



Designation: E351 – 18

Standard Test Methods for Chemical Analysis of Cast Iron—All Types¹

This standard is issued under the fixed designation E351; 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 pig iron, gray cast iron (including alloy and austenitic), white cast iron, malleable cast iron, and ductile (nodular) iron having chemical compositions within the following limits:

Element	Composition Range, %
Aluminum	0.003 to 0.50
Antimony	0.005 to 0.03
Arsenic	0.02 to 0.10
Bismuth	0.001 to 0.03
Boron	0.001 to 0.10
Cadmium	0.001 to 0.005
Carbon	1.25 to 4.50
Cerium	0.005 to 0.05
Chromium	0.01 to 30.00
Cobalt	0.01 to 4.50
Copper	0.03 to 7.50
Lead	0.001 to 0.15
Magnesium	0.002 to 0.10
Manganese	0.06 to 2.50
Molybdenum	0.01 to 5.00
Nickel	0.01 to 36.00
Phosphorus	0.01 to 0.90
Selenium	0.001 to 0.06
Silicon	0.10 to 6.0
Sulfur	0.005 to 0.25
Tellurium	0.001 to 0.35
Tin	0.001 to 0.35
Titanium	0.001 to 0.20
Tungsten	0.001 to 0.20
Vanadium	0.005 to 0.50
Zinc	0.005 to 0.20

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

	Sections
Carbon, Graphitic, by the Direct Combustion Infrared Absorption Method (1 % to 3 %)	108–115
Carbon, Total by the Combustion Gravimetric Method (1.25 % to 4.50 %)— <i>Discontinued 2012</i>	97–107

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.

Current edition approved July 1, 2018. Published September 2018. Originally approved in 1968. Last previous edition approved in 2013 as E351 – 13. DOI: 10.1520/E0351-18.

Cerium and Lanthanum by the Direct Current Plasma Atomic Emission Spectrometry Method (Ce: 0.003 % to 0.5 %; La: 0.001 % to 0.30 %)	237–245
Chromium by the Atomic Absorption Method (0.006 % to 1.00 %)	208–217
Chromium by the Peroxydisulfate Oxidation—Titration Method (0.05 % to 30.0 %)	218–226
Chromium by the Peroxydisulfate-Oxidation Titrimetric Method (0.05 % to 30.0 %)— <i>Discontinued 1980</i>	144–151
Cobalt by the Ion-Exchange—Potentiometric Titration Method (2.0 % to 4.5 %)	53–60
Cobalt by the Nitroso-R-Salt Spectrophotometric Method (0.01 % to 4.50 %)	61–70
Copper by the Neocuproine Spectrophotometric Method (0.03 % to 7.5 %)	116–125
Copper by the Sulfide Precipitation-Electrodeposition Gravimetric Method (0.03 % to 7.5 %)	81–88
Lead by the Ion-Exchange—Atomic Absorption Spectrometry Method (0.001 % to 0.15 %)	126–135
Magnesium by the Atomic Absorption Spectrometry Method (0.002 % to 0.10 %)	71–80
Manganese by the Periodate Spectrophotometric Method (0.10 % to 2.00 %)	9–18
Manganese by the Peroxydisulfate-Arsenite Titrimetric Method (0.10 % to 3.5 %)	152–159
Molybdenum by the Ion Exchange–8-Hydroxyquinoline Gravimetric Method	257–264
Molybdenum by the Thiocyanate Spectrophotometric Method (0.01 % to 1.5 %)	196–207
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 % to 36.00 %)	168–175
Nickel by the Ion Exchange-Atomic Absorption Spectrometry Method (0.005 % to 1.00 %)	176–185
Phosphorus by the Alkalimetric Method (0.02 % to 0.90 %)	160–167
Phosphorus by the Molybdenum Blue Spectrophotometric Method (0.02 % to 0.90 %)	19–30
Silicon by the Gravimetric Method (0.1 % to 6.0 %)	46–52
Sulfur by the Gravimetric Method— <i>Discontinued 1988</i>	30–36
Sulfur by the Combustion-Iodate Titration Method (0.005 % to 0.25 %)— <i>Discontinued 2012</i>	37–45
Sulfur by the Chromatographic Gravimetric Method— <i>Discontinued 1980</i>	136–143
Tin by the Solvent Extraction-Atomic Absorption Spectrometry Method (0.002 % to 0.10 %)	186–195
Tin by the Sulfide Precipitation-Iodometric Titration Method (0.01 % to 0.35 %)	89–96
Titanium by the Diantipyrylmethane Spectrophotometric Method (0.006 % to 0.35 %)	246–256
Vanadium by the Atomic Absorption Spectrometry Method (0.006 % to 0.15 %)	227–236

1.3 Procedures for the determination of carbon and sulfur not included in these test methods 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, 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 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
- 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
- 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 Inert Gas 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

2.2 Other Document: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 Committee 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 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 method.

5.1.1 In the methods specifying spectrophotometric testing, the cells utilized to contain the reference material solutions and 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 Practices E60 for details.

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.⁵ 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.

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>.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. 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.

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 to sample the material, refer to Practice E1806.

8. Interlaboratory Studies and Rounding Calculated Values

8.1 These test methods have been evaluated as directed in Practice E173 (withdrawn 1997) or ISO 5725. Practice E173 has been replaced by Practice E1601. The Reproducibility R2 of E173 corresponds to the Reproducibility Index R of E1601. The Repeatability R1 of E173 corresponds to the Repeatability Index r of E1601.

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

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

9.1 This test method covers the determination of manganese from 0.10 % to 2.00 %.

10. Summary of 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 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 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 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 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 the 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
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

Transfer it to a 300-mL Erlenmeyer flask.

16.1.2 To dissolve samples that do not require HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO₃ 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 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, 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 by adding 8 mL to 10 mL of HCl (1 + 1), and heating. 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 16.1.1.

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 20 mL aliquots, 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 100 mL of HNO₃-H₃PO₄ 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 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 mass, 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. Although a sample covered by this method with manganese composition of approximately 2.0 % was not available, the precision data for this composition should be similar to those obtained for material 5.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Spectrophotometric Method

Test Specimen	Manganese Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
1. White cast iron (NIST 3a, 0.317 Mn)	0.318	0.006	0.017
2. Cast iron (NIST 4i, 0.793 Mn)	0.793	0.018	0.028
3. Cast iron (B.C.S. 236/2, 1.14 Mn)	1.15	0.03	0.06
4. White cast iron (NIST 1175, 1.64 Mn)	1.64	0.02	0.08
5. Low-alloy steel (NIST 100b, 1.89 Mn)	1.91	0.02	0.04

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 method covers the determination of phosphorus from 0.02 % to 0.90 %.

20. Summary of Method

20.1 The sample is dissolved in mixed acids and the solution is fumed with HClO_4 . 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 H_2SO_4 to 500 mL of water and cool. Add 20 g of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 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 $(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4$ 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 $(\text{Na}_2\text{HPO}_4)$, 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.

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 HClO_4 (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 HClO_4 (1 + 5), dilute to volume, and mix.

25.7 *Sodium Sulfite Solution* (100 g/L)—Dissolve 100 g of sodium sulfite (Na_2SO_3) 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 mL, 10 mL, 15 mL, 25 mL, and 50 mL of Phosphorus Standard Solution B (1 mL = 0.01 mg P) to 100-mL volumetric flasks. Add 20 mL of HClO_4 , 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 HClO_4 (1 + 5) to a 100-mL borosilicate glass volumetric flask.

26.3 Color Development:

26.3.1 Add 15 mL of Na_2SO_3 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 the 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 mL, 10 mL, 15 mL, 20 mL, 25 mL, 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 the milligrams of phosphorus per 100 mL of solution.

28. Procedure

28.1 Test Solution:

28.1.1 Select and weigh a sample as follows:

Phosphorus, %	Sample Mass, g	Tolerance in Sample Mass, mg
0.020 to 0.30	1.0	0.5
0.30 to 0.60	0.5	0.3
0.60 to 0.90	0.25	0.1

Transfer it to a 250-mL Erlenmeyer flask.

28.1.2 If the sample is other than white iron, proceed as directed in 28.1.2.1 and 28.1.2.2.

28.1.2.1 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.

28.1.2.2 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.

28.1.3 Treat samples of white iron as directed in 28.1.3.1 and 28.1.3.2.

28.1.3.1 Crush the material in an iron mortar and weigh only particles passing through a 300-μm (No. 50) sieve. Transfer the weighed sample to a 250-mL Erlenmeyer flask. Add 15 mL of HNO₃ and 5 mL of HBr. Heat until dissolution is complete. Add 10 mL of HClO₄, evaporate to copious white fumes; 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.

28.1.3.2 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 28.1.2.2 or 28.1.3.2, 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 28.1.2.2 or 28.1.3.2. 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 composition 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:

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

TABLE 2 Statistical Information—Phosphorus—Molybdenum Blue—Spectrophotometric Method

Test Specimen	Phosphorus Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
1. Cast iron 15Ni-2Cr-5Cu (NIST 115, 0.114 P)	0.107	0.013	0.014
2. Cast iron (NIST 5k, 0.263 P)	0.257	0.016	0.012
3. Cast iron (NIST 7g, 0.794 P)	0.779	0.020	0.053

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 method and obtained the data summarized in Table 2.

30.2 *Bias*—The accuracy of this test method exhibits a slight negative bias 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 30 through 36, was discontinued in 1988.

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

This test method, which consisted of Sections 37 through 45, was discontinued in 2012.

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

46.1 This method covers the determination of silicon from 0.1 % to 6.1 %.

47. Summary of Test Method

47.1 After dissolution of the sample, silicic acid is dehydrated by fuming with H_2SO_4 or $HClO_4$. 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 ordinarily 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 Perchloric Acid ($HClO_4$):

49.2.1 Select a lot of $HClO_4$ 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 $HClO_4$ (Note 5) to each of two 400-mL beakers. To one of the beakers transfer an additional 50 mL of $HClO_4$. Using a pipet, transfer 20 mL of Na_2SiO_3 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 $HClO_4$ 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 $HClO_4$ 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 H_2SO_4 (1 + 49). Transfer the papers to platinum crucibles.

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 H_2SO_4 (1 + 1) to moisten the SiO_2 , and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 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 SiO_2 when 65 mL of $HClO_4$ was taken, g,
 B = final mass of crucible plus impurities when 65 mL of $HClO_4$ was taken, g,
 C = initial mass of crucible plus impure SiO_2 when 15 mL of $HClO_4$ was taken, g,
 D = final mass of crucible plus impurities when 15 mL of $HClO_4$ was taken, g, and
 E = nominal mass (80 g) of 50 mL of $HClO_4$.

49.3 *Sodium Silicate Solution*—Transfer 11.0 g of sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) 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 $HClO_4$.

49.4 *Tartaric Acid Solution* (20.6 g/L)—Dissolve 20.6 g of tartaric acid ($C_4H_6O_6$) in water, dilute to 1 L, and filter.

49.5 *Water*—Use freshly prepared Type II water known to be free of silicon. Water distilled from glass, demineralized in