



Designation: **E350 – 12 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:

	Sections
Aluminum, Total, by the 8-Quinolinol Gravimetric Method (0.20% to 1.5%)	124 — 131
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

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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	Sections
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 Argon Plasma Atomic –Emission Spectroscopy 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 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 Spec- trometry –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 %)	164–174
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
Nickel by the Ion-Exchange Atomic Absorption Spectrometry –Method (0.005 % to 1.00 %)	188–197
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 Combustion-Iodate Titration Method (0.005 % to 0.3 %)	37–45
Tin by the Sulfide-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, Total, by the Diantipyrylmethane Spectrophotometric –Method (0.025 % to 0.30 %)	258–268
Vanadium by the Atomic Absorption Spectrometry –Method (0.006 % to 0.15 %)	239–248
Sections	
Aluminum, Total, by the 8-Quinolinol Gravimetric Method (0.20 % to 1.5 %)	124–131
Aluminum, Total, by the 8-Quinolinol Spectrophotometric Method (0.003 % to 0.20 %)	76–86

	Sections
<u>Aluminum, Total or Acid-Soluble, by the Atomic Absorption Spectrometry Method</u> (0.005 % to 0.20 %)	<u>308–317</u>
<u>Antimony by the Brilliant Green Spectrophotometric Method</u> (0.0002 % to 0.030 %)	<u>142–151</u>
<u>Bismuth by the Atomic Absorption Spectrometry Method</u> (0.02 % to 0.25 %)	<u>298–307</u>
<u>Boron by the Distillation-Curcumin Spectrophotometric Method</u> (0.0003 % to 0.006 %)	<u>208–219</u>
<u>Calcium by the Direct-Current Plasma Atomic Emission Spectrometry Method</u> (0.0005 % to 0.010 %)	<u>289–297</u>
<u>Carbon, Total, by the Combustion Gravimetric Method</u> (0.05 % to 1.80 %)— <i>Discontinued 1995</i>	
<u>Cerium and Lanthanum by the Direct Current Plasma Atomic Emission Spectrometry Method</u> (0.003 % to 0.50 % Cerium, 0.001 % to 0.30 % Lanthanum)	<u>249–257</u>
<u>Chromium by the Atomic Absorption Spectrometry Method</u> (0.006 % to 1.00 %)	<u>220–229</u>
<u>Chromium by the Peroxydisulfate Oxidation-Titration Method</u> (0.05 % to 3.99 %)	<u>230–238</u>
<u>Cobalt by the Nitroso-R Salt Spectrophotometric Method</u> (0.01 % to 0.30 %)	<u>53–62</u>
<u>Copper by the Sulfide Precipitation-Iodometric Titration Method</u> (<i>Discontinued 1989</i>)	<u>87–94</u>
<u>Copper by the Atomic Absorption Spectrometry Method</u> (0.004 % to 0.5 %)	<u>279–288</u>
<u>Copper by the Neocuproine Spectrophotometric Method</u> (0.005 % to 1.50 %)	<u>114–123</u>
<u>Lead by the Ion-Exchange—Atomic Absorption Spectrometry Method</u> (0.001 % to 0.50 %)	<u>132–141</u>
<u>Manganese by the Atomic Absorption Spectrometry Method</u> (0.005 % to 2.0 %)	<u>269–278</u>
<u>Manganese by the Metaperiodate Spectrophotometric Method</u> (0.01 % to 2.5 %)	<u>9–18</u>
<u>Manganese by the Peroxydisulfate-Arsenite Titrimetric Method</u> (0.10 % to 2.50 %)	<u>164–171</u>
<u>Molybdenum by the Thiocyanate Spectrophotometric Method</u> (0.01 % to 1.50 %)	<u>152–163</u>
<u>Nickel by the Atomic Absorption Spectrometry Method</u> (0.003 % to 0.5 %)	<u>318–327</u>
<u>Nickel by the Dimethylglyoxime Gravimetric Method</u> (0.1 % to 5.00 %)	<u>180–187</u>
<u>Nickel by the Ion-Exchange-Atomic-Absorption Spectrometry Method</u> (0.005 % to 1.00 %)	<u>188–197</u>
<u>Nitrogen by the Distillation-Spectrophotometric Method</u> (<i>Discontinued 1988</i>)	<u>63–75</u>
<u>Phosphorus by the Alkalimetric Method</u> (0.02 % to 0.25 %)	<u>172–179</u>
<u>Phosphorus by the Molybdenum Blue Spectrophotometric Method</u> (0.003 % to 0.09 %)	<u>19–30</u>
<u>Silicon by the Molybdenum Blue Spectrophotometric Method</u> (0.01 % to 0.06 %)	<u>103–113</u>
<u>Silicon by the Gravimetric Titration Method</u> (0.05 % to 3.5 %)	<u>46–52</u>
<u>Sulfur by the Gravimetric Method</u> (<i>Discontinued 1988</i>)	<u>31–36</u>
<u>Sulfur by the Combustion-Iodate Titration Method</u> (0.005 % to 0.3 %) (<i>Discontinued 2017</i>)	<u>37–45</u>
<u>Tin by the Sulfide Precipitation-Iodometric Titration Method</u> (0.01 % to 0.1 %)	<u>95–102</u>
<u>Tin by the Solvent Extraction-Atomic Absorption Spectrometry Method</u> (0.002 % to 0.10 %)	<u>198–207</u>
<u>Titanium by the Diantiprylmethane Spectrophotometric Method</u> (0.025 % to 0.30 %)	<u>258–268</u>
<u>Vanadium by the Atomic Absorption Spectrometry Method</u> (0.006 % to 0.15 %)	<u>239–248</u>

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

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

E319 Practice for the Evaluation of Single-Pan Mechanical Balances

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

E1097E1601 Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry 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 ISO Standard: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 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.

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>.

5.1.1 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 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.

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 for sampling to sample the material, reference shall be made 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_s , of Practice E173 corresponds to the reproducibility index, R , of Practice E1601. The repeatability, R_r , of Practice E173 corresponds to the repeatability index, r , of Practice E1601.

8.2 ~~Calculated values shall be rounded to the desired number of places in accordance~~ Rounding of test results obtained using these test methods shall be performed as directed in Practice E29 with the Rounding Method of Practice, Rounding Method, unless an alternative E29 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 in compositions from 0.01 % to 2.5 %.

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 perchloric HClO_4 acid so that the effect of metaperiodate ion is limited to the oxidation of manganese. Spectrophotometric absorbance measurement is made at approximately 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. Perchloric HClO_4 acid treatment, which is used in the procedure, yields solutions which can be highly colored due to the presence of Cr (VI) ions. Although these ions and other colored ions in the sample

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.uspc.org.

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 HNO₃ 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 HNO₃ and 400 mL of H₃PO₄ 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 (KIO₄) in 200 mL of hot HNO₃ (1 + 1), add 400 mL of H₃PO₄, cool, dilute to 1 L, and mix.

14.4 *Water, Pretreated with Metaperiodate*—Add 20 mL of KIO₄ 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 KIO₄ 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 KIO₄ solution, and heat the solutions at not less than 90 °C for 20 min to 30 min (Note 2). Cool, dilute to volume with pretreated water, and mix.

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

15.4 *Spectrophotometry:*

15.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using the Reference Solution (15.2) in absorption cells with a 1-cm light path and using a light band centered at approximately 545 nm. Using the test cell, take the spectrophotometric 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 approximately 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 in accordance with the following as follows:

Manganese, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
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 in accordance with 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 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 in a 300-mL Erlenmeyer flask 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~~ 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, ~~in accordance with~~ as directed in 16.1.1, to two 50-mL borosilicate glass volumetric flasks. Treat one portion ~~in accordance with~~ as directed in 16.3. Treat the other portion ~~in accordance with~~ 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 ~~in accordance with~~ 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 ~~in accordance with~~ 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 ~~in accordance with~~ 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: <https://standards.iteh.ai/catalog/standards/sist/8416120b-5045-4ed3-bca2-902b5d9ad105/astm-e350-18>

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*—~~No information on the accuracy of this test method is known. The accuracy of this test method may be judged by comparing accepted reference values with~~ has been deemed satisfactory based upon the data for the certified reference materials in Table 1 the corresponding arithmetic average obtained by interlaboratory testing. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

TABLE 1 Statistical Information—Manganese—Metaperiodate Spectrophotometric Method

Test Material	Manganese Found, %	Repeatability (<i>R</i> ₁ , E173)	Reproducibility (<i>R</i> 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

PHOSPHORUS BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD
19. Scope

~~19.1 This test method covers the determination of phosphorus in compositions 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 in accordance with 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.~~

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 ~~perchloric acid~~ HClO_4 acid. 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 ~~hydrochloric acid~~ 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 ($\text{NH}_4(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), 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 (Na_2HPO_4), previously dried to constant weight/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, 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 ~~in accordance with~~ 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 ~~approximately~~ 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 ~~approximately~~ 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 ~~in accordance with~~ as directed in 26.2.

27.3 *Color Development*—Proceed ~~in accordance with~~ 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 ~~approximately~~ 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 ~~approximately~~ 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 ~~in accordance with~~ as directed in 28.3 and the other ~~in accordance with~~ 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, ~~in accordance with~~ 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) in accordance with directed in 26.5 or 27.5 depending upon the estimated composition 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:

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

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—No information on the accuracy of this test method is known. The accuracy of this test method may be judged by comparing accepted reference values with has been deemed satisfactory based upon the data for the certified reference materials in Table 2 the corresponding arithmetic average obtained by interlaboratory testing. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

(http://www.astm.org) **SULFUR BY THE GRAVIMETRIC METHOD**
Document Preview

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

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

37. Scope

37.1 This test method covers the determination of sulfur in compositions from 0.005 % to 0.3 %.

37.2 The upper limit of the scope has been set at 0.3 % because sufficient numbers of test materials containing higher sulfur compositions were unavailable for testing in accordance with 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 0.6 %. Users of this test method are cautioned that its use above 0.3 % is not supported by interlaboratory testing.

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

38. Summary of Test Method

38.1 A major part of the sulfur in the sample is converted to sulfur dioxide (SO₂) by combustion in a stream of oxygen. During the combustion, the SO₂ is absorbed in an acidified starch-iodide solution and titrated with potassium iodate solution. The latter is standardized against steels of known sulfur composition to compensate for characteristics of a given apparatus and for day-to-day variation in the percentage of sulfur recovered as SO₂. Compensation is made for the blank due to accelerators and boats (or crucibles):

39. Interferences

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

TABLE 2 Statistical Information—Phosphorus—Molybdenum Blue Spectrophotometric Method

Test Material	Phosphorus Found, %	Repeatability (R ₁ , E173)	Reproducibility (R 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

40. Apparatus

40.1 *Apparatus for Determination of Sulfur by Direct Combustion*—The apparatus must be suitable for the combustion of the sample in oxygen to form sulfur dioxide (SO_2) and must provide an absorption vessel in which the SO_2 is titrated. A typical arrangement is shown in Fig. 1.

40.1.1 *Oxygen Purifiers*—The regular commercial tank oxygen is satisfactory. It must be passed through two pressure reduction valves (approximately 207 kPa (30 psig) and 14 kPa to 28 kPa (2 psig to 4 psig), respectively) or a suitable two-stage reduction valve to provide an even and adequate flow of oxygen through a tower containing H_2SO_4 and through an absorption tower containing 20-mesh to 30-mesh inert base impregnated with NaOH and anhydrous magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$). A flowmeter and quick-acting shut-off valve for use during preheating periods must precede the resistance furnace assembly. A flowmeter must also precede the induction furnace assembly.

40.1.2 *Combustion Furnace*—An electric tube furnace capable of continuous operation at 1425 °C to 1450 °C is recommended, since this temperature is required for some alloys. The combustion may be accomplished either by resistance or induction heating. With the former, the temperature must be controlled as specified for each type of alloy. With the latter a rheostat to control the power input to the induction coil is required to avoid heating some types of samples too rapidly during the early stages of combustion. The combustion zone of the resistance furnace must be 200 mm to 250 mm (8 in. to 10 in.) in length and that of the induction furnace must amply provide for adequate heating of the sample.

40.1.3 *Combustion Tube*—The combustion tube of the resistance furnace must be of a low-sulfur refractory type that will withstand the maximum operating temperature without becoming porous. The tube must be of a suitable size to fit the particular furnace used and have an inside diameter large enough to accommodate the thimble, boat, and cover. A tapered-end tube is recommended.

40.1.4 *Combustion Boats, Crucibles, and Covers*—The boats and crucibles for use with the respective types of furnaces must be of adequate thickness to retain the molten slag and have a blank as low and consistent as possible. The boats for use with resistance furnaces should be 90 mm to 100 mm (3.5 in. to 4 in.) in length and may be provided with suitable covers. The crucibles for use with induction furnaces must have adequate capacity and may be provided with suitable covers. The blank requirements that apply to the boats and crucibles also apply to their covers. Prior to use, the boats and covers must be pre-fired at least 15 min at 1100 °C and then stored in a desiccator.

40.1.5 *Ceramic Thimble*—A porous ceramic thimble or liner with a small orifice drilled in the closed end is placed (closed end first) in the hot zone of the tube of the resistance furnace to prolong the life of the combustion tube by absorbing spattered slag, and to act as a filter to remove metal oxide fumes from the gas stream.

40.1.6 *Ceramic Filter*—If a ceramic thimble is not available, a porous ceramic filter is placed in the hot zone of the furnace to remove metallic oxide fumes from the gas stream; it can be constructed from porous insulating fire brick capable of withstanding the operating temperatures. In induction furnaces suitable precautions must be taken to prevent metallic oxides from entering the titration vessel.

40.1.7 *Connections*—A metal breech connector at the entrance of the combustion tube is recommended. If a rubber stopper is used it must be protected by heat-reflecting baffles, preferably of the double-disk type. Connection between the outlet end of the combustion tube and the absorption and titration assembly must be as short and free of bends as possible, with glass connections butted to minimize areas of rubber tubing exposed to gases. All rubber stoppers and tubing must be essentially free of sulfur.

40.1.8 *Absorption and Titration Apparatus*—The apparatus should consist of an absorption and titration vessel of appropriate volume and containing an inlet bubbler tube for the sulfur gases with a float valve to prevent back flow of liquid when the sample is starting to consume oxygen. The vessel must be shaped to effect complete absorption of SO_2 in a small volume of solution. The buret should be approximately 10 mL in capacity. Automatic titrations which utilize a photoelectric cell to activate a solution inlet valve are commercially available and may be used.

41. Reagents

41.1 *Copper (Low-Sulfur) Accelerator*—Rectangular strips for combustion boats used with a resistance furnace, or rings for crucibles used with an induction furnace.

41.2 *Iron (Low-Sulfur) Accelerator*—Iron chips or iron powder.

41.3 *Potassium Iodate Standard Solution A* (Approximate sulfur equivalent = 0.1 mg S/mL)—Dissolve 0.2225 g of potassium iodate (KIO_3) in 900 mL of water containing 1 g of sodium hydroxide (NaOH) and dilute to 1 L.

41.4 *Potassium Iodate Standard Solution B* (Approximate sulfur equivalent = 0.02 mg S/mL)—Transfer 200 mL of KIO_3 Standard Solution A (approximate sulfur equivalent = 0.1 mg S/mL) to a 1-L volumetric flask, dilute to volume, and mix.

NOTE 5—The stated sulfur equivalents are based on complete conversion of sulfur to SO_2 ; this is a phenomenon that seldom, if ever, occurs.

41.5 *Starch-Iodide Solution*—Transfer 9 g of soluble (or arrowroot) starch to a 50-mL beaker, add 5 mL to 10 mL of water, and stir until a smooth paste is obtained. Pour the mixture slowly into 500 mL of boiling water. Cool, add 15 g of potassium iodide (KI), and stir until the KI is dissolved. Dilute to 1 L.

41.6 *Tin (Low-Sulfur) Accelerator*, granular.

42. Calibration

42.1 Select a minimum of three reference materials (**Note 6**), two with sulfur composition near the high and low limits of the range for a given sample weight (**43.1.3**) and also one near the median. The median reference material may be simulated, if necessary, by taking one half the sample weight of each of the other two.

NOTE 6—The accuracy of this test method is dependent to a large extent upon the accuracy of the methods used to certify the sulfur composition in the calibration reference materials.

42.2 For sulfur compositions greater than 0.02 % use KIO₃ Standard Solution A. For sulfur compositions less than 0.02 % use KIO₃ Standard Solution B.

42.3 Select a suitable homogenous sample with low sulfur composition and make several determinations in accordance with **43.1** or **43.2** until the system is stabilized as shown by reproducible titrations. Avoid the use of certified reference materials for instrument stabilization evaluation.

42.4 Continue with multiple portions of each reference material, in accordance with **43.1** or **43.2**, running these in ascending order of sulfur composition.

42.5 Prepare a calibration curve by plotting the percentage of sulfur in each reference material against the average of the millilitres of KIO₃ Standard Solution (or apparent percentage of sulfur for “direct-reading” burets). Prepare a separate calibration curve for each sample weight/sulfur range (**43.1.3**).

42.6 Repeat the calibration: (1) when another KIO₃ standard solution or another starch-iodide solution is used, (2) when a different lot of boats (or crucibles) is used, (3) when a different lot of accelerator is used, (4) when a different cylinder of oxygen is used, (5) when the system has not been in use for 1 h, or less than 1 h if the oxygen flow rate has not been maintained during that period, (6) when the system has been in use continuously for 8 h, (7) when the operating temperature has been changed, and (8) when a change in sample weight in accordance with **43.1.3** is required.

43. Procedure

43.1 Combustion with Resistance Furnace:

43.1.1 Adjust the temperature of the furnace to 1400 °C to 1425 °C.

43.1.2 Add 65 mL to 70 mL of HCl (1 + 99) and 2 mL of starch-iodide solution to the absorption vessel. Pass oxygen through the system at a constant rate which is the maximum compatible with the particular absorption system used but not less than 1.0 L/min and not more than 1.5 L/min. Add KIO₃ Standard Solution from the buret until the intensity of the blue color is that which is to be taken as the end point of the final titration. Read the buret and record as the initial reading, and refill the buret. Turn off the oxygen.

43.1.3 Select and weigh a sample in accordance with the following:

Sulfur, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.005 to 0.10	1.000	1.0
0.10 to 0.25	0.500	0.5
0.25 to 0.60	0.250	0.5

Transfer the sample to a preignited combustion boat and spread it in a layer of uniform thickness.

43.1.4 Cover the sample with 0.5 g of iron accelerator and approximately 0.25 g of copper accelerator. Place a preignited cover on the boat and introduce it into the center of the combustion zone. Close the tube and allow the sample to heat for 1.5 min. Start the flow of oxygen at the rate used in **43.1.2**.

43.1.5 Titrate the evolved SO₂ continuously with the appropriate KIO₃ standard solution at such a rate as to maintain as nearly as possible the initial intensity of the blue color. Continue the flow of oxygen for 10 min, record the buret reading, and subtract the initial reading obtained in **43.1.2**. Drain the absorption vessel. If the net volume differs by more than a factor of three from that required for the sample previously analyzed, disregard the result and repeat the analysis a sufficient number of times to stabilize the system before proceeding in accordance with **44.1**.

43.2 Combustion with Induction Furnace:

43.2.1 Turn on the power of the induction furnace and allow the electronic circuit to heat to operating temperature. Depress the starting button until the ammeter indicates that the current is flowing through the induction coil.

43.2.2 Proceed in accordance with **43.1.2**.

43.2.3 Proceed in accordance with **43.1.3** substituting a crucible for the combustion boat.

43.2.4 Add 0.5 g of iron accelerator, 1.0 g of tin, and approximately 0.5 g of copper accelerator. Place a preignited cover on the crucible and introduce it into the center of the combustion zone. Close the tube, start the flow of oxygen at the rate used in **43.2.2**, turn on the power, and increase it to the maximum at such a rate that spattering of the molten sample is avoided.

43.2.5 Proceed in accordance with **43.1.5**, but discontinue the flow of oxygen after 4 min to 5 min or when the titration is complete. Turn off the power to the induction coil.

44. Calculation

44.1 Read the percentage of sulfur in the sample from the appropriate curve plotted in accordance with ~~42.5~~.

45. Precision and Bias

45.1 *Precision*—Twenty-two laboratories cooperated in testing this test method; six used resistance furnaces and reported eight sets of values (*Note 7*); sixteen used induction furnaces (*Note 8*). They obtained the data summarized in *Table 3* for Specimens 3 through 7. Although samples covered by this test method with sulfur composition near the lower limit and the median of the scope were not available for testing, the precision data obtained using the test methods indicated in *Table 3* should apply. None was available to permit a test near the upper limit of the scope.

NOTE 7—The recovery of sulfur as SO₂ ranged from 72 % to 97 % with an average value of 83 % based on calibration reference materials designated B, C, and D in *Table 3*.

NOTE 8—The recovery of sulfur as SO₂ ranged from 80 % to 96 % with an average value of 88 % based on calibration reference materials designated B, C, and D in *Table 3*.

45.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be judged by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

46.1 This test method covers the determination of silicon in compositions 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 in accordance with 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.

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 sulfuric H₂SO₄ or perchloric HClO₄ acid. The solution is filtered, and the impure silica is ignited and weighed. The silica is then volatilized with hydrofluoric acid, HF. The residue is ignited and weighed; the loss in weight~~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 ~~make certain~~ ensure, by analyzing blanks and other checks, that possible silicon contamination of reagents will not significantly bias the results.

49.2 *Perchloric HClO₄ Acid*:

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 in accordance with as directed in *49.2.2 – 49.2.6*.

49.2.2 Transfer 15 mL of HClO₄ (*Note 95*) 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~~wash~~ 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.

49.2.4 Dry the papers and heat at 600 °C until the carbon is removed. Finally ignite at 1100 °C to 1150 °C or to constant weight/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 weight of crucible plus impure SiO₂ when 65 mL of HClO₄ was taken, g,
- B = final weight of crucible plus impurities when 65 mL of HClO₄ was taken, g,
- C = initial weight of crucible plus impure SiO₂ when 15 mL of HClO₄ was taken, g,
- D = final weight of crucible plus impurities when 15 mL of HClO₄ was taken, g, and
- E = nominal weight (80 g) of 50 mL of HClO₄.

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 in accordance with the following as follows:

Silicon, % H ₂ SO ₄ (1 + 4)	Sample Weight, g HClO ₄	Tolerance in Sample Weight, mg	Dehydrating Acid, mL	
			Dehydrating Acid, %	Sample mass, g
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 in accordance with as directed in 50.2 or 50.3.

50.2 Sulfuric H₂SO₄ Acid-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 in accordance with as directed in 50.4.

50.3 Perchloric HClO₄ Acid-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 in accordance with 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 in accordance with as directed in 50.4.