



Designation: E 350 – 95 (Reapproved 2000)^{ε1}

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 E 350; 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 Department of Defense.

^{ε1} NOTE—Editorial changes were made in November 2000.

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	Concentration 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 Photometric Method (0.003 to 0.20 %)	76–86
Aluminum, Total or Acid-Soluble, by the Atomic Absorption Method (0.005 to 0.20 %)	308–317
Antimony by the Brilliant Green Photometric Method (0.0002 to 0.030 %)	142–151
Bismuth by the Atomic Absorption Method (0.02 to 0.25 %)	298–307
Boron by the Distillation-Curcumin Photometric Method (0.0003 to 0.006 %)	208–219
Calcium by the Direct-Current Argon Plasma Optical Emission Spectroscopy Method (0.0005 to 0.010 %)	289–297
Carbon, Total, by the Combustion Gravimetric Method (0.05 to 1.80 %)—Discontinued 1995	
Cerium and Lanthanum by the D-C Plasma Optical Emission Method (0.003 to 0.50 % Cerium, 0.001 to 0.30 % Lanthanum)	249–257
Chromium by the Atomic Absorption 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 Photometric Method (0.01 to 0.30 %)	53–62
Copper by the Atomic Absorption Method (0.004 to 0.5 %)	279–288
Copper by the Neocuproine Photometric Method (0.005 to 1.50 %)	114–123
Lead by the Ion-Exchange—Atomic Absorption Method (0.001 to 0.50 %)	132–141
Manganese by the Atomic Absorption Method (0.005 to 2.0 %)	269–278
Manganese by the Metaperiodate Photometric Method (0.01 to 2.5 %)	8–17
Manganese by the Peroxydisulfate-Arsenite Titrimetric Method (0.10 to 2.50 %)	164–171
Molybdenum by the Thiocyanate Photometric Method (0.01 to 1.50 %)	152–163
Nickel by the Atomic Absorption 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 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 Photometric Method (0.003 to 0.09 %)	18–29
Silicon by the Molybdenum Blue Photometric Method (0.01 to 0.06 %)	103–113
Silicon by the Gravimetric Titration Method (0.01 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 Method (0.002 to 0.10 %)	198–207
Titanium, Total, by the Diantiprylmethane Spectrophotometric Method (0.025 to 0.30 %)	258–268

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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1.3 Test methods for the determination of several elements not included in this standard can be found in Test Methods E 30 and Test Methods E 1019.

1.4 Some of the concentration 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 Practice E 380 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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 5 and in special “Warning” paragraphs throughout these test methods.

2. Referenced Documents

2.1 ASTM Standards:

- D 1193 Specification for Reagent Water²
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications³
- E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open Hearth Iron, and Wrought Iron⁴
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁵
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁵
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁶
- E 319 Practice for the Evaluation of Single-Pan Mechanical Balances³
- E 351 Test Methods for Chemical Analysis of Cast Iron—All Types⁵
- E 352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels⁵
- E 353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys⁵
- E 354 Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys⁵
- E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)⁷
- E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁵

E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, Oxygen, and Hydrogen in Steel and in Iron, Nickel, and Cobalt Alloys⁵

E 1024 Guide for Chemical Analysis of Metals and Metal-Bearing Ores by Flame Atomic Absorption Spectrophotometry⁵

E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis⁵

E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition⁸

2.2 ISO Standard:

ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests⁹

3. Significance and Use

3.1 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 A-1 on Steel, Stainless Steel, and Related Alloys and A-4 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 E 882.

4. Apparatus, Reagents, and Instrumental Practices

4.1 *Apparatus*—Specialized apparatus requirements are listed in the “Apparatus” Section in each test method. In some cases reference may be made to Practices E 50.

4.2 Reagents:

4.2.1 *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.¹⁰ 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.

4.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

5. Hazards

5.1 For precautions to be observed in the use of certain reagents and equipment in these test methods, refer to Practices E 50.

⁸ *Annual Book of ASTM Standards*, Vol 03.06.

⁹ Available from American National Standards Institute, 11 West 42nd St., 13th Floor, New York, NY 10036.

¹⁰ *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 14.02.

⁴ Discontinued 1995; see 1994 *Annual Book of ASTM Standards*, Vol 03.05.

⁵ *Annual Book of ASTM Standards*, Vol 03.05.

⁶ Discontinued 1998; see 1997 *Annual Book of ASTM Standards*, Vol 03.05.

⁷ Discontinued 1997; see IEEE/ASTM SI 10—Standard, Vol 14.04.

6. Sampling

6.1 For procedures for sampling the material, reference shall be made to Practice E 1806.

7. Interlaboratory Studies and Rounding Calculated Values

7.1 These test methods have been evaluated using Practice E 173 or ISO 5725.

7.2 Calculated values shall be rounded to the desired number of places in accordance with 3.4 to 3.6 of Practice E 29.

MANGANESE BY THE METAPERIODATE PHOTOMETRIC METHOD

8. Scope

8.1 This test method covers the determination of manganese in concentrations from 0.01 to 2.5 %.

9. Summary of Test Method

9.1 Manganous ions are oxidized to permanganate ions by reaction with metaperiodate ions. Solutions of the samples are fumed with perchloric acid so that the effect of metaperiodate ion is limited to the oxidation of manganese. Photometric measurement is made at approximately 545 nm.

10. Concentration Range

10.1 The recommended concentration range is from 0.15 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.

11. Stability of Color

11.1 The color is stable for at least 24 h.

12. Interferences

12.1 The elements ordinarily present do not interfere. Perchloric acid treatment, which is used in the procedure, yields solutions which can be highly colored due to the presence of Cr (VI) ions. Although these ions and other colored ions in the sample solution undergo no further change in color quality upon treatment with metaperiodate ion, the following precautions must be observed when filter photometers are used: Select a filter with maximum transmittance between 545 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.

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

13. Reagents

13.1 *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.

13.2 *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.

13.3 *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.

13.4 *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 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.

14. Preparation of Calibration Curve

14.1 *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 14.3.

14.2 *Reference Solution*—Transfer approximately 25 mL of water to a 50-mL borosilicate glass volumetric flask. Proceed as directed in 14.3.

14.3 *Color Development*—Add 10 mL of KIO₄ solution, and heat the solutions at not less than 90°C for 20 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.

14.4 *Photometry:*

14.4.1 *Multiple-Cell Photometer*—Measure the cell correction using the Reference Solution (14.2) 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 photometric readings of the calibration solutions versus the reference solution (14.2).

14.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution (14.2) to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 545 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

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

15. Procedure

15.1 *Test Solution:*

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

Manganese, %	Sample Weight, g	Tolerance in Sample Weight, 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 or 500-mL borosilicate glass volumetric flask in accordance with the above table or to a 300-mL Erlenmeyer flask if HF is to be used in sample dissolution.

15.1.2 To dissolve samples that do not require HF, add 8 to 10 mL of HCl (1+1), and heat. Add HNO₃ as needed to hasten dissolution, and then add 3 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 or 500-mL volumetric flask as indicated in 16.1.1. Proceed to 16.1.4.

15.1.3 For samples whose dissolution is hastened by HF, treat them in a 300-mL Erlenmeyer flask by adding 8 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 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 or 500-mL volumetric flask as indicated in 15.1.1.

15.1.4 Cool the solution to room temperature, dilute to volume, and mix. Allow insoluble matter to settle, or dryfilter through a coarse paper and discard the first 15 to 20 mL of the filtrate, before taking aliquots.

15.1.5 Using a pipet, transfer 10 to 20-mL aliquots, in accordance with 15.1.1, to two 50-mL borosilicate glass volumetric flasks. Treat one portion in accordance with 15.3. Treat the other portion in accordance with 15.4.1.

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

15.3 *Color Development*—Proceed in accordance with 14.3.

15.4 *Reference Solutions*:

15.4.1 *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 to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

15.4.2 *Reagent Blank Reference Solution*—Transfer the reagent blank solution (15.2) 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 15.3 and use as reference solution for test samples. Treat the other in accordance with 15.4.1 and use as reference solution for Background Color Solutions.

15.5 *Photometry*—Establish the cell corrections with the reagent blank reference solution to be used as a reference

solution for background color solutions. Take the photometric readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference Solutions in accordance with 14.4.

16. Calculation

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

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

where:

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

17. Precision and Bias

17.1 *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 concentration of approximately 2.5 % was not available, the precision data for this concentration should be similar to those obtained for Material 7.

17.2 *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.

PHOSPHORUS BY THE MOLYBDENUM BLUE PHOTOMETRIC METHOD

18. Scope

18.1 This test method covers the determination of phosphorus in concentrations from 0.003 to 0.09 %.

18.2 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 E 173. However, recognizing that the chemical principles used in this test method are capable of handling higher concentrations, the test method includes a calibration

TABLE 1 Statistical Information—Manganese—Metaperiodate Photometric Method

Test Material	Manganese Found, %	Repeat-ability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
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 (NBS 72f, 0.545 Mn)	0.551	0.010	0.020
4. Low-alloy steel (NBS 139a, 0.780 Mn)	0.780	0.009	0.030
5. Alloy steel (NBS, 159, 0.807 Mn)	0.819	0.010	0.034
6. Carbon steel (NBS 13f, 0.889 Mn)	0.892	0.015	0.027
7. Low-alloy steel (NBS 100b, 1.89 Mn)	1.91	0.02	0.04

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. Summary of Test Method

19.1 The sample is dissolved in mixed acids and the solution is fumed with perchloric 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. Photometric measurement is made at 650 nm or 825 nm, depending upon the concentration.

20. Concentration Range

20.1 The recommended concentration range is from 0.005 to 0.05 mg of phosphorus per 100 mL of solution when measured at 825 nm and from 0.05 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.

21. Stability of Color

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

22. Interferences

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

23. Apparatus

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

24. Reagents

24.1 *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.

24.2 *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.

24.3 *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.

24.4 *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 at 105°C, to a 500-mL volumetric flask; dissolve in about 100 mL of water, dilute to volume, and mix.

24.5 *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 $\text{HClO}_4(1+5)$, dilute to volume, and mix.

24.6 *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 $\text{HClO}_4(1+5)$, dilute to volume, and mix.

24.7 *Sodium Sulfite Solution* (100 g/L)—Dissolve 100 g of sodium sulfite (Na_2SO_3) in water, dilute to 1 L, and mix.

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

25.1 *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 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 in accordance with 25.3.

25.2 *Reagent Blank*—Transfer 12 mL of $\text{HClO}_4(1+5)$ to a 100-mL borosilicate glass volumetric flask.

25.3 Color Development:

25.3.1 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.

25.3.2 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.

25.4 *Reference Solution*—Water.

25.5 Photometry:

25.5.1 *Multiple-Cell Photometer*—Measure the reagent blank (which includes the cell correction) versus the reference solution (25.4) 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 photometric readings of the calibration solutions versus the reference solution.

25.5.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution (25.4) to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting using a light band centered at approximately 825 nm. While maintaining this adjustment, take the photometric readings of the reagent blank solution and of the calibration solutions.

25.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of phosphorus per 100 mL of solution.

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

26.1 *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 HClO_4 , dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 100-mL borosilicate glass volumetric flask.

26.2 *Reagent Blank*—Proceed in accordance with 25.2.

26.3 *Color Development*—Proceed in accordance with 25.3.

26.4 *Reference Solution*—Water.

26.5 *Photometry*:

26.5.1 *Multiple-Cell Photometer*—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 a light band centered at approximately 650 nm. Using the test cell, take the photometric readings of the calibration solutions versus the reference solution.

26.5.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution (26.4) to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting using a light band (no change) centered at approximately 650 nm. While maintaining this adjustment, take the photometric readings of the reagent blank solution and of the calibration solutions.

26.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of phosphorus per 100 mL of solution.

27. Procedure

27.1 Test Solution:

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

27.1.2 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.

27.1.3 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 27.3 and the other in accordance with 27.4.2.

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

27.3 *Color Development*—Proceed with one of the 10-mL portions obtained in 27.1.3, in accordance with 25.3.

27.4 Reference Solutions:

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

27.4.2 *Background Color Reference Solution*—Add 15 mL of Na₂SO₃ solution to the second 10-mL portion obtained in 27.1.3. 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.

27.5 *Photometry*—Take the photometric readings of the reagent blank solution and of the test solution (using the respective reference solutions) in accordance with 25.5 or 26.5 depending upon the estimated concentration of phosphorus in the sample.

28. Calculation

28.1 Convert the net photometric reading of the test solution and of the reagent blank solution to milligrams of phosphorus

by means of the appropriate calibration curve. Calculate the percent of phosphorus as follows:

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

where:

A = phosphorus found in 100 mL of the final test solution, mg,

B = phosphorus found in 100 mL of the final reagent blank solution, mg, and

C = sample represented in 100 mL of the final test solution, g.

29. Precision and Bias

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

29.2 *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.

SULFUR BY THE GRAVIMETRIC METHOD

This test method, which consisted of Sections 30 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 concentrations 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 contents were unavailable for testing in accordance with Practice E 173. However, recognizing that the chemical principles used in this test method are capable of handling higher concentrations, 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.

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 content 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

TABLE 2 Statistical Information—Phosphorus—Molybdenum Blue Photometric Method

Test Material	Phosphorus Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. Ingot iron (NBS 55e, 0.003 P)	0.002	0.001	0.002
2. Carbon steel (NBS 12g, 0.014 P)	0.014	0.002	0.003
3. Carbon steel (NBS 10g, 0.086 P)	0.084	0.006	0.009

accelerators and boats (or crucibles).

39. Interferences

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

40. Apparatus

40.1 *Apparatus for Determination of Sulfur by Direct Combustion*—Apparatus No. 13, Practices E 50.

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 (KIO₃) 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 KIO₃ 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 SO₂; 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 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 standards (Note 6), two with sulfur contents 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 standard 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 concentration in the calibration standards.

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

42.3 Select the standard with the lowest sulfur concentration and make several determinations in accordance with 43.1 or 43.2 until the system is stabilized as shown by reproducible titrations.

42.4 Continue with multiple portions of each additional standard, in accordance with 43.1 or 43.2, running the standards in ascending order of sulfur concentration.

42.5 Prepare a calibration curve by plotting the percentage of sulfur in each standard 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 to 1425°C.

43.1.2 Add 65 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 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 concentration 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.

TABLE 3 Statistical Information—Sulfur—Combustion-Iodate Titration Method

Test Material	Sulfur Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
Induction Furnace			
1. No. 1, E 352	0.006 ^A	0.002	0.003
2. No. 2, E 352	0.008 ^A	0.001	0.004
3. Low-alloy steel (NBS 11 lb, 0.015S)	0.014 ^A	0.003	0.003
4. Carbon steel (NBS 13f, 0.016S)	0.016 ^A	0.002	0.002
5. Carbon steel (NBS 152, 0.027S)	0.026 ^B	0.003	0.004
6. Carbon steel (NBS 16d, 0.033 S)	0.032 ^B	0.003	0.005
7. Carbon steel (NBS 129b + 8i (Mixed), 0.144 S)	0.141 ^C	0.007	0.013
8. No. 7, E 353	0.286 ^D	0.014	0.020
Resistance Furnace			
1. No. 1, E 352	0.006 ^A	0.001	0.002
2. No. 2, E 352	0.009 ^A	0.001	0.002
3. Low-alloy steel (NBS 11 lb, 0.015S)	0.014 ^A	0.001	0.003
4. Carbon steel (NBS 13f, 0.016S)	0.015 ^A	0.002	0.003
5. Carbon steel (NBS 152, 0.027S)	0.027 ^B	0.004	0.004
6. Carbon steel (NBS 16d, 0.033S)	0.032 ^B	0.003	0.004
7. Carbon steel (NBS 129b + 8i (Mixed), 0.144S)	0.140 ^C	0.007	0.011
8. No. 7, E 353	0.288 ^D	0.012	0.021

^A Calibration Standards: NBS 169, Ni-Base Alloy, 0.02S; NBS 125a, 0.013S; NBS 32e, 1.2 Ni-0.7 Cr, 0.021S.

^B Calibration Standards: NBS 32e, 1.2 Ni-0.7 Cr, 0.021S; NBS 8i, Low-Alloy Steel, 0.064S; NBS 10g, Low-Alloy Steel, 0.109S.

^C Calibration Standards: NBS 10g, Carbon Steel, 0.109S; NBS 32e, 1.2 Ni-0.7 Cr, 0.021S + NBS 133a, 13 Cr-0.3 Mo, 0.326S: 0.174S; NBS 129b, Low-Alloy Steel, 0.221S.

^D Calibration Standards: NBS 129b, Low-Alloy Steel, 0.221S; NBS 129b, Low-Alloy Steel, 0.221S + NBS 133a, 13 Cr-0.3 Mo, 0.329S: 0.273S; NBS 133a, 13 Cr-0.3 Mo, 0.329S.

NOTE 7—The recovery of sulfur as SO₂ ranged from 72 to 97 % with an average value of 83 % based on calibration standards 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 standards 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. Reagents

46.1 This test method covers the determination of silicon in concentrations 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 E 173. However, recognizing that the chemical principles used in this test method are capable of handling higher concentrations, 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 or perchloric acid. The solution is filtered, and the impure silica is ignited and weighed. The silica is then volatilized with hydrofluoric acid. The residue is ignited and weighed; the loss in weight represents silica.

48. Interferences

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

49. Reagents

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

49.2 Perchloric 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 49.2.2–49.2.6.

49.2.2 Transfer 15 mL of HClO₄ (Note 9) 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 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 to 50°C).

NOTE 9—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 lowash 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 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 to 1150°C or to constant weight (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 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 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.

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.

49.5 *Water*—Use freshly prepared Type II water known to be free of silicon. Water distilled from glass, demineralized in columns containing silicon compounds, or stored for extended periods in glass, or combination thereof, has been known to pick up silicon.

50. Procedure

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

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

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

50.2 Sulfuric 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 to 3 min. Cool sufficiently, and add 100 mL of water (40 to 50°C). Stir to dissolve the salts and heat, if necessary, but do not boil. Proceed immediately in accordance with 50.4.

50.3 Perchloric 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 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 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 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 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 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 50.4.

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

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

51. Calculation

51.1 Calculate the percent of silicon as follows:

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

where:

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

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

C = sample used, g.

52. Precision and Bias

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

52.2 *Bias*—No information on the bias of this test method is known. The bias of this test method may be judged by

TABLE 4 Statistical Information—Silicon—Gravimetric Method

Test Material	Silicon Found, %	Repeat-ability (R_1 , E 173)	Reproducibility (R_2 , E 173)
HClO ₄ Dehydration			
1. Carbon steel	0.053	0.015	0.036
2. Carbon steel (NBS 14d, 0.126 Si)	0.127	0.011	0.011
3. Carbon steel (NBS 19g, 0.186 Si)	0.186	0.011	0.010
4. Carbon steel (NBS 12g, 0.187 Si)	0.187	0.011	0.012
5. Low-alloy steel (NBS 32e, 0.278 Si)	0.280	0.011	0.012
6. Carbon steel (NBS 20f, 0.299 Si)	0.300	0.012	0.016
7. Electrical steel (NBS 125a, 3.32 Si)	3.33	0.07	0.07
H ₂ SO ₄ Dehydration			
1. Carbon steel	0.046	0.009	0.013
2. Carbon steel (NBS 14d, 0.126 Si)	0.128	0.016	0.016
3. Carbon steel (NBS 19g, 0.186 Si)	0.186	0.014	0.019
4. Carbon steel (NBS 12g, 0.187 Si)	0.188	0.007	0.016
5. Low-alloy steel (NBS 32e, 0.278 Si)	0.282	0.015	0.024
6. Carbon steel (NBS 20f, 0.299 Si)	0.302	0.015	0.015
7. Electrical steel (NBS 125a, 3.32 Si)	3.33	0.05	0.05

comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

COBALT BY THE NITROSO-R-SALT PHOTOMETRIC METHOD

53. Scope

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

54. Summary of Test Method

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

55. Concentration Range

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

NOTE 10—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

56. Stability of Color

56.1 The color is stable for at least 3 h.

57. Interferences

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

Colored complexes of nickel, manganese, and copper are destroyed by treating the hot solution with nitric acid.

58. Reagents

58.1 *Cobalt, Standard Solution* (1 mL = 0.06 mg Co)—Dry a weighing bottle and stopper in an oven at 130°C for 1 h, cool in a desiccator, and weigh. Transfer approximately 0.789 g of cobalt sulfate (CoSO₄)¹¹ that has been heated at 550°C for 1 h to the weighing bottle. Dry the bottle and contents at 130°C for 1 h, cool in a desiccator, stopper the bottle, and weigh. The difference in weight is the exact amount of CoSO₄ taken. Transfer the weighed CoSO₄ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 10 mL of HCl, and heat to dissolve the salts. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix. By means of a pipet, transfer a 50-mL aliquot of this solution to a 500-mL volumetric flask, dilute to volume, and mix. The exact concentration (in milligrams of cobalt per millilitre) of the final solution is the exact weight of CoSO₄ taken multiplied by 0.076046.

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

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

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

59. Preparation of Calibration Curve

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

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

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

59.4 Photometry:

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

59.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution (59.2) to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting,

¹¹ Cobalt sulfate (99.9 % minimum) prepared from the hexamine salt by G. Frederick Smith Chemical Co., Columbus, OH, is satisfactory for this purpose.

using a light band centered at approximately 520 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

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

60. Procedure

60.1 Test Solution:

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

60.1.2 Add ZnO suspension in portions of about 5 mL until the iron is precipitated and a slight excess of ZnO is present. Shake thoroughly after each addition of the precipitant and avoid a large excess (Note 11). Dilute to volume, and mix. Allow the precipitate to settle; filter a portion of the solution through a dry, fine-porosity filter paper and collect it in a dry, 150-mL beaker after having discarded the first 10 to 20 mL. Using a pipet, transfer 10 mL of the filtrate to a 50-mL borosilicate glass volumetric flask. Proceed as in accordance with 60.3.

NOTE 11—When sufficient ZnO has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is indicated by a slightly white and milky supernatant liquid.

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

60.3 *Color Development*—Proceed in accordance with 59.3.

60.4 *Photometry*—Take the photometric reading of the test solution in accordance with 59.4.

61. Calculation

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

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

where:

A = cobalt found in 50 mL of the final test solution, mg, and

B = sample represented in 50 mL of the final test solution, g.

62. Precision and Bias¹²

62.1 Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 5.

62.2 *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.

TABLE 5 Statistical Information—Cobalt—Nitroso-R-Salt Photometric Method

Test Material	Cobalt Found, %	Repeat-ability (R_1 , E 173)	Repro-ducibility (R_2 , E 173)
1. Carbon steel (NIST 19g, 0.012 Co)	0.011	0.005	0.007
2. Low-alloy steel (NIST 461, 0.26 Co)	0.253	0.006	0.024

NITROGEN BY THE DISTILLATION-PHOTOMETRIC METHOD

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

TOTAL ALUMINUM BY THE 8-QUINOLINOL PHOTOMETRIC METHOD

76. Scope

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

77. Summary of Test Method

77.1 Interfering elements are removed by means of mercury-cathode, cupferron, and sodium hydroxide separations. Aluminum quinolate is formed and is extracted with chloroform and determined photometrically. Photometric measurement is made at approximately 395 nm.

78. Concentration Range

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

NOTE 12—This procedure has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

79. Stability of Color

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

80. Interferences

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

81. Apparatus

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

81.2 *Mercury Cathode*—Apparatus No. 10B.

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

82. Reagents

¹² Supporting data are available from ASTM Headquarters. Request RR:E03-1024.

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

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

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

82.4 *Chloroform* ($CHCl_3$).

82.5 *Cupferron Solution* (60 g/L)—Reagent No. 115.

82.6 *8-Quinolinol Solution* (50 g/L)—Dissolve 25 g of 8-quinolinol in 60 mL of acetic acid, dilute to 300 mL with warm water, filter through a medium filter paper, and dilute to 500 mL. Store in an amber bottle away from direct sunlight. Do not use a solution that is more than one month old.

82.7 *Sodium Cyanide* (100 g/L)—Dissolve 100 g of sodium cyanide (NaCN) in a polyethylene bottle with water and dilute to 1 L.

NOTE 13—**Warning:** The preparation, storage, and use of NaCN solution require care and attention. Avoid inhalation of fumes and exposure of the skin to the chemical and its solutions. **Precaution**—Work in a well-ventilated hood. Refer to the Safety Precautions section of Practices E 50. Because of the strongly alkaline properties of NaCN solution, contact with glass may result in appreciable aluminum contamination of the reagent.

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

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

83. Preparation of Calibration Curve

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

83.2 *Reference Solution*— $CHCl_3$.

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

83.4 *Color Development:*

83.4.1 Treat the solutions singly as follows: Add 1 mL of ammonium acetate solution and 10 mL of NaCN solution (**Warning: Precaution**—Note 13). Using a pH meter, adjust the pH to 9.0 ± 0.2 with NH_4OH or HCl (1+1).

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

transfer to the 25-mL volumetric flask, taking care to avoid transferring any Na_2SO_4 . Dilute to volume with $CHCl_3$, and mix.

83.5 *Photometry:*

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

83.5.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 395 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions and of the reagent blank solution.

83.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of aluminum per 25 mL of solution.

84. Procedure

84.1 *Test Solution:*

84.1.1 Select a sample weighed to the nearest 1 mg in accordance with the following:

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

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

84.1.2 Add 30 mL of HCl and 10 mL of HNO_3 , and digest at a low temperature until dissolution is complete. Add 30 mL of $HClO_4$, heat to fumes, and continue fuming until chromium, if present, is oxidized and the white $HClO_4$ vapors are present only in the neck of the flask. Add, with care, 1.0 to 1.5 mL of HCl allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming the solution until the volume is reduced to 10 mL. Remove from the hot plate and cool. Add 25 mL of water to dissolve the salts. If iron hydrolyzes, indicating that the sample was fumed too long, add 1 to 2 mL of HCl and 5 mL of $HClO_4$ and again take to fumes. Dilute to 75 mL with water and boil to remove chlorine.

84.1.3 Filter through an 11-cm medium filter paper into a 400-mL beaker. Wash the paper and residue two or three times with hot $HClO_4$ (2+98) and then several times with hot water to ensure removal of $HClO_4$. Reserve the filtrate.

84.1.4 Transfer the paper to a platinum crucible, dry the paper and residue, and then heat at about $600^\circ C$ until the carbon is removed. Finally ignite at $1100^\circ C$ to remove volatile oxides. Cool, and add a few drops of H_2SO_4 (1+1), followed by 4 to 5 mL of HF. Evaporate to dryness, and then heat at a gradually increasing rate until the H_2SO_4 is removed. Cool, add 2 to 3 g of sodium hydrogen sulfate, fuse and heat until a clear melt is obtained. Cool the crucible, transfer it to a 250-mL beaker, add 50 mL of water, and then digest until the melt is dissolved. Remove and rinse the crucible with water.

84.1.5 If the solution is clear, add it to the filtrate reserved in 84.1.3. If the solution is turbid, filter through an 11-cm medium

filter paper containing paper pulp into the beaker containing the reserved filtrate. Wash the paper three or four times with hot H₂SO₄(3+97). Discard the paper and residue.

84.1.6 Transfer the solution to the mercury cathode cell. Dilute to 150 to 200 mL and electrolyze at 15 A until the iron is removed (Note 14). Without interrupting the current, transfer the solution from the cell to a 400-mL beaker. Thoroughly rinse the cell and electrodes several times with water and add the rinsings to the solution.

NOTE 14—The completeness of the removal of iron, which usually requires 1 to 3 h, can easily be determined by the following test: Transfer 1 drop of the electrolyte to a cover glass or spot test plate. Add 1 drop of H₂SO₄(1+1), 1 drop of saturated potassium permanganate (KMnO₄) solution, and 1 drop of sodium thiocyanate (NaCNS) solution (500 g/L). When only a faint pink color is observed, the electrolysis may be considered to be complete.

84.1.7 Filter the solution through a 12.5-cm medium filter paper containing paper pulp (Note 15) into a 600-mL beaker, and wash 3 or 4 times with hot water. To the filtrate add 10 mL of H₂SO₄(1+1) and 10 mL of (NH₄)₂S₂O₈ solution. Heat to boiling, and evaporate to about 75 mL. Cool in an ice bath to about 5°C.

NOTE 15—This filtration removes any mercurous chloride that may have formed and any metallic mercury that may have been transferred from the cell.

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

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

84.1.10 Transfer an aliquot to a 250-mL beaker, selecting the size in accordance with the following:

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

Adjust the volume to 50 mL. Proceed in accordance with 84.3.

84.2 *Reagent Blank*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with

the sample omitted. Transfer an aliquot of the same volume as that taken from the test solution, to a 250-mL beaker, and adjust the volume to 50 mL. Proceed in accordance with 84.3.

84.3 *Color Development*—Proceed in accordance with 83.4.

84.4 *Reference Solution*—CHCl₃.

84.5 *Photometry*—Take the photometric readings of the reagent blank solution and of the test solution in accordance with 83.5.

85. Calculation

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

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

where:

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

86. Precision

86.1 Samples covered by this test method were not tested. However, the precision data obtained for other types of alloys, using the methods indicated in Table 6, should apply.

COPPER BY THE SULFIDE PRECIPITATION-ELECTRODEPOSITION GRAVIMETRIC METHOD

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

TIN BY THE SULFIDE-IODOMETRIC TITRATION METHOD

95. Scope

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

96. Summary of Test Method

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

TABLE 6 Statistical Information—Aluminum—8-Quinolinol Photometric Method

Test Material	Aluminum Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 1, E 353	0.004	0.001	0.003
2. No. 2, E 353	0.045	0.006	0.010
3. No. 3, E 353	0.083	0.004	0.009
4. No. 4, E 353	0.19	0.01	0.04

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

97. Interferences

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

98. Apparatus

98.1 *Apparatus for Reduction of Tin*—Apparatus 7A or 7B. If Apparatus 7B is used, extend the CO₂ delivery tube to within 2.5 cm of the bottom of the flask.

99. Reagents

99.1 *Ammonium Sulfate-Hydrogen Sulfide Solution*—Dissolve 50 g of ammonium sulfate ((NH₄)₂SO₄) in about 800 mL of H₂SO₄(1+99), dilute to 1 L with H₂SO₄(1+99), and saturate with hydrogen sulfide (H₂S).

99.2 *Antimony Trichloride Solution* (20 g/L)—Dissolve 2 g of antimony trichloride (SbCl₃) in 50 mL of HCl, and dilute to 100 mL.

99.3 *Ferric Chloride Solution* (2 g Fe/L)—Dissolve 10 g of ferric chloride hexahydrate (FeCl₃·6H₂O) in about 800 mL of HCl (1 + 99) and dilute to 1 L with HCl (1+99).

99.4 *Potassium Iodate, Standard Solution* (1 mL = approximately 0.0005 g Sn)—For samples containing not more than 0.10 % Sn—Dissolve 0.300 g of potassium iodate (KIO₃) in 200 mL of water containing 1 g of sodium hydroxide (NaOH) and add 10 g of potassium iodide (KI). Dilute to 1 L, and mix. Determine the tin equivalent of the solution as follows:

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

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

where:

A = tin titrated, g.

B = KIO₃ solution required to titrate the tin, mL, and

C = KIO₃ solution required to titrate the blank, mL.

99.5 *Potassium Iodate, Standard Solution* (1 mL = approximately 0.0015 g Sn)—For samples containing not less than 0.10% Sn—Dissolve 0.900 g of KIO₃ in 200 mL of water containing 1 g of NaOH and add 10 g of KI. Dilute to 1 L. Determine the tin equivalent of the solution in accordance with 99.4 but use 25 mL of the tin solution (1 mL = 0.001 g Sn).

99.6 *Starch Solution* (10 g/L)—Reagent No. 110.

99.7 *Test Lead*, granular.

99.8 *Tin, Standard Solution* (1 mL = 0.001 g Sn)—Reagent No. 19.

100. Procedure

100.1 For the range from 0.01 to 0.05 % tin, transfer a 10-g sample, weighed to the nearest 10 mg, to each of two 1-L Erlenmeyer flasks; use a single 10-g sample for the range from 0.05 to 0.10 %.

100.2 When two 10-g samples are used, proceed in accordance with 100.3–100.8. When a single 10-g sample is used, proceed in accordance with 100.5–100.8.

100.3 Dissolve the precipitates by passing 100 mL of hot HCl (1+1) in increments through each of the two papers, collecting the solutions in a single 800-mL beaker. Wash each paper alternately with hot water and small increments of hot HCl (1+1) until 20 mL of the latter has been used. Finally, wash each paper with about ten 5-mL portions of hot HCl (2+98).

100.4 Add NH₄OH (1+1) until neutral to litmus paper to precipitate iron, tin, chromium, etc., and then add 1 to 2 mL in excess. Add paper pulp, and heat the solution to boiling to coagulate the precipitate. Filter using a coarse filter paper and wash 5 to 10 times with hot NH₄OH (1+99). Discard the filtrate.

100.5 Pass 10 mL of hot HCl (1+1) in increments through the paper, collecting the solution in a 500-mL Erlenmeyer flask. Wash the paper alternately with hot water and small increments of hot HCl (1+1) until 20 mL of the latter has been used. Finally, wash the paper with about ten 5-mL portions of hot HCl (2+98).

100.6 Add 20 mL of HCl and dilute the solution to about 300 mL. Add 1 mL of SbCl₃ solution and 10 g of test lead. Stopper the flask with the 3-hole stopper containing the condenser, the glass rod, and the carbon dioxide inlet tube. Start the flow of carbon dioxide, boil the solution gently until the iron is reduced, and continue boiling for 30 to 40 min.

100.7 Replace the glass rod with a thermometer, increase the flow rate of the carbon dioxide to prevent air from entering the flask, and cool the solution to about 8°C by immersing the flask in ice water.

NOTE 16—If Apparatus 7A is used, ignore the reference to the flow of carbon dioxide in 100.6 and 100.7. When reduction is complete, dip the end of the siphon into a saturated solution of sodium hydrogen carbonate (NaHCO₃) and cool the solution in the flask to about 8°C by immersing it in ice water.

100.8 Remove the thermometer and, using a pipet, add 5 mL of starch solution through the open hole. Insert the tip of a 25-mL buret containing the appropriate KIO₃ solution and titrate the supernatant solution until a faint blue color is produced. Swirl the flask to bring the lead chloride into suspension, let it settle, and again titrate to the end point. Bring the lead chloride into suspension again, and let it settle; when the faint blue color is unaffected by this procedure the titration of the tin is complete.

NOTE 17—If Apparatus 7A is used, remove the stopper and the siphon and replace immediately with a two-hole stopper with a CO₂ delivery tube through which CO₂ is flowing; adjust the delivery tube so that it extends to within 2.5 cm of the bottom of the flask. Add starch solution, insert the buret tip in the other hole, and proceed in accordance with 100.8.

101. Calculation

101.1 Calculate the percent of tin as follows:

$$\text{Tin, \%} = [(A - B) \times C/D] \times 100 \quad (8)$$

where: