.

50.7 Add enough H₂SO₄ (1 + 1) to moisten the impure SiO₂, and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H₂SO₄ is removed. Ignite at 1100 °C to 1150 °C for 15 min, cool in a desiccator, and weigh.

51. Calculation

51.1 Calculate the percent of silicon as follows:

$$\text{Silicon, \%} = [(A - B) \times 0.4674]/C \times 100 \quad (4)$$

where:

A = initial mass of crucible and impure SiO₂, g,

B = final mass of crucible and residue, g, and

C = sample used, g.

52. Precision and Bias

52.1 *Precision*—Eleven laboratories cooperated in testing this test method and obtained the data summarized in Table 3.

52.2 *Bias*—The accuracy of this test method has been deemed satisfactory based upon the data for the certified reference materials in Table 3. Users are encouraged to use

TABLE 3 Statistical Information—Silicon—Gravimetric Method

Test Material	Silicon Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
HClO ₄ Dehydration			
1. Carbon steel	0.053	0.015	0.036
2. Carbon steel (NIST 14d, 0.126 Si)	0.127	0.011	0.011
3. Carbon steel (NIST 19g, 0.186 Si)	0.186	0.011	0.010
4. Carbon steel (NIST 12g, 0.187 Si)	0.187	0.011	0.012
5. Low-alloy steel (NIST 32e, 0.278 Si)	0.280	0.011	0.012
6. Carbon steel (NIST 20f, 0.299 Si)	0.300	0.012	0.016
7. Electrical steel (NIST 125a, 3.32 Si)	3.33	0.07	0.07
H ₂ SO ₄ Dehydration			
1. Carbon steel	0.046	0.009	0.013
2. Carbon steel (NIST 14d, 0.126 Si)	0.128	0.016	0.016
3. Carbon steel (NIST 19g, 0.186 Si)	0.186	0.014	0.019
4. Carbon steel (NIST 12g, 0.187 Si)	0.188	0.007	0.016
5. Low-alloy steel (NIST 32e, 0.278 Si)	0.282	0.015	0.024
6. Carbon steel (NIST 20f, 0.299 Si)	0.302	0.015	0.015
7. Electrical steel (NIST 125a, 3.32 Si)	3.33	0.05	0.05

these or similar reference materials to verify that the test method is performing accurately in their laboratories.

COBALT BY THE NITROSO-R-SALT SPECTROPHOTOMETRIC METHOD

53. Scope

53.1 This test method covers the determination of cobalt from 0.01 % to 0.30 %.

54. Summary of Test Method

54.1 The sample solution is treated with zinc oxide to remove iron, chromium, and vanadium. Nitroso-R-salt solution is added to a portion of the filtrate which has been buffered with sodium acetate to produce an orange-colored complex with cobalt. The addition of nitric acid stabilizes the cobalt complex and also destroys certain interfering complexes. Spectrophotometric absorbance measurement is made at 520 nm.

55. Concentration Range

55.1 The recommended concentration range is from 0.005 mg to 0.15 mg of cobalt per 50 mL of solution, using a 1-cm cell.

NOTE 6—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

56. Stability of Color

56.1 The color is stable for at least 3 h.

57. Interferences

57.1 Nickel, manganese, and copper form complexes with nitroso-R-salt that deplete the reagent and inhibit the formation of the colored cobalt complex. A sufficient amount of nitroso-R-salt is used to provide full color development with 0.15 mg of cobalt in the presence of 41 mg of nickel, 1.5 mg of manganese, and 5 mg of copper, or 48 mg of nickel only. Colored complexes of nickel, manganese, and copper are destroyed by treating the hot solution with HNO₃.

58. Reagents

58.1 *Cobalt, Standard Solution* (1 mL = 0.06 mg Co)—Dry a weighing bottle and stopper in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer approximately 0.789 g of cobalt sulfate (CoSO₄)⁶ that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in a desiccator, stopper the bottle, and weigh. The difference in mass is the exact amount of CoSO₄ taken. Transfer the weighed CoSO₄ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 10 mL of HCl, and heat to dissolve the salts. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix. By means of a pipet, transfer a 50-mL aliquot of this solution to a 500-mL volumetric flask, dilute to volume, and mix. The exact concentration (in milligrams of cobalt per millilitre) of the final solution is the exact mass of CoSO₄ taken multiplied by 0.076046.

58.2 *Nitroso-R Salt Solution* (7.5 g/L)—Dissolve 1.50 g of 1-nitroso-2-naphthol-3,6-disulfonic acid disodium salt (nitroso-R salt) in about 150 mL of water, filter, and dilute to 200 mL. This solution is stable for 1 week.

58.3 *Sodium Acetate Solution* (500 g/L)—Dissolve 500 g of sodium acetate trihydrate (CH₃COONa·3H₂O) in about 600 mL of water, filter, and dilute to 1 L.

58.4 *Zinc Oxide Suspension* (166 g/L)—Add 10 g of finely divided zinc oxide (ZnO) to 60 mL of water and shake thoroughly. Prepare fresh daily as needed.

59. Preparation of Calibration Curve

59.1 *Calibration Solutions*—Using pipets, transfer (2, 5, 10, 15, 20, and 25) mL of cobalt standard solution (1 mL = 0.06 mg Co) to six 100-mL volumetric flasks, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 50-mL borosilicate glass volumetric flask. Proceed as directed in 59.3.

59.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed as directed in 59.3.

⁶ Cobalt sulfate (99.9 % minimum) prepared from the hexamine salt by G. Frederick Smith Chemical Co., Columbus, OH, is satisfactory for this purpose.

59.3 *Color Development*—Add 5 mL of sodium acetate solution, and mix. Using a pipet, add 10 mL of nitroso-R-salt solution, and mix. Place the flask in a boiling water bath. After 6 min to 10 min, add 5 mL of HNO₃ (1 + 2), and mix. Continue the heating for 2 min to 4 min. Cool the solution to room temperature, dilute to volume, and mix.

59.4 *Spectrophotometry*:

59.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction with water using absorption cells with a 1-cm light path and using a light band centered at 520 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions versus the reference solution (59.2).

59.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (59.2) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at 520 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

59.5 *Calibration Curve*—Follow the instrument manufacturer’s instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of cobalt per 50 mL of solution.

60. Procedure

60.1 Test Solution:

60.1.1 Transfer a 0.50-g sample, weighed to the nearest 0.2 mg, to a 100-mL borosilicate glass volumetric flask. Add 5 mL of a mixture of 1 volume of HNO₃ and 3 volumes of HCl. Heat gently until the sample is dissolved. Boil the solution until brown fumes have been expelled. Cool, add 50 mL to 55 mL of water, and cool again.

60.1.2 Add ZnO suspension in portions of about 5 mL until the iron is precipitated and a slight excess of ZnO is present. Shake thoroughly after each addition of the precipitant and avoid a large excess (Note 7). Dilute to volume, and mix. Allow the precipitate to settle; filter a portion of the solution through a dry, fine-porosity filter paper and collect it in a dry, 150-mL beaker after having discarded the first 10 mL to 20 mL. Using a pipet, transfer 10 mL of the filtrate to a 50-mL borosilicate glass volumetric flask. Proceed as directed in 60.3.

NOTE 7—When sufficient ZnO has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is indicated by a slightly white and milky supernatant liquid.

60.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed as directed in 60.3.

60.3 *Color Development*—Proceed as directed in 59.3.

60.4 *Spectrophotometry*—Take the spectrophotometric absorbance reading of the test solution as directed in 59.4.

61. Calculation

61.1 Convert the net spectrophotometric absorbance reading of the test solution to milligrams of cobalt by means of the calibration curve. Calculate the percent of cobalt as follows:

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

where:

- A = cobalt found in 50 mL of the final test solution, mg, and
- B = sample represented in 50 mL of the final test solution, g.

62. Precision and Bias⁷

62.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 4.

62.2 *Bias*—The accuracy of this test method has been deemed satisfactory based upon the data for the certified reference materials in Table 4. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories

NITROGEN BY THE DISTILLATION-SPECTROPHOTOMETRIC METHOD

(This test method, which consisted of Sections 63 through 75 of this standard, was discontinued in 1988.)

TOTAL ALUMINUM BY THE 8-QUINOLINOL SPECTROPHOTOMETRIC METHOD

76. Scope

76.1 This test method covers the determination of total aluminum from 0.003 % to 0.20 %. It is not applicable to silicon electrical steel.

77. Summary of Test Method

77.1 Interfering elements are removed by means of mercury-cathode, cupferron, and NaOH separations. Aluminum quinolate is formed and is extracted with chloroform and determined spectrophotometrically. Spectrophotometric absorbance measurement is made at 395 nm.

78. Concentration Range

78.1 The recommended concentration range is from 0.015 mg to 0.10 mg of aluminum per 25 mL of solution using a 1-cm cell.

NOTE 8—This procedure has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1083.

TABLE 4 Statistical Information—Cobalt—Nitroso-R-Salt Spectrophotometric Method

Test Material	Cobalt Found, %	Repeatability (R ₁ , E173)	Reproducibility (R ₂ , E173)
1. Carbon steel (NIST 19g, 0.012 Co)	0.011	0.005	0.007
2. Low-alloy steel (NIST 461, 0.26 Co)	0.253	0.006	0.024

79. Stability of Color

79.1 The color is relatively stable, but readings should be made within 5 min.

80. Interferences

80.1 This test method is not applicable to silicon electrical steel. None of the elements usually present in the other ferrous materials interfere if their compositions are under the maximum limits shown in 1.1.

81. Apparatus

81.1 *Glassware*—To prevent contamination of the sample, all glassware must be cleaned with hot HCl (1 + 1) before use. It is recommended that a set of glassware be reserved for the determination of aluminum below 0.01 %.

81.2 *Mercury Cathode*—An efficient apparatus for mercury cathode separations is that employing a rotating mercury pool cathode. With this instrument the movement of the cathode causes a fresh surface of mercury to be exposed during electrolysis, thus accelerating the separation. This instrument permits use of a current of 15 A in a 400-mL beaker. The electrolyte may be removed from the cell through a stopcock located just above the level of the mercury or siphoned from it. When 1 % or more of aluminum or titanium is present and these are to be determined, it should be initially ascertained if any of the aluminum or titanium is lost to the cathode.

81.3 *Spectrophotometer*—A spectrophotometer, rather than a filter photometer, is recommended because of the increased sensitivity that it provides.

82. Reagents

82.1 *Aluminum, Standard Solution* (1 mL = 0.005 mg Al)—Transfer 0.4396 g of potassium aluminum sulfate ($K_2Al_2(SO_4)_4 \cdot 24H_2O$) to a 250-mL volumetric flask, dissolve in water, add 15 mL of HCl (1 + 1), dilute to volume, and mix. Using a pipet, transfer 50 mL to a 1-L volumetric flask, dilute to volume, and mix. Store the solution in a polyethylene bottle.

82.2 *Ammonium Acetate Solution* (180 g/L)—Dissolve 90 g of ammonium acetate (CH_3COONH_4) in water and dilute to 500 mL.

82.3 *Ammonium Peroxydisulfate Solution* (100 g/L)—Dissolve 20 g of ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) in water and dilute to 200 mL.

82.4 *Chloroform* ($CHCl_3$).

82.5 *Cupferron Solution* (60 g/L)—Dissolve 6 g of cupferron in 80 mL of cold water, dilute to 100 mL, and filter. Prepare fresh as needed.

82.6 *Potassium Permanganate Solution*—Saturated $KMnO_4$.

82.7 *8-Quinolinol Solution* (50 g/L)—Dissolve 25 g of 8-quinolinol in 60 mL of acetic acid, dilute to 300 mL with warm water, filter through a medium filter paper, and dilute to 500 mL. Store in an amber bottle away from direct sunlight. Do not use a solution that is more than one month old.

82.8 *Sodium Cyanide Solution* (100 g/L)—Dissolve 100 g of sodium cyanide (NaCN) in a polyethylene bottle with water and dilute to 1 L. (**Warning**—The preparation, storage, and use of NaCN solution requires care and attention. Avoid inhalation of fumes and exposure of the skin to the chemical and its solutions. **Precaution**—Work in a well-ventilated hood. Refer to the Safety Precautions section of Practices E50. Because of the strongly alkaline properties of NaCN solution, contact with glass may result in appreciable aluminum contamination of the reagent.)

82.9 *Sodium Hydrogen Sulfate, Fused* (a mixture of $Na_2S_2O_7$ and $NaHSO_4$).

82.10 *Sodium Hydroxide Solution* (200 g/L)—Dissolve 100 g of NaOH in water in a platinum dish or in a plastic beaker and dilute to 500 mL. Store the solution in a polyethylene bottle.

82.11 *Sodium Sulfate*—Anhydrous $NaSO_4$.

82.12 *Sodium Thiocyanate Solution* (500 g/L)—Dissolve 50 g of sodium thiocyanate (NaCNS) in water and dilute to 100 mL.

83. Preparation of Calibration Curve

83.1 *Calibration Solutions*—Using pipets, transfer (2, 5, 10, 15, and 20) mL of aluminum solution (1 mL = 0.005 mg Al) to 250-mL beakers containing 40 mL of water and 2 mL of HCl (1 + 1). Proceed as directed in 83.4.

83.2 *Reference Solution*— $CHCl_3$.

83.3 *Reagent Blank*—Transfer 40 mL of water and 2 mL of HCl (1 + 1) to a 250-mL beaker and proceed as directed in 83.4.

83.4 *Color Development*:

83.4.1 Treat the solutions singly as follows: Add 1 mL of ammonium acetate solution and 10 mL of NaCN solution (see **Warning**—82.8). Using a pH meter, adjust the pH to 9.0 ± 0.2 with NH_4OH or HCl (1 + 1).

83.4.2 Transfer the solution to a 125-mL conical separatory funnel. Add 1 mL of 8-quinolinol solution and mix. Add 10 mL of $CHCl_3$ and shake vigorously for 20 s. Allow the phases to separate and drain the $CHCl_3$ layer into a dry, 50-mL beaker. Add 10 mL of $CHCl_3$ to the separatory funnel and extract as before. Combine the two extracts. Sprinkle 0.5 g of anhydrous Na_2SO_4 over the surface of the $CHCl_3$ extract in the beaker and then decant the $CHCl_3$ into a 25-mL volumetric flask. Rinse the beaker with 3 mL to 5 mL of $CHCl_3$ and transfer to the 25-mL volumetric flask, taking care to avoid transferring any Na_2SO_4 . Dilute to volume with $CHCl_3$, and mix.

83.5 *Spectrophotometry*:

83.5.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at 395 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions and of the reagent blank solution.

83.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial

setting, using a light band centered at 395 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions and of the reagent blank solution.

83.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against milligrams of aluminum per 25 mL of solution.

84. Procedure

84.1 Test Solution:

84.1.1 Select a sample weighed to the nearest 1 mg as follows:

Aluminum, %	Sample mass, g
0.003 to 0.10	2.00
0.08 to 0.20	1.00

Transfer the sample to a 500-mL, wide-mouth Erlenmeyer flask.

84.1.2 Add 30 mL of HCl and 10 mL of HNO₃, and digest at a low temperature until dissolution is complete. Add 30 mL of HClO₄, heat to fumes, and continue fuming until chromium, if present, is oxidized and the white HClO₄ vapors are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming the solution until the volume is reduced to 10 mL. Remove from the hot plate and cool. Add 25 mL of water to dissolve the salts. If iron hydrolyzes, indicating that the sample was fumed too long, add 1 mL to 2 mL of HCl and 5 mL of HClO₄ and again take to fumes. Dilute to 75 mL with water and boil to remove chlorine.

84.1.3 Filter through an 11-cm medium filter paper into a 400-mL beaker. Wash the paper and residue two times or three times with hot HClO₄ (2 + 98) and then several times with hot water to ensure removal of HClO₄. Reserve the filtrate.

84.1.4 Transfer the paper to a platinum crucible, dry the paper and residue, and then heat at about 600 °C until the carbon is removed. Finally ignite at 1100 °C to remove volatile oxides. Cool, and add a few drops of H₂SO₄ (1 + 1), followed by 4 mL to 5 mL of HF. Evaporate to dryness, and then heat at a gradually increasing rate until the H₂SO₄ is removed. Cool, add 2 g to 3 g of sodium hydrogen sulfate, fuse and heat until a clear melt is obtained. Cool the crucible, transfer it to a 250-mL beaker, add 50 mL of water, and then digest until the melt is dissolved. Remove and rinse the crucible with water.

84.1.5 If the solution is clear, add it to the filtrate reserved in 84.1.3. If the solution is turbid, filter through an 11-cm medium filter paper containing paper pulp into the beaker containing the reserved filtrate. Wash the paper three times or four times with hot H₂SO₄ (3 + 97). Discard the paper and residue.

84.1.6 Transfer the solution to the mercury cathode cell. Dilute to 150 mL to 200 mL and electrolyze at 15 A until the iron is removed. Without interrupting the current, transfer the solution from the cell to a 400-mL beaker. Thoroughly rinse the

cell and electrodes several times with water and add the rinsings to the solution.

84.1.6.1 The completeness of the removal of iron, which usually requires 1 h to 3 h, can easily be determined by the following test: Transfer 1 drop of the electrolyte to a cover glass or spot test plate. Add 1 drop of H₂SO₄ (1 + 1), 1 drop of saturated KMnO₄ solution, and 1 drop of NaCNS solution (500 g/L). When only a faint pink color is observed, the electrolysis may be considered to be complete.

84.1.7 Filter the solution through a 12.5-cm medium filter paper containing paper pulp (Note 9) into a 600-mL beaker, and wash 3 times or 4 times with hot water. To the filtrate add 10 mL of H₂SO₄ (1 + 1) and 10 mL of (NH₄)₂S₂O₈ solution. Heat to boiling, and evaporate to about 75 mL. Cool in an ice bath to about 5 °C.

NOTE 9—This filtration removes any mercurous chloride that may have formed and any metallic mercury that may have been transferred from the cell.

84.1.8 Transfer the solution to a 250-mL conical separatory funnel, and without delay, add 15 mL of cupferron solution. Reserve the beaker. Shake for 30 s and allow the precipitate to settle. Add 20 mL of CHCl₃ and shake for 1 min. Allow the layers to separate. Draw off and discard the CHCl₃ layer. Repeat the extractions until the extract is colorless. Transfer the aqueous solution to the reserved 600-mL beaker and evaporate to 35 mL to 40 mL. Add 25 mL of HNO₃, cover with a ribbed cover glass, evaporate to fumes of H₂SO₄, and cool. Dilute to 50 mL to 100 mL, heat to boiling, and cool.

84.1.9 Transfer the solution to a platinum dish or a quartz, high-silica glass, or tetrafluoroethylene beaker. Neutralize to litmus with NaOH solution and add 10 mL in excess. Add 1 mL of H₂O₂ and digest near boiling for 5 min to 7 min to coagulate the manganese precipitate. Cool, and filter through a 12.5-cm medium filter paper, previously washed with hot dilute NaOH solution (20 g/L), into a 400-mL beaker. Wash the paper and precipitate 4 times or 5 times with hot water. Immediately add HCl to the filtrate until acid to litmus paper. Transfer the acidified filtrate to a 200-mL volumetric flask, dilute to volume, and mix.

84.1.10 Transfer an aliquot to a 250-mL beaker, selecting the size as follows:

Aluminum, %	Sample mass, g	Aliquot Volume, mL	Equivalent Sample mass in Aliquot, mg
0.003 to 0.02	2.00	50	500
0.01 to 0.04	2.00	25	250
0.02 to 0.1	2.00	10	100
0.08 to 0.2	1.00	10	50

Adjust the volume to 50 mL. Proceed as directed in 84.3.

84.2 *Reagent Blank*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with the sample omitted. Transfer an aliquot of the same volume as that taken from the test solution, to a 250-mL beaker, and adjust the volume to 50 mL. Proceed as directed in 84.3.

84.3 *Color Development*—Proceed as directed in 83.4.

84.4 *Reference Solution*—CHCl₃.

84.5 *Spectrophotometry*—Take the spectrophotometric absorbance readings of the reagent blank solution and of the test solution as directed in 83.5.

85. Calculation

85.1 Convert the net spectrophotometric absorbance readings of the test solution and of the reagent blank solution to milligrams of aluminum by means of the calibration curve. Calculate the percentage of total aluminum as follows:

$$\text{Aluminum, \%} = (A - B)/(C \times 10) \quad (6)$$

where:

- A = aluminum found in 25 mL of the final test solution, mg,
- B = aluminum found in 25 mL of the final reagent blank solution, mg, and
- C = sample represented in 25 mL of the final test solution, g.

86. Precision and Bias

86.1 *Precision*—Samples covered by this test method were not tested. However, the precision data obtained for other types of alloys, using the methods indicated in Table 5, should apply.

86.2 *Bias*—No information on the bias of this method is known because at the time of the interlaboratory study, suitable reference materials were not available or were not tested. The user of this method is encouraged to employ acceptable reference materials, if available, to determine the presence or absence of bias.

COPPER BY THE SULFIDE PRECIPITATION- IODOMETRIC TITRATION METHOD

(This test method, which consisted of Sections 87 through 94 of this standard, was discontinued in 1989.)

TIN BY THE SULFIDE PRECIPITATION- IODOMETRIC TITRATION METHOD

95. Scope

95.1 This test method covers the determination of tin from 0.01 % to 0.1 %.

96. Summary of Test Method

96.1 Tin is precipitated as the sulfide from dilute acid containing chloride and nitrate ions. After dissolution of the precipitate, iron is added and tin is separated from copper by double precipitation with NH_4OH . This precipitate is dissolved in HCl, and the tin is reduced with lead and titrated with

standard iodate solution in an inert atmosphere. Starch is used to indicate the end point.

97. Interferences

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

98. Apparatus

98.1 *Apparatus for Reduction of Tin*—When tin is to be reduced to the stannous state and determined by titration with standard iodine or iodate solution, air must be excluded during the reduction and titration to prevent oxidation of the stannous tin. This exclusion of air is usually accomplished by keeping the solution under a blanket of gaseous CO_2 and may be accomplished in a variety of ways. One of the simplest methods is by means of the apparatus shown in Fig. 1 in which the reduction of the tin solution is made in a flask capped with a rubber stopper containing an L-shape siphon tube. When reduction is complete, the end of the siphon is dipped into a saturated solution of NaHCO_3 and set aside to cool. When cool, the stopper is removed and the solution titrated.

98.2 For work of high accuracy, it is best to keep the tin solution under gaseous CO_2 . Fig. 2 shows one of the many forms of apparatus that may be used when gaseous CO_2 is employed. It consists of a flask closed with a three-hole rubber stopper containing an inlet tube for CO_2 , an air condenser, and a hole for the buret (glass plugged). During reduction a very slow stream of CO_2 is passed through the flask. Extend the CO_2 delivery tube to within 2.5 cm of the bottom of the flask. When reduction is complete, the flow is increased to maintain a protecting blanket of CO_2 during the cooling and titration.

99. Reagents

99.1 *Ammonium Sulfate-Hydrogen Sulfide Solution*—Dissolve 50 g of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) in about 800 mL of H_2SO_4 (1 + 99), dilute to 1 L with H_2SO_4 (1 + 99), and saturate with hydrogen sulfide (H_2S).

99.2 *Antimony Trichloride Solution* (20 g/L)—Dissolve 2 g of antimony trichloride (SbCl_3) in 50 mL of HCl, and dilute to 100 mL.

99.3 *Ferric Chloride Solution* (2 g Fe/L)—Dissolve 10 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in about 800 mL of HCl (1 + 99) and dilute to 1 L with HCl (1 + 99).

99.4 *Potassium Iodate, Standard Solution* (1 mL = approximately 0.0005 g Sn)—For samples containing not more than 0.10 % Sn—Dissolve 0.300 g of potassium iodate (KIO_3) in

TABLE 5 Statistical Information—Aluminum—8-Quinolinol Spectrophotometric Method

Test Material	Aluminum Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
1. No. 1, E353 (Type 304 stainless steel 18Cr-8Ni)	0.004	0.001	0.003
2. No. 2, E353 (Type 304 stainless steel 18Cr-8Ni)	0.045	0.006	0.010
3. No. 3, E353 (Type 304 stainless steel 18Cr-8Ni)	0.083	0.004	0.009
4. No. 4, E353 (Type A286 stainless steel 15Cr-26Ni)	0.19	0.01	0.04

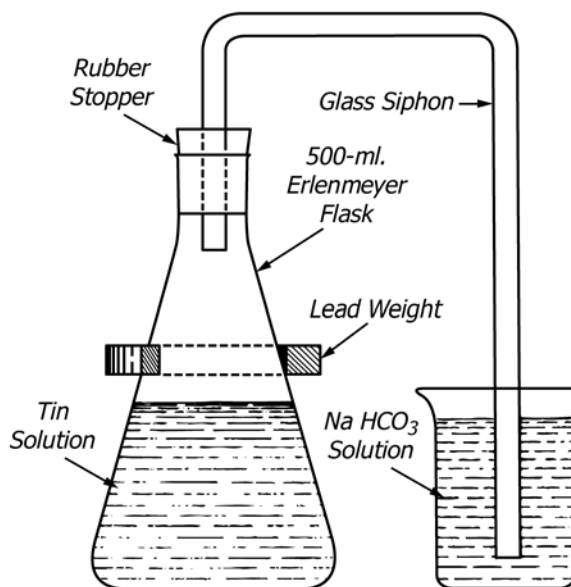


FIG. 1 Apparatus for Reduction of Tin

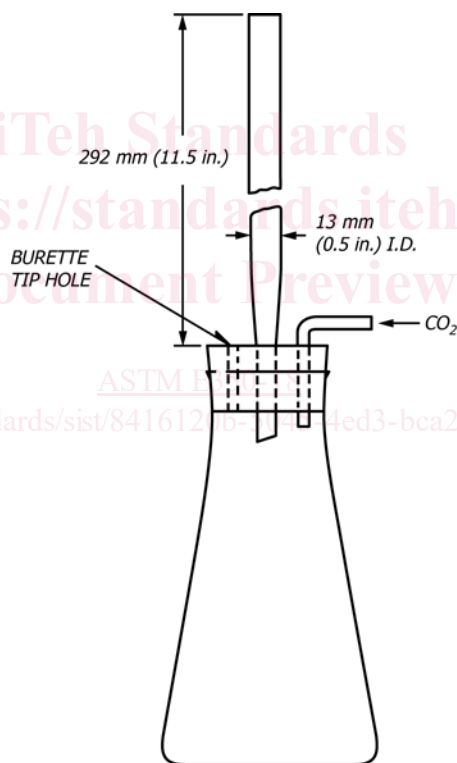


FIG. 2 Apparatus for Reduction of Tin

200 mL of water containing 1 g of NaOH and add 10 g of potassium iodide (KI). Dilute to 1 L, and mix. Determine the tin equivalent of the solution as follows:

99.4.1 Using a pipet, transfer 10 mL of the tin solution (1 mL = 0.001 g Sn) to a 500-mL Erlenmeyer flask, add 10 mL of FeCl₃ solution, 120 mL of HCl (1 + 1), and proceed as directed in 100.6 – 100.8. Determine a blank using the same amounts of all reagents with tin omitted. Calculate the tin equivalent of the potassium iodate solution as follows:

$$\text{Tin equivalent, g Sn/mL} = A / (B - C) \quad (7)$$

where:

- A = tin titrated, g,
- B = KIO₃ solution required to titrate the tin, mL, and
- C = KIO₃ solution required to titrate the blank, mL.

99.5 Potassium Iodate, Standard Solution (1 mL = approximately 0.0015 g Sn)—For samples containing not less than 0.10% Sn—Dissolve 0.900 g of KIO₃ in 200 mL of water