Designation: E350 – 12

Standard Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron[1]

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:

[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
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

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 and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 6 and in special "Warning" paragraphs throughout these test methods.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)[3]

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]

E1097 Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry

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.

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.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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

[5] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC, www.chemistry.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, http://www.usp.org.

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 the material, reference shall be made to Practice E1806.

8. Interlaboratory Studies and Rounding Calculated Values

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

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

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

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

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

14. Reagents

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

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

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

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

15. Preparation of Calibration Curve

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

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

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

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

15.4 *Spectrophotometry:*

15.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using the Reference Solution (15.2) in absorption

cells with a 1-cm light path and using a light band centered at approximately 545 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions versus the reference solution (15.2).

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

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

16. Procedure

16.1 *Test Solution:*

16.1.1 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-mL 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.

16.1.2 To dissolve samples that do not require HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO_3 as needed to hasten dissolution, and then add 3 mL to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of $HClO_4$; evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, and digest if necessary to dissolve the salts. Cool and transfer the solution to either a 100-mL or 500-mL volumetric flask as indicated in 16.1.1. Proceed to 16.1.4.

16.1.3 For samples whose dissolution is hastened by HF, treat them in a 300-mL Erlenmeyer flask by adding 8 mL to 10 mL of HCl (1 + 1), and heating. Add HNO_3 and a few drops of HF as needed to hasten dissolution, and then add 3 mL to 4 mL of HNO_3. When dissolution is complete, cool, then add 10 mL of $HClO_4$, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to either a 100-mL or 500-mL volumetric flask as indicated in 16.1.1.

16.1.4 Cool the solution to room temperature, dilute to volume, and mix. Allow insoluble matter to settle, or dryfilter 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 16.1.1, to two 50-mL borosilicate glass volumetric flasks. Treat one portion in accordance with 16.3. Treat the other portion in accordance with 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 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). 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 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 readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference Solutions in accordance with 15.4.

17. Calculation

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

TABLE 1 Statistical Information—Manganese—Metaperiodate Spectrophotometric Method

Test Material	Manganese Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Alloy steel (BCS 252, 0.016 Mn)	0.022	0.004	0.006
2. Alloy steel (BCS 255/1 0.16 Mn)	0.161	0.004	0.010
3. Low-alloy steel (NIST 72f, 0.545 Mn)	0.551	0.010	0.020
4. Low-alloy steel (NIST 139a, 0.780 Mn)	0.780	0.009	0.030
5. Alloy steel (NIST, 159, 0.807 Mn)	0.819	0.010	0.034
6. Carbon steel (NIST 13f, 0.889 Mn)	0.892	0.015	0.027
7. Low-alloy steel (NIST 100b, 1.89 Mn)	1.91	0.02	0.04

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 the corresponding arithmetic average obtained by interlaboratory testing.

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.

20. Summary of Test Method

20.1 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. Spectrophotometric 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 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 $(NH_4)_6Mo_7O_{24}·4H_2O$), 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 ($(NH_2)_2·H_2SO_4$) 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 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 $HClO_4$, 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 26.3.

26.2 *Reagent Blank*—Transfer 12 mL of $HClO_4$ (1 + 5) to a 100-mL borosilicate glass volumetric flask.

26.3 *Color Development:*

26.3.1 Add 15 mL of Na_2SO_3 solution, boil gently for 30 s, and add 50 mL of ammonium molybdate-hydrazine sulfate solution that has been prepared within the hour.

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

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

26.4 *Reference Solution*—Water.

26.5 *Spectrophotometry:*

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

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 $HClO_4$, 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 26.2.

27.3 *Color Development*—Proceed in accordance with 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 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 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.

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 HNO_3 and 3 volumes of HCl, slowly and in small portions. When the reaction has ceased, add 10 mL of $HClO_4$ and evaporate to fumes. Remove the flask immediately to avoid undue loss of $HClO_4$, cool, and add 20 mL of HBr (1 + 4). Evaporate the solution to copious whit 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 $HClO_4$ (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 28.3 and the other in accordance with 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 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 Na_2SO_3 solution to the second 10-mL portion obtained in 28.1.3. Boil gently for 30 s, add 50 mL of H_2SO_4 (3 + 37), cool, dilute to volume, and mix. Use this as the reference solution for the test solution.

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

29. Calculation

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

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

where:

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

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

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

30. Precision and Bias

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

30.2 *Bias*—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 31 through 36 of this standard, was discontinued in 1988.)

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

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.

38. Summary of Test Method

38.1 A major part of the sulfur in the sample is converted to sulfur dioxide (SO_2) by combustion in a stream of oxygen. During the combustion, the SO_2 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 SO_2. Compensation is made for the blank due to accelerators and boats (or crucibles).

39. Interferences

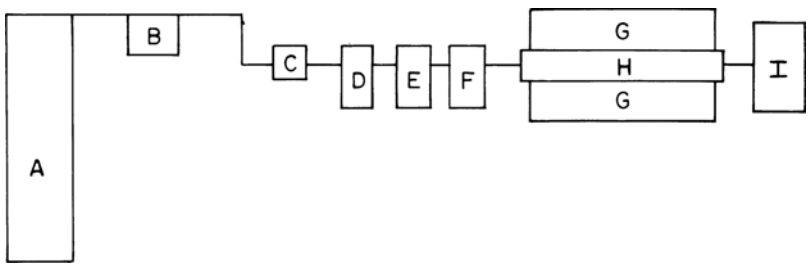
39.1 The elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1.

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 ($Mg(ClO_4)_2$). 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.



A = Oxygen tank
B = Reduction valve
C = Quick-acting shut-off valve
D = Tower containing H_2SO_4
E = Tower containing CO_2 absorber and anhydrous $Mg(ClO_4)_2$
F = Flowmeter
G = Furnace, induction or resistance-type
H = Combustion tube
I = Absorption and titration assembly

FIG. 1 Typical Arrangement for Determination of Sulfur by the Direct-Combustion Method

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 prefired 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 KIO_3 Standard Solution A. For sulfur compositions less than 0.02 % use KIO_3 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 matetrial, 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 KIO_3 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 KIO_3 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 KIO_3 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 SO_2 continuously with the appropriate KIO_3 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.

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

Test Material	Sulfur Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
Induction Furnace			
1. No. 1, E352	0.006[A]	0.002	0.003
2. No. 2, E352	0.008[A]	0.001	0.004
3. Low-alloy steel (NIST 11 lb, 0.015S)	0.014[A]	0.003	0.003
4. Carbon steel (NIST 13f, 0.016S)	0.016[A]	0.002	0.002
5. Carbon steel (NIST 152, 0.027S)	0.026[B]	0.003	0.004
6. Carbon steel (NIST 16d, 0.033 S)	0.032[B]	0.003	0.005
7. Carbon steel (NIST 129b + 8i (Mixed), 0.144 S)	0.141[C]	0.007	0.013
8. No. 7, E353	0.286[D]	0.014	0.020
Resistance Furnace			
1. No. 1, E352	0.006[A]	0.001	0.002
2. No. 2, E352	0.009[A]	0.001	0.002
3. Low-alloy steel (NIST 11 lb, 0.015S)	0.014[A]	0.001	0.003
4. Carbon steel (NIST 13f, 0.016S)	0.015[A]	0.002	0.003
5. Carbon steel (NIST 152, 0.027S)	0.027[B]	0.004	0.004
6. Carbon steel (NIST 16d, 0.033S)	0.032[B]	0.003	0.004
7. Carbon steel (NIST 129b + 8i (Mixed), 0.144S)	0.140[C]	0.007	0.011
8. No. 7, E353	0.288[D]	0.012	0.021

[A] Calibration reference materials: NIST 169, Ni-Base Alloy, *002S*; NIST 125a, *0.013S*; NIST 32e, 1.2 Ni-0.7 Cr, *0.021S*.
[B] Calibration reference materials: NIST 32e, 1.2 Ni-0.7 Cr, *0.021S*; NIST 8i, Low-Alloy Steel, *0.064S*; NIST 10g, Low-Alloy Steel, *0.109S*.
[C] Calibration reference materials: NIST 10g, Carbon Steel, *0.109S*, NIST 32e, 1.2 Ni-0.7 Cr, 0.021S + NIST 133a, 13 Cr-0.3 Mo, 0.326S: *0.174S*; NIST 129b, Low-Alloy Steel, *0.221S*.
[D] Calibration reference materials: NIST 129b, Low-Alloy Steel, *0.221S*; NIST 129b, Low-Alloy Steel, 0.221S + NIST 133a, 13 Cr-0.3 Mo, 0.329S: *0.273S*; NIST 133a, 13 Cr-0.3 Mo, *0.329S*.

NOTE 7—The recovery of sulfur as SO_2 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 SO_2 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.

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 compositions 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 $HClO_4$ that contains not more than 0.0002 % silicon for the analysis of samples containing silicon in the range from 0.02 % to 0.10 % and not more than 0.0004 % silicon for samples containing more than 0.10 % by determining duplicate values for silicon in accordance with 49.2.2 – 49.2.6.

49.2.2 Transfer 15 mL of $HClO_4$ (Note 9) to each of two 400-mL beakers. To one of the beakers transfer an additional 50 mL of $HClO_4$. Using a pipet, transfer 20 mL of Na_2SiO_3 solution (1 mL = 1.00 mg Si) to each of the beakers. Evaporate the solutions to fumes and heat for 15 min to 20 min at such a rate that $HClO_4$ refluxes on the sides of the beakers. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C).

NOTE 9—The 15-mL addition of $HClO_4$ can be from the same lot as the one to be tested. Once a lot has been established as having less than 0.0002 % silicon, it should preferably be used for the 15-mL addition in all subsequent tests of other lots of acid.

49.2.3 Add paper pulp and filter immediately, using 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 mL to 5 mL portions of hot HCl (1 + 19) and hot water, for a total of 6 times. Finally wash the papers twice with H_2SO_4 (1 + 49). Transfer the papers to platinum crucibles.

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

49.2.5 Add enough H_2SO_4 (1 + 1) to moisten the SiO_2, and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Ignite for 15 min at 1100 °C to 1150 °C, cool in a desiccator, and weigh.

49.2.6 Calculate the percent of silicon as follows:

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

where:

A = initial weight of crucible plus impure SiO_2 when 65 mL of $HClO_4$ was taken, g,
B = final weight of crucible plus impurities when 65 mL of $HClO_4$ was taken, g,
C = initial weight of crucible plus impure SiO_2 when 15 mL of $HClO_4$ was taken, g,
D = final weight of crucible plus impurities when 15 mL of $HClO_4$ was taken, g, and
E = nominal weight (80 g) of 50 mL of $HClO_4$.

49.3 *Sodium Silicate Solution*—Transfer 11.0 g of sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) to a 400-mL beaker. Add 150 mL of water and dissolve the salt. Filter through a medium paper, collecting the filtrate in a 1-L volumetric flask, dilute to volume, and mix. Store in a polyethylene bottle. Use this solution to determine the suitability of the $HClO_4$.

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

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_2SO_4 (1 + 4)	Dehydrating Acid, mL $HClO_4$
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 HNO_3, or mixtures and dilutions of these acids, that are sufficient to dissolve the sample; and then add the H_2SO_4 (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 50.4.

50.3 *Perchloric Acid Dehydration:*

50.3.1 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample, and cover. Heat until dissolution is complete. Add HNO_3 to provide a total of 35 mL to 40 mL, followed by $HClO_4$ 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 $HClO_4$ 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 H_2SO_4 (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 HNO_3 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 °C to 1150 °C to constant weight (at least 30 min). Cool in a desiccator and weigh.

50.7 Add enough H_2SO_4 (1 + 1) to moisten the impure SiO_2, and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Ignite at 1100 °C to 1150 °C for 15 min, cool in a desiccator, and weigh.

51. Calculation

51.1 Calculate the percent of silicon as follows:

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

where:

A = initial weight of crucible and impure SiO_2, 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 comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

COBALT BY THE NITROSO-R-SALT SPECTROPHOTOMETRIC METHOD

53. Scope

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

54. Summary of Test Method

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

TABLE 4 Statistical Information—Silicon—Gravimetric Method

Test Material	Silicon Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
$HClO_4$ Dehydration			
1. Carbon steel	0.053	0.015	0.036
2. Carbon steel (NIST 14d, 0.126 Si)	0.127	0.011	0.011
3. Carbon steel (NIST 19g, 0.186 Si)	0.186	0.011	0.010
4. Carbon steel (NIST 12g, 0.187 Si)	0.187	0.011	0.012
5. Low-alloy steel (NIST 32e, 0.278 Si)	0.280	0.011	0.012
6. Carbon steel (NIST 20f, 0.299 Si)	0.300	0.012	0.016
7. Electrical steel (NIST 125a, 3.32 Si)	3.33	0.07	0.07
H_2SO_4 Dehydration			
1. Carbon steel	0.046	0.009	0.013
2. Carbon steel (NIST 14d, 0.126 Si)	0.128	0.016	0.016
3. Carbon steel (NIST 19g, 0.186 Si)	0.186	0.014	0.019
4. Carbon steel (NIST 12g, 0.187 Si)	0.188	0.007	0.016
5. Low-alloy steel (NIST 32e, 0.278 Si)	0.282	0.015	0.024
6. Carbon steel (NIST 20f, 0.299 Si)	0.302	0.015	0.015
7. Electrical steel (NIST 125a, 3.32 Si)	3.33	0.05	0.05

55. Composition Range

55.1 The recommended composition range is from 0.005 mg 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 ($CoSO_4$)[6] that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in a desiccator, stopper the bottle, and weigh. The difference in weight is the exact amount of $CoSO_4$ taken. Transfer the weighed $CoSO_4$ 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 composition (in milligrams of cobalt per millilitre) of the final solution is the exact weight of $CoSO_4$ 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 ($CH_3COONa{\cdot}3H_2O$) 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 min to 10 min, add 5 mL of HNO_3 (1 + 2), and mix. Continue the heating for 2 min to 4 min. Cool the solution to room temperature, dilute to volume, and mix.

59.4 *Spectrophotometry:*

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

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

59.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

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 HNO_3 and 3 volumes of HCl. Heat gently until the sample is dissolved. Boil the solution until brown fumes have been expelled. Cool, add 50 mL to 55 mL of water, and cool again.

60.1.2 Add ZnO suspension in portions of about 5 mL until the iron is precipitated and a slight excess of ZnO is present. Shake thoroughly after each addition of the precipitant and avoid a large excess (Note 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 mL 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 *Spectrophotometry*—Take the spectrophotometric reading of the test solution in accordance with 59.4.

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

61. Calculation

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

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

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 Bias[7]

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.

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 SPECTROPHOTOMETRIC METHOD

76. Scope

76.1 This test method covers the determination of total aluminum in compositions 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 quinolinate is formed and is extracted with chloroform and determined photometrically. Spectrophotometric measurement is made at approximately 395 nm.

78. Composition Range

78.1 The recommended composition range is from 0.015 mg 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.

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

79. Stability of Color

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

80. Interferences

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

81. Apparatus

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

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

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

82. Reagents

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

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

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

82.4 *Chloroform* ($CHCl_3$).

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

82.6 *8-Quinolinol Solution* (50 g/L)—Dissolve 25 g of 8-quinolinol in 60 mL of acetic acid, dilute to 300 mL with

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

Test Material	Cobalt Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Carbon steel (NIST 19g, 0.012 Co)	0.011	0.005	0.007
2. Low-alloy steel (NIST 461, 0.26 Co)	0.253	0.006	0.024

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. (**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 E50. 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 (see **Warning—**82.7). 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 mL to 5 mL of $CHCl_3$ and transfer to the 25-mL volumetric flask, taking care to avoid transferring any Na_2SO_4. Dilute to volume with $CHCl_3$, and mix.

83.5 *Spectrophotometry:*

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

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

83.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

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 mL to 1.5 mL of HCl allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming the solution until the volume is reduced to 10 mL. Remove from the hot plate and cool. Add 25 mL of water to dissolve the salts. If iron hydrolyzes, indicating that the ample was fumed too long, add 1 mL 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 °C until the carbon is removed. Finally ignite at 1100 °C to remove volatile oxides. Cool, and add a few drops of H_2SO_4 (1 + 1), followed by 4 mL 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 g to 3 g of sodium hydrogen sulfate, fuse and heat until a clear melt is obtained. Cool the crucible, transfer it to a 250-mL beaker, add 50 mL of water, and then digest until the melt is dissolved. Remove and rinse the crucible with water.

84.1.5 If the solution is clear, add it to the filtrate reserved in 84.1.3. If the solution is turbid, filter through an 11-cm medium filter paper containing paper pulp into the beaker containing the reserved filtrate. Wash the paper three or four times with hot H_2SO_4 (3 + 97). Discard the paper and residue.

84.1.6 Transfer the solution to the mercury cathode cell. Dilute to 150 mL to 200 mL and electrolyze at 15 A until the iron is removed (Note 13). 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 13—The completeness of the removal of iron, which usually requires 1 h to 3 h, can easily be determined by the following test: Transfer 1 drop of the electrolyte to a cover glass or spot test plate. Add 1 drop of

H_2SO_4 (1 + 1), 1 drop of saturated potassium permanganate ($KMnO_4$) 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 14) into a 600-mL beaker, and wash 3 or 4 times with hot water. To the filtrate add 10 mL of H_2SO_4 (1 + 1) and 10 mL of $(NH_4)_2S_2O_8$ solution. Heat to boiling, and evaporate to about 75 mL. Cool in an ice bath to about 5 °C.

NOTE 14—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 $CHCl_3$ and shake for 1 min. Allow the layers to separate. Draw off and discard the $CHCl_3$ layer. Repeat the extractions until the extract is colorless. Transfer the aqueous solution to the reserved 600-mL beaker and evaporate to 35 mL to 40 mL. Add 25 mL of HNO_3, cover with a ribbed cover glass, evaporate to fumes of H_2SO_4, and cool. Dilute to 50 mL 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 H_2O_2 and digest near boiling for 5 min to 7 min to coagulate the manganese precipitate. Cool, and filter through a 12.5-cm medium filter paper, previously washed with hot dilute NaOH solution (20 g/L), into a 400-mL beaker. Wash the paper and precipitate 4 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*—$CHCl_3$.

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

85. Calculation

85.1 Convert the net spectrophotometric 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:

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

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

97. Interferences

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

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

Test Material	Aluminum Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E353	0.004	0.001	0.003
2. No. 2, E353	0.045	0.006	0.010
3. No. 3, E353	0.083	0.004	0.009
4. No. 4, E353	0.19	0.01	0.04

98. Apparatus

98.1 *Apparatus for Reduction of Tin*—When tin is to be reduced to the stannous state and determined by titration with standard iodine or iodate solution, air must be excluded during the reduction and titration to prevent oxidation of the stannous tin. This exclusion of air is usually accomplished by keeping the solution under a blanket of gaseous CO_2 and may be accomplished in a variety of ways. One of the simplest methods is by means of the apparatus shown in Fig. 2 in which the reduction of the tin solution is made in a flask capped with a rubber stopper containing an L-shape siphon tube. When reduction is complete, the end of the siphon is dipped into a saturated solution of $NaHCO_3$ and set aside to cool. When cool, the stopper is removed and the solution titrated.

98.2 For work of high accuracy, it is best to keep the tin solution under gaseous CO_2. Fig. 3 shows one of the many forms of apparatus that may be used when gaseous CO_2 is employed. It consists of a flask closed with a three-hole rubber stopper containing an inlet tube for CO_2, an air condenser, and a hole for the buret (glass plugged). During reduction a very slow stream of CO_2 is passed through the flask. Extend the CO_2 delivery tube to within 2.5 cm of the bottom of the flask. When reduction is complete, the flow is increased to maintain a protecting blanket of CO_2 during the cooling and titration.

99. Reagents

99.1 *Ammonium Sulfate-Hydrogen Sulfide Solution*—Dissolve 50 g of ammonium sulfate ($(NH_4)_2SO_4$) in about 800 mL of H_2SO_4 (1 + 99), dilute to 1 L with H_2SO_4 (1 + 99), and saturate with hydrogen sulfide (H_2S).

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

99.3 *Ferric Chloride Solution* (2 g Fe/L)—Dissolve 10 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in about 800 mL of HCl (1 + 99) and dilute to 1 L with HCl (1 + 99).

99.4 *Potassium Iodate, Standard Solution* (1 mL = approximately 0.0005 g Sn)—For samples containing not more than 0.10 % Sn)—Dissolve 0.300 g of potassium iodate (KIO_3) in 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 $FeCl_3$ 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:

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

where:

A = tin titrated, g,
B = KIO_3 solution required to titrate the tin, mL, and
C = KIO_3 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 KIO_3 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)—Add about 5 mL of water gradually to 1 g of soluble (or arrowroot) starch, with stirring, until a paste is formed, and add this to 100 mL of boiling water. Cool, add 5 g of potassium iodide (KI), and stir until the KI is dissolved. Prepare fresh as needed.

99.7 *Test Lead,* granular.

99.8 *Tin, Standard Solution* (1 mL = 0.001 g Sn)—Transfer 1.0000 g of tin (purity, 99.9% min) to a 400-mL beaker, and cover. Add 300 mL of HCl (1 + 1) and warm gently until the metal is dissolved. If dissolution is difficult, add 0.5 g to 1.0 g of potassium chlorate ($KClO_3$). Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

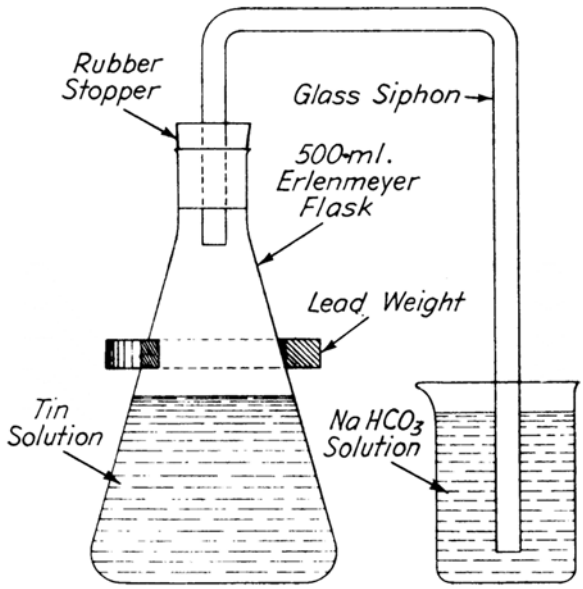


FIG. 2 Apparatus for Reduction of Tin

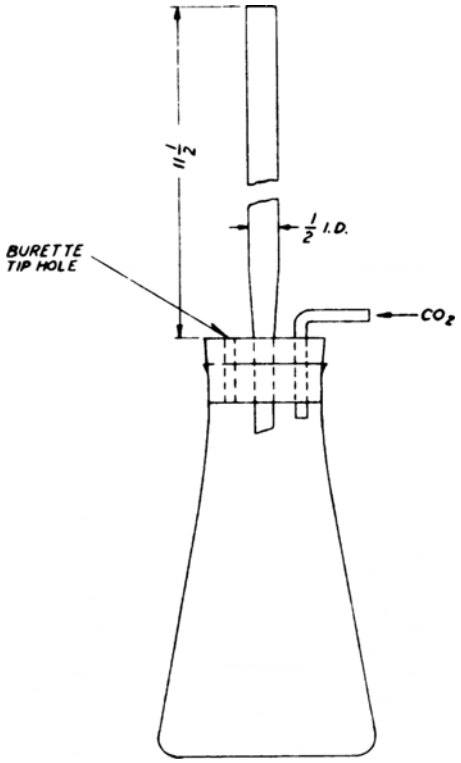


FIG. 3 Apparatus for Reduction of Tin

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 NH_4OH (1 + 1) until neutral to litmus paper to precipitate iron, tin, chromium, etc., and then add 1 mL 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 NH_4OH (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 $SbCl_3$ 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 min 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 15—If Apparatus in 98.1 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 ($NaHCO_3$) 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 KIO_3 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 16—If Apparatus in 98.1 is used, remove the stopper and the siphon and replace immediately with a two-hole stopper with a CO_2 delivery tube through which CO_2 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:

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

where:

A = KIO_3 solution required to titrate the tin in the sample, mL,
B = KIO_3 solution required to titrate the blank, mL,
C = tin equivalent of the KIO_3 solution, and
D = sample used, g.

102. Precision

102.1 Five to seven laboratories cooperated in testing this test method, three of them submitting one additional set of data, all of which are summarized in Table 7.

SILICON BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD

103. Scope

103.1 This test method covers the determination of silicon in compositons from 0.01 % to 0.06 %.

104. Summary of Test Method

104.1 The sample is carefully dissolved in dilute acid to avoid the formation of polymeric forms of silicic acid. Silica present in the sample is separated, along with other acid insolubles, and fused in sodium carbonate. After leaching, the oxides of silicon are in the form of orthosilicic acid, which is combined with the original sample solution. Ammonium molybdate is added to form the molybdosilicate complex, which is reduced with ascorbic acid to form the blue complex. Spectrophotometric measurement is made at approximately 810 nm against a reference solution that compensates for background color.

105. Concentration Range

105.1 The recommended concentration range is from 0.02 mg to 0.12 mg of silicon per 100 mL of solution, using a 1-cm cell.

NOTE 17—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.

106. Stability of Color

106.1 The color develops in 30 min, and is stable for at least 1 h.

107. Interferences

107.1 The formation of molybdophosphate, molybdoarsenate, and molybdovanadate complexes is prevented by the addition of oxalic acid and by maintaining high acidity.

108. Apparatus

108.1 *Polyethylene Reagent Bottles and 150-mL Poly(tetrafluoroethylene) Beakers.*

NOTE 18—Neutral or alkaline solutions should not remain in contact with glassware longer than necessary; such solutions may be prepared in glass volumetric flasks, provided they are transferred promptly to polyethylene bottles. Acidic solutions may remain in contact with glassware for as long as 2 h without becoming contaminated with silica.

108.2 *Platinum Crucibles,* 8-mL and 25-mL capacity.

108.3 *Filter Holder and Filter Membranes*—47-mm diameter cellulose disks having a 0.5-µm average pore diameter.

109. Reagents

109.1 *Ammonium Molybdate Solution* (100 g/L)—Dissolve 100 g of ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 500 mL of water, dilute to 1 L, and transfer to a polyethylene bottle. Allow the reagent to stand for at least 1 day, filter, and store in a polyethylene bottle.

109.2 *Ascorbic Acid Solution* (40 g/L)—Dissolve 4.0 g of ascorbic acid in water, dilute to 100 mL, and transfer promptly to a polyethylene bottle. Do not use a solution that has stood for more than 1 day.

109.3 *Distilled Water*—Do not use water that has been stored in a glass container.

109.4 *Oxalic Acid Solution* (80 g/L)—Dissolve 80 g of oxalic acid dihydrate in 800 mL of water, dilute to 1 L, filter if necessary, and transfer promptly to a polyethylene bottle.

109.5 *Silicon, Standard Solution A* (1 mL = 0.4 mg Si)—Transfer 0.8557 g of silicon dioxide (SiO_2) (purity: 71.5 % minimum), previously dried for 1 h at 150 °C, to a 25-mL platinum crucible. Add 8 g of sodium carbonate (Na_2CO_3), mix well, heat to obtain a clear melt, and cool. Place the crucible in a poly(tetrafluoroethylene) beaker, add 100 mL of water, and heat at approximately 90 °C to dissolve the melt. Using a plastic rod, remove and rinse the crucible with water, and cool. Transfer the solution to a 1-L volumetric flask, dilute to volume, and mix. Transfer promptly to a polyethylene bottle. If SiO_2 of the designated purity is not available, proceed in accordance with 109.5.1.

109.5.1 Using a pipet, transfer 25-mL portions of silicon Solution A to 400-mL beakers. Add 50 mL of $HClO_4$ which contains less than 0.0002 % silicon (see Section 49). Evaporate the solutions to fumes and heat at such a rate for 15 min to 20 min that $HClO_4$ refluxes on the sides of the beakers. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C). Proceed in accordance with 49.2.2 – 49.2.6 of these test methods.

109.5.2 Calculate the silicon concentration of standard Solution A as follows:

TABLE 7 Statistical Information—Tin—Iodimetric Titration Method

Test Material	Tin Found, %	Number of Laboratories	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Low-alloy steel (NIST 36a, 0.011 Sn)	0.011	5	0.002	0.003
2. Low-alloy steel	0.011	6	0.002	0.004
3. Low-alloy steel (NIST 152a, 0.032 Sn)	0.028	5	0.002	0.001
4. Low-alloy steel	0.087	7	0.009	0.010
5. Low-carbon steel	0.113	7	0.009	0.020

$$\text{Silicon, mg/mL} = [(A - B) \times 0.4675 \times 1000]/25 \quad (9)$$

where:

A = initial weight of crucible and impure SiO_2, g, and
B = final weight of crucible and residue, g.

109.6 *Silicon, Standard Solution B* (1 mL = 0.04 mg Si)—Using a pipet, transfer 50 mL of silicon Solution A to a 500-mL volumetric flask, dilute to volume, and mix. Transfer promptly to a polyethylene bottle.

110. Preparation of Calibration Curve

110.1 *Calibration Solutions:*

110.1.1 Transfer 2.000 g of iron (purity: 71.8 % minimum, silicon: 0.001 maximum) to each of seven 150-mL poly(tetrafluoroethylene) beakers. Using a pipet (Note 19), add 25 mL of H_2SO_4 (3 + 20), cover the beaker with a plastic cover, and heat at 90 °C until dissolution is complete.

NOTE 19—The amount of H_2SO_4 (3 + 20) added is critical. This amount of acid will minimize the formation of polymeric forms of silicic acid, which require excessive time to react with ammonium molybdate.

110.1.2 Add 1 g of potassium nitrate (KNO_3) and 50 mL of water. Mark the beaker at this volume. Boil for 5 min to 8 min to remove oxides of nitrogen, while maintaining the volume by additions of water from a wash bottle. Cool, and transfer the solutions to 200-mL volumetric flasks.

110.1.3 Using pipets, transfer (5, 10, 15, 20, 25, and 30) mL of silicon Solution B (1 mL = 0.04 mg Si) to the flasks, dilute to volume, and mix. Do not allow these solutions to remain in the glassware for more than 1 h.

110.1.4 Using a pipet, transfer 20 mL of each solution to a 100-mL volumetric flask, and dilute to 70 mL. Proceed in accordance with 110.3.

110.2 *Reference Solution*—Dilute the remaining seventh solution, prepared in accordance with 121.1.2, to volume, and mix. Using a pipet, transfer 20 mL to a 100-mL volumetric flask, and dilute to 70 mL. Proceed in accordance with 110.3.

110.3 *Color Development:*

110.3.1 Add 10 mL of ammonium molybdate solution. After 20 min, add in order, and with swirling after each addition, 5 mL of H_2SO_4 (1 + 1), 5 mL of oxalic acid solution, and 5 mL of ascorbic acid solution. Dilute to volume, and mix.

110.3.2 Allow the solutions to stand for 30 min at 25 °C, and proceed in accordance with 110.4.

110.4 *Spectrophotometry:*

110.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 810 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

110.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 810 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

110.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

111. Procedure

111.1 *Test Solution:*

111.1.1 Transfer a 2.00-g sample, weighed to the nearest 1 mg, to a 150-mL poly(tetrafluoroethylene) beaker. Using a pipet (Note 20), add 25 mL of H_2SO_4 (3 + 20), cover the beaker with a plastic cover, and heat at 90 °C until dissolution is complete.

111.1.2 Filter on a membrane filter, and wash three to five times with 5-mL portions of hot water. Transfer the filtrate and the washings to the original poly(tetrafluoroethylene) beaker, and reserve. Wash the filter with two 5-mL portions of methanol, and discard these washings.

111.1.3 Transfer the paper to an 8-mL platinum crucible, dry the paper, and then heat at about 600 °C until the carbon is removed. Ignite the crucible and contents at 980 °C for 1 h.

111.1.4 Add 100 mg of Na_2CO_3, heat until a clear melt is obtained, and cool. Place the crucible in the beaker containing the reserved filtrate. Add 40 mL of water, cover the beaker, and heat at 90 °C, if necessary, until the melt is dissolved.

111.1.5 Using a plastic rod, remove the crucible and rinse with 10 mL of water. Add 1 g of KNO_3, mark the beaker at the liquid level, and boil to remove oxides of nitrogen for 5 min to 8 min while maintaining the volume by additions of water from a wash bottle. Cool, transfer the solution to a 200-mL volumetric flask, dilute to volume, and mix.

111.1.6 Using a pipet, promptly transfer 20-mL portions to two 100-mL volumetric flasks, add 50 mL of water, and treat one in accordance with 111.3 and the other in accordance with 111.5.

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

NOTE 20—The Na_2CO_3 must be fused in a platinum crucible in preparing this solution.

111.3 *Color Development*—Proceed in accordance with 110.3.

111.4 *Background Color Reference Solution*—To the other portion obtained in 111.1.6, add in order, and with swirling after each addition (Note 21), 5 mL of H_2SO_4 (1 + 1), 10 mL of ammonium molybdate solution, 5 mL of oxalic acid solution, and 5 mL of ascorbic acid solution. Dilute to volume, and mix. Allow the solution to stand for 30 min.

NOTE 21—The addition of H_2SO_4 (1 + 1) before the ammonium molybdate prevents the formation of the colored complex.

111.5 *Spectrophotometry*—Take the spectrophotometric readings of the reagent blank solution and of the test solution (using the respective background color reference solutions and determining the cell correction with each of them) in accordance with 111.4.

112. Calculation

112.1 Convert the net spectrophotometric readings of the test solution and of the reagent blank solution to milligrams of silicon by means of the calibration curve. Calculate the percent of silicon as follows:

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

where:

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

113. Precision

113.1 Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 8.

COPPER BY THE NEOCUPROINE SPECTROPHOTOMETRIC METHOD

114. Scope

114.1 This test method covers the determination of copper in compositions from 0.005 % to 1.50 %.

115. Summary of Test Method

115.1 Copper is separated as cuprous copper from other metals by extraction of the copper-neocuproine complex with chloroform. Photometric measurement is made at approximately 455 nm.

116. Concentration Range

116.1 The recommended concentration range is from 0.01 mg to 0.30 mg of copper per 50 mL of solution, using a 1-cm cell.

NOTE 22—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.

117. Stability of Color

117.1 The color develops within 5 min and the extracted complex is stable for at least 1 week; however, because of the volatile nature of the solvent, it is advisable to take spectrophotometric readings promptly.

118. Interferences

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

119. Reagents

119.1 *Chloroform* ($CHCl_3$).

119.2 *Citric Acid Solution* (300 g/L)—Dissolve 300 g of citric acid in water and dilute to 1 L. The addition of 1 g of benzoic acid per litre will prevent bacterial growth.

119.3 *Copper, Standard Solution* (1 mL = 0.01 mg Cu)—Transfer 0.4000 g of copper (purity: 99.9 % minimum) to a 250-mL Erlenmeyer flask, and dissolve in 20 mL of HNO_3 (1 + 1). Add 10 mL of $HClO_4$ and evaporate to $HClO_4$ fumes to expel HNO_3. Cool, add 100 mL of water, transfer to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 25 mL to a 1-L volumetric flask, dilute to volume, and mix. Do not use a solution that has stood more than one week.

119.4 *2,9-Dimethyl-1,10-Phenanthroline (Neocuproine) Solution* (1 g/L)—Dissolve 0.1 g of neocuproine in 100 mL of absolute ethanol.

NOTE 23—In addition to absolute ethanol, 95 % ethanol or denatured No. 30 or 3A alcohol have been found suitable for preparing this solution.

119.5 *Hydroxylamine Hydrochloride Solution* (100 g/ L)—Dissolve 5.0 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 50 mL of water. Prepare fresh as needed.

119.6 *Water*—Use deionized water or water distilled in all-glass or all-quartz apparatus.

120. Preparation of Calibration Curve

120.1 *Calibration Solutions*—Using pipets, transfer (5, 10, 15, 20, 25, and 30) mL of copper solution (1 mL = 0.01 mg Cu) to 150-mL beakers, and dilute to 50 mL. Proceed in accordance with 120.3.

120.2 *Reagent Blank Solution*—Transfer 50 mL of water to a 150-mL beaker. Proceed in accordance with 120.3.

120.3 *Color Development:*

120.3.1 Add 5 mL of $NH_2OH{\cdot}HCl$ solution and 10 mL of citric acid solution. Stir for 30 s. Using a pH meter (Note 24), adjust the pH to 5.0 ± 1.0 with NH_4OH (1 + 1). Add 10 mL of neocuproine solution.

NOTE 24—Test paper may be used, except for highly colored solutions, by affixing it to the inner wall of the beaker, and rinsing it with water before removing it.

120.3.2 Transfer the solution to a 125-mL conical separatory funnel, rinsing the beaker with 10 mL to 15 mL of water. Add 15 mL of $CHCl_3$ and shake for 30 s. Allow the phases to separate. Place a small roll of filter paper which has been washed with $CHCl_3$, in the stem of a small funnel. Drain the $CHCl_3$ layer through the funnel into a 50-mL volumetric flask containing 6 mL to 7 mL of ethanol. Add 10 mL of $CHCl_3$ to the separatory funnel, extract as before, and drain the $CHCl_3$ layer through the funnel into the 50-mL volumetric flask. Repeat the extraction just described. Wash the paper and the funnel with 4 mL to 5 mL of ethanol, and collect the washings in the volumetric flask. Dilute to volume with ethanol, and mix.

120.4 *Reference Solution*—$CHCl_3$.

120.5 *Spectrophotometry:*

120.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at

TABLE 8 Statistical Information—Silicon—Molybdenum Blue Spectrophotometric Method

Test Material	Silicon Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Low-alloy steel (NIST 10g, 0.020 Si)	0.021	0.003	0.016
2. Low-alloy steel	0.031	0.003	0.011
3. Low-alloy steel (NIST 170a, 0.036 Si)	0.037	0.005	0.012

approximately 455 nm. Using the test cell, take the photometric readings of the calibration solutions.

120.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 455 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

120.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

121. Procedure

121.1 *Test Solution:*

121.1.1 Select a sample in accordance with the following:

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.005 to 0.15	1.00	1.0	100	20
0.10 to 0.25	1.00	1.0	250	30
0.20 to 0.50	1.00	0.5	250	15
0.40 to 1.00	0.50	0.5	250	15
0.80 to 1.50	0.50	0.1	250	10

Transfer the sample to a 250-mL Erlenmeyer flask.

121.1.2 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample. Heat until dissolution is complete. Add HNO_3 to provide a total of at least 5 mL. Add 15 mL of $HClO_4$ and a sufficient amount of HF to volatilize the silica.

121.1.3 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 mL to 1.5 mL of HCl allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming the solution until the volume has been reduced to about 10 mL. Cool, add 7 mL of water, and digest if necessary to dissolve the salts. Cool to room temperature, add 1 mL of HCl, and transfer the solution (Note 25) to a volumetric flask that provides for the dilution in accordance with 121.1.1. Dilute to volume and mix.

NOTE 25—If silver is present in the alloy it must be removed by filtration at this point.

121.1.4 Allow insoluble matter to settle, or dry-filter through a coarse paper and discard the first 15 mL to 20 mL of the filtrate before taking the aliquot. Using a pipet, transfer a portion as specified in 121.1.1 to a 150-mL beaker, and dilute to 50 mL. Proceed as directed in 121.4.

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

121.3 *Reference Solution*—$CHCl_3$.

121.4 *Color Development*—Proceed in accordance with 120.3.

121.5 *Spectrophotometry*—Take the spectrophotometric reading of the test solution in accordance with 120.5.

122. Calculation

122.1 Convert the net spectrophotometric readings of the test solution and of the reagent blank solution to milligrams of copper by means of the calibration curve. Calculate the percent of copper as follows:

$$\text{Copper, \%} = (A - B)/(C \times 10) \quad (11)$$

where:

A = copper found in 50 mL of the final test solution, mg,
B = copper found in 50 mL of the final reagent blank solution, mg, and
C = sample represented in 50 mL of the final test solution, g.

123. Precision

123.1 Ten laboratories cooperated in testing this test method and obtained the data summarized in Table 9. Although samples covered by this test method with copper compositions near the lower and upper limits of the scope were not available for testing, the precision data obtained for the other specimens by the methods indicated should apply.

TOTAL ALUMINUM BY THE 8-QUINOLINOL GRAVIMETRIC METHOD

124. Scope

124.1 This test method covers the determination of total aluminum in compositions from 0.20 % to 1.5 % except in silicon electrical steel.

125. Summary of Test Methods

125.1 Following dissolution, acid-insoluble aluminum is separated, fused, and recombined. Interfering elements are removed by mercury-cathode, cupferron, and sodium hydroxide separations. Aluminum quinolinate is precipitated and weighed.

TABLE 9 Statistical Information—Copper—Neocuproine Spectrophotometric Method

Test Material	Copper Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E354	0.006	0.001	0.004
2. No. 2, E354	0.014	0.002	0.006
3. Carbon steel (NIST 152a, 0.023 Cu)	0.021	0.004	0.010
4. Low-alloy steel (NIST 12h, 0.073 Cu)	0.074	0.009	0.010
5. Low-alloy steel (NIST 19g, 0.093 Cu)	0.092	0.007	0.005
6. Low-alloy steel (NIST 36a, 0.114 Cu)	0.110	0.004	0.011
7. Low-alloy steel	0.750	0.023	0.046
8. No. 5, E351	1.51	0.04	0.05

126. Interferences

126.1 This test method is not applicable to silicon electrical steel. The elements ordinarily present in the other ferrous materials do not interfere if their compositions are under the maximum limits shown in 1.1.

127. Apparatus

127.1 *Filtering Crucible,* medium-porosity fritted-glass, low-form, 30-mL capacity.

127.2 *Glassware,* to prevent contamination of the sample, all glassware must be cleaned with hot HCl (1 + 1) before use.

127.3 *HCl Gas Generator* (Fig. 4)—A simple HCl gas generator constructed from a stoppered wash bottle and glass tubing.

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

127.5 *pH Meter.*

128. Reagents

128.1 *Ammonium Peroxydisulfate Solution* (100 g/L)—Dissolve 20 g of ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) in water and dilute to 200 mL. Do not use a solution that has stood more than 8 h.

128.2 *Chloroform* ($CHCl_3$).

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

128.4 *8-Quinolinol Solution* (25 g/L)—Dissolve 25 g of 8-quinolinol in 50 mL of acetic acid, dilute to 300 mL with warm water, filter through a medium paper, and dilute to 1 L. Store in an amber bottle away from direct sunlight. Do not use a solution that has stood more than 1 month.

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

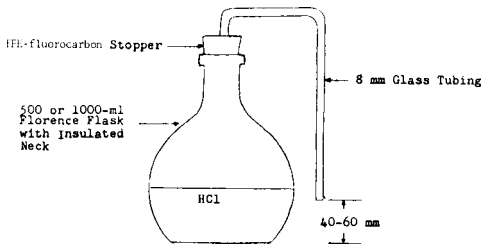


FIG. 4 HCl Gas Generator

128.6 *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 in a polyethylene bottle.

128.7 *Tartaric Acid Solution* (200 g/L)—Dissolve 200 g of tartaric acid in 500 mL of water, filter through a medium paper, and dilute to 1 L.

129. Procedure

129.1 Transfer a 1.000-g sample, weighed to the nearest 0.1 mg, to a 600-mL beaker.

129.2 Carry a reagent blank through the entire procedure, using the same amounts of all reagents but with the sample omitted.

129.3 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. If chromium is present, position the gas generator containing boiling HCl (use a fresh portion of HCl for each sample), so that the tube extends into the beaker and the HCl gas is delivered 20 mm to 30 mm above the surface of the fuming $HClO_4$. Continue boiling the HCl and fuming the sample solution until there is no evidence of yellow chromyl chloride in the fumes. Remove the generator and continue fuming the solution until the volume is reduced to 10 mL. Alternatively, volatilize the chromium as directed in 84.1.2. Remove from the hot plate and cool. Add 25 mL of water to dissolve the salts. If iron hydrolyzes, indicating that the sample was fumed too long, add 1 mL to 2 mL of HCl and 5 mL of $HClO_4$ and again take to fumes. Dilute to 75 mL with water and boil to remove chlorine.

129.4 Filter through an 11-cm medium paper into a 400-mL beaker. Scrub and wipe the inside of the beaker with half a sheet of filter paper. Add this paper to the funnel. Wash the original beaker, the paper, and the residue 2 or 3 times with hot $HClO_4$ (2 + 98) and then 3 or 4 times with hot water to ensure removal of $HClO_4$. Reserve the filtrate.

129.5 Transfer the paper to a platinum crucible, dry it, and then heat at about 600 °C until the carbon has been removed. Finally ignite at 1100 °C, cool, and add a few drops of H_2SO_4 (1 + 1) and 4 mL to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until the H_2SO_4 has been removed. Cool, add 2 g to 3 g of sodium hydrogen sulfate, fused, 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.

129.6 If the solution is clear, add it to the filtrate reserved in 129.4. If the solution is turbid, filter through an 11-cm fine paper containing paper pulp into the beaker containing the reserved filtrate. Wash the paper 3 or 4 times with hot H_2SO_4 (3 + 97). Discard the paper and residue.

129.7 Evaporate to approximately 100 mL, and cool. Transfer the solution to a mercury cathode cell. Dilute to 150 mL to 200 mL and electrolyze at 15 A (Note 26) until the iron has been removed (Note 27). 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 26—Contact between the mercury pool and the platinum cathode may be broken intermittently due to stirring the mercury too rapidly. Since this will cause arcing which will result in the dissolution of some mercury in the electrolyte, it should be avoided by adding more mercury to the cell, using less current, or by proper adjustment of the cathode lead wire so that contact will be ensured.

NOTE 27—The completeness of the removal of iron, which usually requires 1 to 3 h, can be determined by the following test: Transfer 1 drop of the electrolyte to a watch glass or spot test plate. Add 1 drop of H_2SO_4 (1 + 1), 1 drop of saturated potassium permanganate ($KMnO_4$) solution, and 1 drop of sodium thiocyanate (NaSCN) solution (500 g/L). When only a faint pink color is observed, the electrolysis may be considered complete.

129.8 Filter the solution through a 12.5-cm medium paper containing paper pulp (Note 28) into a 600-mL beaker, and wash 3 or 4 times with hot water. To the filtrate add 10 mL of H_2SO_4 (1 + 1) and 10 mL of $(NH_4)_2S_2O_8$ solution. Heat to boiling and evaporate to about 75 mL. Cool in an ice bath to below 10 °C.

NOTE 28—This filtration removes any mercurous chloride that may have formed and any metallic mercury that may have been transferred from the cell.

129.9 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 $CHCl_3$ and shake for 1 min. Allow the layers to separate. Draw off and discard the $CHCl_3$ layer. Repeat the extraction [with 20-mL portions of $CHCL_3$ until the extract is colorless. Transfer the aqueous solution to the reserved 600-mL beaker and evaporate to 35 mL to 40 mL. Add 25 mL of HNO_3, cover with a ribbed cover glass, evaporate to fumes of H_2SO_4,] and cool. Dilute to 50 mL, heat to boiling, and cool.

129.10 Transfer the solution to a platinum, quartz or high-silica glass, or poly(tetrafluoroethylene) beaker. Police thoroughly (Note 29), rinse the beaker, and add the rinsings to the main solution. Neutralize to litmus with sodium hydroxide (NaOH) solution (Note 30), and add a 10-mL excess. Add 1 mL of H_2O_2, digest near the boiling point for 5 min to 7 min, and finally boil for 1 min to 2 min to coagulate the manganese precipitate. Cool, and filter through a 12.5-cm medium paper containing paper pulp previously washed 3 times with hot dilute NaOH solution (20 g/L), into a 600-mL beaker. Wash the paper and precipitate 4 or 5 times with hot water. Immediately add HCl (1 + 1) to the filtrate until acidic to litmus paper, and then add 3 mL to 4 mL in excess.

NOTE 29—This step is necessary whether or not a precipitate is visible.

NOTE 30—Approximately 70 mL will be required.

129.11 Dilute to approximately 250 mL, and add 25 mL of tartaric acid solution. Using a pH meter, adjust the pH to 8.0 with NH_4OH.

129.12 Add 10 mL of H_2O_2 (Note 31), heat to 55 °C, and while stirring add 15 mL of 8-quinolinol solution. Add 5 mL of NH_4OH, and stir continuously for 1 min and then for 5 s to 10 s once a minute for 9 more min while maintaining the temperature at 50 °C to 55 °C.

NOTE 31—Precipitate aluminum in only one sample at a time. A motor-driven stirrer operating continuously for 10 min may be used.

129.13 Allow the solution to cool to room temperature. Filter with suction, using a weighed, medium-porosity, fritted-glass crucible. Police the beaker, rinse with NH_4OH (1 + 100), and wash the precipitate 4 times with warm NH_4OH (1 + 100). Dry for 1.5 h at 135 °C, cool, and weigh as aluminum quinolinate.

130. Calculation

130.1 Calculate the percent of total aluminum as follows:

$$\text{Total aluminum, \%} = [((A - B) \times 0.0587)/C] \times 100 \quad (12)$$

where:

A = aluminum quinolinate found, g,
B = correction for blank, g, and
C = sample used, g.

131. Precision[7]

131.1 Nine laboratories cooperated in testing this test method, with one laboratory reporting a second pair of values; the data are summarized in Table 10. Although samples covered by this test method with aluminum compositions near the lower limit and in the middle range of the scope were not available for testing, the precision data obtained using the test methods indicated in Table 10 should apply.

LEAD BY THE ION-EXCHANGE—ATOMIC ABSORPTION SPECTROMETRY METHOD

132. Scope

132.1 This test method covers the determination of lead in compositions from 0.001 % to 0.50 %.

133. Summary of Test Method

133.1 A hydrochloric acid solution of the sample is passed through an ion-exchange column to separate the lead from most of the other elements, including iron. After elution of lead, the solution is aspirated into an air-acetylene flame. Spectral energy at 217.0 Å from a lead hollow-cathode tube is

TABLE 10 Statistical Information—Aluminum—Quinolinol Gravimetric Method

Test Material	Aluminum Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E353	0.232	0.036	0.041
2. No. 2, E353	1.16	0.06	0.10
3. No. 3, E354	1.21	0.02	0.08
4. Nitralloy-type steel	1.44	0.07	0.16

passed through the flame, and the absorbance is measured. The spectrophotometer is calibrated with solutions of known concentrations of lead.

134. Concentration Range

134.1 The recommended concentration range is from 0.002 mg to 0.030 mg of lead per millilitre of solution.

135. Interferences

135.1 All interfering elements normally present are removed by the ion-exchange separation.

136. Apparatus

136.1 *Atomic Absorption Spectrometer,* capable of resolving the 217.0 nm line, equipped with a neon-filled hollow-cathode tube whose radiant energy is modulated, with a detector system tuned to the same frequency, and with a premix air-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (0.030 mg/mL) produces an absorbance of 0.300 or higher, and a calibration curve whose deviation from linearity is within the limits in accordance with 138.3.

136.2 *Ion-Exchange Column,* approximately 25 mm in diameter and 300 mm long, tapered at one end, and provided with a stopcock or other means to stop the flow. The Jones reductor may be adapted to this test method and has the dimensional requirements shown in Fig. 5. It consists of a column 19 mm in diameter and 250 mm in length, of 20-mesh to 30-mesh amalgamated zinc. To amalgamate the zinc, shake 800 g of zinc (as free of iron as possible) with 400 mL of HgCl 2 solution (25 g/L) in a 1-L flask for 2 min. Wash several times with H_2SO_4 (2 + 98), and then thoroughly with water. The reductor, when idle, should always be kept filled with distilled water to above the top of the zinc.

137. Reagents

137.1 *Ion-Exchange Resin:*

137.1.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a nominal cross-linkage of 8 % and 100 to 200 nominal mesh size.[8]

137.1.2 Transfer a supply of the resin (Note 32) to a beaker, cover with water, and allow at least 30 min for the beads to undergo maximum swelling. Place a No. 60 (250-µm) screen, 150 mm in diameter, over a 2-L beaker. Prepare a thin slurry of the resin and pour a portion of it onto the screen. Wash the fine beads through the screen using a small stream of water. Continue adding small portions of the resin to the screen and washing with a small stream of water until all of the resin has been screened. Discard the large resin beads retained on the screen periodically, if necessary to avoid undue clogging of the openings.

NOTE 32—One pound of resin (45 % moisture) provides enough material for approximately 5 ion-exchange columns.

137.1.3 Allow the bulk of the collected resin to settle for 4 min to 6 min and then decant the excess water. Add 1 L of water, stir vigorously, allow the resin to settle for 4 min to 6 min, decant 900 mL to 950 mL of the suspension, and discard.

[8] Dowex 1, manufactured by The Dow Chemical Co, has been found satisfactory for this purpose.

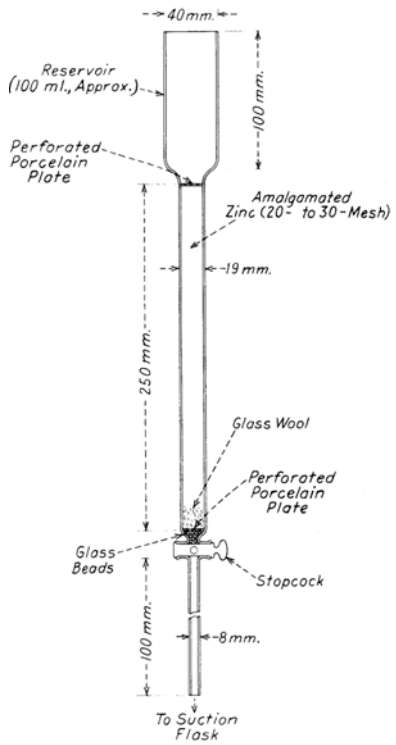


FIG. 5 Jones Reductor

Repeat the treatment twice more, and reserve the coarser resin for the column preparation.

137.1.4 Prepare the column (Note 33) as follows: Place a 10-mm to 20-mm layer of glass wool or poly (vinyl chloride) plastic fiber in the bottom of the column, and add sufficient prepared resin to fill the column to a height of approximately 140 mm. Place a 20-mm layer of glass wool or poly (vinyl chloride) plastic fiber at the top of the resin bed to protect it from being carried into suspension when the solution is added. Add 150 mL of HCl to the column, and when the solution level is 10 mm to 20 mm above the resin bed, add a minimum of 50 mL of HCl (1 + 11) to the column. Drain to 10 mm to 20 mm above the top of the resin bed and close the stopcock.

NOTE 33—If necessary, prepare at least 4 columns, as this number or more of test solutions can be conveniently processed simultaneously through the ion-exchange separation.

137.2 *Lead, Standard Solution* (1 mL = 0.1 mg Pb)—Transfer 0.2500 g of lead (purity: 99.9 % minimum) to a 250-mL borosilicate glass volumetric flask. Add 10 mL of HNO_3 (1 + 1) and heat gently. When dissolution is complete, cool to room temperature, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask, dilute to volume, and mix.

138. Preparation of Calibration Curves

138.1 *Calibration Solutions*—Using pipets, transfer (2, 5, 10, 15, 20, 25, and 30) mL of lead solution (1 mL = 0.1 mg Pb) to 100-mL volumetric flasks, add 2 mL HNO_3, dilute to volume, and mix. Do not use solutions that have stood more than two weeks.

NOTE 34—Prepare the test solution (139.1) and the reagent blank solution (139.2), and have them ready to aspirate immediately after aspirating the calibration solutions.

138.2 *Spectrometry:*

138.2.1 With the lead hollow-cathode tube in position, energized, and stabilized, locate the wavelength setting that gives maximum response to radiant energy at 217.0 nm.

138.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the lead solution with the highest concentration from the series prepared in accordance with 138.1, and adjust the height of the burner, the air and fuel pressures and flow rates, the aspiration rate of the solution, and the position of the capillary to obtain maximum response. Adjust the slit setting and the gain to obtain optimum signal-to-noise ratio.

NOTE 35—Recalibration is required whenever these parameters are changed.

138.2.3 Aspirate the lead solution used in 138.2.2 a sufficient number of times to establish that the absorbance reading is not drifting. Record six readings, and calculate the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (13)$$

where:

A = highest of the six values found, and

B = lowest of the six values found.[9]

138.2.4 Beginning with the calibration solution containing the lowest concentration of lead, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of the six values recorded in 138.2.3 by more than twice the standard deviation, *s*, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposits in the burner or clogged capillary), correct it; and repeat 138.2.1 – 138.2.4.

138.2.5 Proceed immediately as directed in 139.3.

138.3 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \quad (14)$$

where:

C = absorbance value for 0.03 mg Pb/mL,
D = absorbance value for 0.025 mg Pb/mL, and
E = absorbance value for 0.005 mg Pb/mL.

If the calculated value is less than 0.60, correct the indicated malfunction or maladjustment of the instrument or hollow-cathode tube and repeat the calibration.

139. Procedure

139.1 *Test Solution:*

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

Lead, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution (after separation), mL
0.0004 to 0.006	5.00	5	10
0.005 to 0.015	5.00	5	25
0.010 to 0.030	5.00	5	50
0.025 to 0.060	5.00	5	100
0.050 to 0.12	2.50	2	100
0.10 to 0.24	2.50	2	200
0.20 to 0.50	2.50	2	500

Transfer the sample to a 600-mL beaker.

139.1.2 Add 40 mL of HCl and 10 mL of HNO_3, cover the beaker, and heat as required until action ceases. Substitute a ribbed cover glass, and evaporate the solution to dryness. Add 40 mL of HCl (1 + 1) and digest until soluble salts are dissolved.

139.1.3 Dilute to 50 mL and filter through a medium paper into a 250-mL Erlenmeyer flask. Wash the paper and residue alternately 3 or 4 times with 3 mL to 5 mL portions of hot HCl (1 + 9) and hot water. Evaporate the filtrate to a volume between 15 mL and 20 mL. Cool, pour the solution into a 25-mL graduated cylinder without rinsing, and note the volume. Return the solution to the flask and rinse the cylinder with a volume of water equivalent to 5 times the noted volume. Add the rinsings to the solution in the flask.

139.1.4 Place a beaker under the ion-exchange column and open the stopcock. Transfer portions of the sample solution to

[9] The value 0.40, which is used to estimate the standard deviation from the range of six values, is derived from Dixon, W. J., and Massey, F. J., *Introduction to Statistical Analysis*, McGraw-Hill, New York, NY, 1957, p. 404, Table 8b (1).

the column. When the solution has been transferred and has drained to a level 10 mm to 20 mm above the resin bed, rinse the flask with 8 mL to 10 mL of HCl (1 + 11). Add these rinsings to the column in such a manner as to wash the upper part of the column at the same time. Allow the solution to reach a level of 10 mm to 20 mm above the resin bed and then repeat the rinsing of the flask and upper part of the column twice more. Add 80 mL more of HCl (1 + 11) to the column. Allow the solution to reach a level of 10 mm to 20 mm above the resin bed, close the stopcock, and discard the eluate.

139.1.5 Open the stopcock, add 75 mL of concentrated HCl to the column, and collect the eluate in a 150-mL beaker. When the solution level has reached 10 mm to 20 mm above the resin bed, close the stopcock and place a 250-mL beaker under the column. Open the stopcock, mix the solution in the 150-mL beaker, and add it to the column (Note 36). When the solution level is 10 mm to 20 mm above the top of the resin bed, rinse the 150-mL beaker 2 or 3 times with 5-mL portions of HCl and add the rinsings to the column. Continue to add HCl to the column until 150 mL of eluate has been collected. Reserve the 250-mL beaker.

NOTE 36—This is required in order to remove the residual iron present after the first pass through the column.

139.1.6 Precondition the column for the next test solution as follows: Drain the remaining solution in the column to 10 mm to 20 mm above the resin bed, pass 100 mL of water, 200 mL of HNO_3 (1 + 9), 100 mL of water, 150 mL of HCl, and a minimum of 50 mL of HCl (1 + 11) through the column. Drain to 10 mm to 20 mm above the top of the resin bed and close the stopcock.

139.1.7 Cover the 250-mL beaker reserved in 139.1.5 with a ribbed cover glass and evaporate the solution to dryness. Dissolve the residue with 0.5 mL of HNO_3 and 5 mL of water. Digest 2 min to 3 min, cool, and transfer to a volumetric flask, selecting the size in accordance with the dilution specified in 139.1.1 (Note 37). Cool, dilute to volume, and mix.

NOTE 37—Use a 10-mL volumetric flask for the reagent blank.

139.2 *Reagent Blank*—Carry a reagent blank through the entire procedure, using the same amounts of all reagents but with the sample omitted; take the reagents from the same lots as used to prepare the test solution.

139.3 *Spectrometry*—Aspirate the test solution and the reagent blank solution, and record the absorbance values. Measure the absorbance of the calibration solution with the highest concentration of lead. If the value differs from the average of the six values recorded in 138.2.3 by more than twice the standard deviation, *s*, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause, correct it, repeat the calibration procedure, and recheck the readings of the test solution (or solutions).

NOTE 38—A group comprised of as many as four test solutions, together with the reagent blank solution, may be aspirated before applying this test for drift.

140. Calculation

140.1 Convert the absorbance of the test solution and of the reagent blank to milligrams of lead per millilitre of final solution by means of the calibration curve. Calculate the percent of lead as follows:

$$\text{Lead, \%} = [((A \times B) - (C \times 10))/(D \times 10)] \quad (15)$$

where:

A = lead per millilitre of the final test solution, mg,
B = final test solution, mL,
C = lead per millilitre of the final reagent blank solution, mg, and
D = sample used, g.

141. Precision

141.1 Nine laboratories cooperated in testing this test method and obtaining the data for Material 7 summarized in Table 11. Although samples covered by this test method with lead compositions near the lower limit or at the middle range of the scope were not available for testing, the precision data obtained for other types of alloys using the methods indicated in Table 11 should apply.

ANTIMONY BY THE BRILLIANT GREEN SPECTROPHOTOMETRIC METHOD

142. Scope

142.1 This test method covers the determination of antimony in compositions from 0.0002 % to 0.030 %.

143. Summary of Test Method

143.1 After dissolution of the sample and removal of nitric acid with hydrochloric acid, excess chlorine and nitric oxides are destroyed with urea. Iron, tin, and arsenic are complexed with sodium pyrophosphate. The antimony-brilliant green complex is extracted with toluene. Spectrophotometric measurement is made at approximately 645 nm.

TABLE 11 Statistical Information—Lead—Ion-Exchange-Atomic Absorption Spectrometry Method

Test Material	Lead Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E353	0.0004	0.0002	0.0003
2. No. 2, E353	0.0010	0.0001	0.0005
3. No. 3, E353	0.0029	0.0004	0.0004
4. No. 4, E353	0.0063	0.0009	0.0010
5. No. 5, E353	0.0126	0.0012	0.028
6. No. 6, E353	0.106	0.023	0.031
7. Lead-bearing steel (NIST 130, 0.204 Pb)	0.217	0.010	0.049

144. Concentration Range

144.1 The recommended concentration range is from 0.002 mg to 0.025 mg of antimony per 25 mL of solution, using a 1-cm cell.

NOTE 39—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.

145. Stability of Color

145.1 The color is stable for at least 1 h.

146. Interferences

146.1 Gold and thallium interfere.

147. Reagents

147.1 *Antimony, Standard Solution A* (1 mL = 0.100 mg Sb)—Transfer 0.1000 g of antimony (purity: 99.9 % minimum) to a 400-mL beaker. Add 5 mL of H_2SO_4 and dissolve the antimony by fuming. Cool, dilute to 300 mL with HCl, and transfer the solution to a 1-L volumetric flask using HCl as the wash solution. Cool, dilute to volume with HCl, and mix.

147.2 *Antimony, Standard Solution B* (1 mL = 0.0025 mg Sb)—Using a pipet, transfer 25 mL of antimony Solution A (1 mL = 0.100 mg Sb) to a l-L volumetric flask, dilute to volume with HCl, and mix.

147.3 *Brilliant Green – Tartaric Acid Reagent*—Transfer 100 g of tartaric acid and 1.00 g of brilliant green[10] to a mortar. Grind until a blended mixture is obtained.

147.4 *Sodium Pyrophosphate Solution* (100 g/L)—Dissolve 100 g of sodium pyrophosphate decahydrate ($Na_4P_2O_7 \cdot 10H_2O$) in about 900 mL of water and dilute to 1 L.

147.5 *Toluene.*

147.6 *Urea Solution* (100 g/L)—Dissolve 10 g of urea in 100 mL of water. Do not use a solution that is more than one day old.

148. Preparation of Calibration Curve

148.1 *Calibration Solutions:*

148.1.1 Using pipets, transfer (1, 3, 5, 7, 9, and 10) mL of antimony Solution B (1 mL = 0.0025 mg Sb) to six 400-mL beakers.

148.1.2 Dilute to 20 mL with HCl and add 10 mL of HNO_3. Do not use a cover glass. Heat rapidly to reduce the volume to approximately 3 mL (Note 40) (hot-plate temperature, 300 °C to 325 °C). Wash the sides of the beaker with 4 mL of HCl and again rapidly reduce volume to approximately 3 mL. Add 30 mL of HCl and cool to less than 10 °C in an ice bath.

NOTE 40—The spectrophotometry must be completed within 1 h after this step is begun.

148.2 *Reagent Blank*—Add 5 mL of HCl to a 400-mL beaker and proceed in accordance with 148.1.2.

148.3 *Color Development:*

148.3.1 Using a pipet, transfer 25 mL of toluene to a 500-mL separatory funnel.

148.3.2 To the 400-mL beakers from 148.1.2, add 125 mL of water, swirl once, and add 7 mL of urea solution. Remove residual chlorine in the atmosphere above the solution in the beaker by blowing into the beaker. Swirl for 30 s. Add 200 mL of $Na_4P_2O_7$ solution and approximately 0.25 g of the brilliant green-tartaric acid reagent and immediately transfer to the 500-mL separatory funnel containing the toluene. Shake vigorously for 1 min and allow the layers to separate. Discard the aqueous layer and drain the toluene into a dry 50-mL beaker.

148.4 *Reference Solution*—Toluene.

148.5 *Spectrophotometry:*

148.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at approximately 645 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

148.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 645 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

148.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

149. Procedure

149.1 *Test Solution:*

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

Antimony, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.0002 to 0.0025	1.00	1.0	...	...
0.0010 to 0.0050	0.50	1.0	...	...
0.0020 to 0.0100	0.250	0.5	...	...
0.0050 to 0.0250	1.000	0.5	100	10
0.0100 to 0.0500	0.500	0.5	100	10

Transfer the sample to a 400-mL beaker.

149.1.2 Add 20 mL of HCl and 10 mL of HNO_3. Do not use a cover glass. Heat gently to dissolve (Note 41). When dissolution is complete, reduce the volume to approximately 3 mL by heating rapidly on a hot plate at 300 °C to 325 °C. Wash the sides of the beaker with 4 mL of HCl and again rapidly reduce the volume to approximately 3 mL. Add 30 mL of HCl and cool to less than 10 °C in an ice bath. If dilution is required, as indicated in 149.1, transfer the solution to a 100-mL volumetric flask. Dilute to volume with HCl and mix. Using a pipet, transfer 10 mL to a 400-mL beaker and add 30 mL of HCl. Cool to less than 10 °C in an ice bath.

NOTE 41—The determination must be completed within 1 h after dissolution of sample.

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

149.3 *Color Development*—Proceed in accordance with 148.3.

[10] Brilliant Green from J. T. Baker, 1170 Clifton Ave., Clifton, NJ 07013, has been found satisfactory for this purpose.

149.4 *Reference Solution*—Toluene.

149.5 *Spectrophotometry*—Take the spectrophotometric readings of the reagent blank solution and test solutions in accordance with 148.5.

150. Calculation

150.1 Convert the net spectrophotometric readings of the test solution and of the reagent blank solution to milligrams of antimony by means of the calibration curve. Calculate the percent of antimony as follows:

$$\text{Antimony, \%} = (A - B)/(C \times 10) \quad (16)$$

where:

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

151. Precision[7]

151.1 Nine laboratories cooperated in testing this test method. The data are summarized in Table 12.

MOLYBDENUM BY THE THIOCYANATE SPECTROPHOTOMETRIC METHOD

152. Scope

152.1 This test method covers the determination of molybdenum in compositions from 0.01 % to 1.50 %.

153. Summary of Test Method

153.1 The test solution is treated with thiocyanate to develop the molybdenum and iron thiocyanate complexes. Molybdenum and iron are reduced with stannous chloride, and the molybdenum complex is extracted with butyl acetate. Spectrophotometric measurement is made at approximately 475 nm.

154. Concentration Range

154.1 The recommended concentration range is from 0.0003 mg to 0.003 mg of molybdenum per millilitre of solution using a 1-cm cell.

NOTE 42—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.

155. Stability of Color

155.1 The color is stable for at least 2 h; however, spectrophotometric readings should be taken promptly because of the volatile nature of the solvent.

156. Interferences

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

157. Reagents

157.1 *Butyl Acetate.*

157.2 *Dissolving Solution*—While stirring, add 300 mL of H_3PO_4 and 300 mL of HNO_3 to 1400 mL of $HClO_4$.

157.3 *Iron* (purity: 99.8 % minimum) molybdenum 0.001 % maximum.

157.4 *Iron Solution A* (1 mL = 70 mg Fe)—Dissolve 25 g of ferric sulfate ($Fe_2(SO_4)_3 \cdot 9H_2O$) in 75 mL of hot water. Cool and add 10 mL of H_2SO_4. Cool, and dilute to 100 mL.

157.5 *Iron Solution B* (1 mL = 0.84 mg Fe)—Add 12 mL of iron Solution A to 175 mL of H_2SO_4 (1 + 1), and dilute to 1 L.

157.6 *Molybdenum, Standard Solution A* (1 mL = 0.2 mg Mo)—Transfer 0.2000 g of molybdenum metal (purity: 99.8 % min) to a 150-mL beaker and dissolve in 10 mL of HCl and HNO_3 added dropwise. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

157.7 *Molybdenum, Standard Solution B* (1 mL = 0.1 mg Mo)—Using a pipet, transfer 50 mL of molybdenum Solution A to a 100-mL volumetric flask, dilute to volume, and mix.

157.8 *Molybdenum, Standard Solution C* (1 mL = 0.01 mg Mo)—Using a pipet, transfer 10 mL of molybdenum Solution A to a 200-mL volumetric flask, dilute to volume, and mix.

157.9 *Sodium Thiocyanate Solution* (100 g/L)—Dissolve 100 g of sodium thiocyanate (NaSCN) in about 500 mL of water, filter, and dilute to 1 L. Store in a dark bottle.

157.10 *Stannous Chloride Solution* (350 g/L)—Transfer 350 g of stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) and 200 g of tartaric acid to a 1-L beaker, add 400 mL of HCl (1 + 1), and heat at 60 °C to 70 °C until dissolution is complete. Cool, and dilute to 1 L. Add several pieces of metallic tin and store in a stoppered bottle.

158. Preparation of Calibration Curve for Compositions from 0.01 % to 0.05 %

158.1 *Calibration Solutions:*

158.1.1 Transfer 0.3 g of iron to each of four 300-mL Erlenmeyer flasks. Using pipets, transfer (2, 5, 10, and 15) mL of molybdenum Solution C (1 mL = 0.01 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

TABLE 12 Statistical Information—Antimony—Brilliant Green Spectrophotometric Method

Test Material	Antimony Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Low-alloy steel (1.8 Cr, 3.5 Ni, 0.5 Mo, 0.15 V)	0.0005	0.0001	0.0002
2. Open-hearth iron (NIST 55e)	0.0013	0.0002	0.0003
3. Low-alloy steel	0.0020	0.0002	0.0006
4. Low-alloy steel	0.0019	0.0001	0.0003
5. Low-alloy steel (BCS 326, 0.005 Sb)	0.0050	0.0006	0.0008
6. Low-alloy steel (BCS 329, 0.018 Sb)	0.0183	0.0019	0.0019
7. Low-alloy steel (BCS 382, 0.026 Sb)	0.0259	0.0011	0.0019

158.1.2 Increase the temperature and evaporate to $HClO_4$ fumes. Cool, add 50 mL of water and 70 mL of H_2SO_4 (1 + 1). Heat to boiling and cool in a water bath.

158.1.3 Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 158.3.

158.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 300-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 158.1.2, 158.1.3, and 158.3.

158.3 *Color Development*—Using a pipet, transfer 100 mL to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of $SnCl_2$ solution, and 25 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell.

158.4 *Reference Solution*—Butyl acetate.

158.5 *Spectrophotometry:*

158.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at approximately 475 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

158.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 475 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank.

158.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

159. Preparation of Calibration Curve for Compositions from 0.05 % to 0.50 %

159.1 *Calibration Solutions:*

159.1.1 Transfer 0.3 g of iron to each of four 300-mL Erlenmeyer flasks. Using pipets, transfer (2, 5, 10, and 15) mL of molybdenum Solution B (1 mL = 0.1 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

159.1.2 Increase the temperature and evaporate to $HClO_4$ fumes. Cool, add 50 mL of water and 70 mL of H_2SO_4 (1 + 1). Heat to boiling and cool in a water bath.

159.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed in accordance with 159.3.

159.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 300-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed in accordance with 159.1.2, 159.1.3, and 159.3.

159.3 *Color Development*—Using a pipet, transfer 50 mL to a 250-mL 14paratory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of $SnCl_2$ solution, and 50 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell.

159.4 *Reference Solution*—Butyl acetate.

159.5 *Spectrophotometry:*

159.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at approximately 475 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

159.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 475 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank.

159.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

160. Preparation of Calibration Curve for Compositions from 0.40 % to 1.50 %

160.1 *Calibration Solutions:*

160.1.1 Transfer 0.3 g of iron to each of five 300-mL Erlenmeyer flasks. Using pipets, transfer (5, 10, 15, 20, and 25) mL of molybdenum Solution A (1 mL = 0.2 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

160.1.2 Increase the temperature and evaporate to $HClO_4$ fumes. Cool, and add 50 mL of water and 70 mL of H_2SO_4 (1 + 1). Heat to boiling and cool in a water bath.

160.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed in accordance with 160.3.

160.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 300-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed in accordance with 160.1.2, 160.1.3, and 160.3.

160.3 *Color Development*—Using a pipet, transfer 25 mL of iron Solution B and 25 mL of the calibration solution to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of $SnCl_2$ solution, and 100 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell.

160.4 *Reference Solution*—Butyl acetate.

160.5 *Spectrophotometry:*

160.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at approximately 475 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

160.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 475 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank.

160.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

161. Procedure

161.1 *Test Solution:*

161.1.1 Transfer a 0.3-g sample, weighed to the nearest 1 mg, to a 300-mL Erlenmeyer flask. Add 30 mL of dissolving solution, and heat until dissolution is complete.

161.1.2 Increase the temperature and heat to $HClO_4$ fumes. Continue fuming until chromium, if present, is oxidized and the white $HClO_4$ fumes are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl, allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been volatilized. Continue fuming the solution until the volume has been reduced to about 15 mL. Cool, add 50 mL of water and 70 mL of H_2SO_4 (1 + 1), heat to boiling, and cool in a water bath.

161.1.3 Transfer to a volumetric flask that provides for dilution in accordance with the following aliquot guide, dilute to volume, and mix.

Molybdenum, %	Dilution, mL	Aliquot Volume, mL
0.01 to 0.05	200	100
0.05 to 0.55	500	50
0.40 to 1.50	500	25

Proceed in accordance with 161.3.

161.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 300-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed in accordance with 161.1.2, 161.1.3, and 161.3, using the same dilution and aliquots used for the test solution.

161.3 *Color Development*—Using a pipet, transfer the appropriate aliquot to a 250-mL separatory funnel containing the appropriate amount of iron solution for the specified aliquot. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of $SnCl_2$ solution, and, measured with a pipet, the amount of butyl acetate specified in the aliquot guide. Stopper the separatory funnel and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, and drain off and discard the aqueous phase. Drain enough of the solvent layer through a funnel containing a dry filter paper to fill an absorption cell.

161.4 *Reference Solution*—Butyl acetate.

161.5 *Spectrophotometry*—Take the spectrophotometric reading of the test solution and of the reagent blank solution in accordance with 160.5.

162. Calculation

162.1 Convert the net spectrophotometric reading of the test solution to milligrams of molybdenum in the final solution by means of the appropriate calibration curve. Calculate the percent of molybdenum as follows:

$$\text{Molybdenum, \%} = A/(B \times 10) \quad (17)$$

where:

A = molybdenum found in (25, 50, or 100) mL, as appropriate, of butyl acetate, mg, and

B = sample represented in (25, 50, or 100) mL, as appropriate, of butyl acetate, g, (see aliquot guide 161.1.3).

Iron Solution B, mL	Butyl Acetate, mL	Weight of Sample in Final Butyl Acetate Solution, g
None	25	0.15
None	50	0.03
25	100	0.015

163. Precision[7]

163.1 Eleven laboratories cooperated in testing this test method and obtained the data summarized in Table 13.

MANGANESE BY THE PEROXYDISULFATE-ARSENITE TITRIMETRIC METHOD

164. Scope

164.1 This test method covers the determination of manganese in compositions from 0.10 % to 2.50 %.

165. Summary of Test Methods

165.1 Manganese ions in a sulfuric-phosphoric-nitric acid medium, or in this medium with perchloric acid present, are

TABLE 13 Statistical Information—Molybdenum—Thiocyanate Spectrophotometric Method

Test Material	Molybdenum Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Plain carbon steel (NIST 14e, 0.013 Mo)	0.012	0.001	0.005
2. Low alloy steel, 1 Cr-0.30c	0.050	0.001	0.003
3. Low-alloy steel 1.75 Ni	0.163	0.012	0.03
4. Low-alloy steel (NIST 364, 0.49 Mo)	0.51	0.02	0.06
5. Low-alloy steel (NIST 36b, 0.996 Mo)	1.03	0.04	0.07
6. Low-alloy steel, 1.3c-1.8 Si-1.5 Ni	1.50	0.05	0.08

oxidized to permanganic acid by ammonium peroxydisulfate in the presence of silver ions. The permanganic acid is titrated with standard sodium arsenite solution.

166. Interferences

166.1 Elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1. Chromium obscures the end point when more than 5 mg is present. If the sample contains between 5 mg and 15 mg of chromium, the color is compensated for by the addition of potassium dichromate solution to the solution used for standardization. When the sample contains more than 15 mg of chromium, it is necessary to remove it by volatilization as chromyl chloride or by precipitation with zinc oxide.

167. Apparatus

167.1 *Platinum Cones.*

168. Reagents

168.1 *Ammonium Peroxydisulfate Solution* (250 g/L)—Dissolve 25 g of ammonium peroxydisulfite [$(NH_4)_2S_2O_8$] in water and dilute to 100 mL. Do not use a solution that has stood more than 1 day.

168.2 *Iron, Low in Manganese*—Use iron with maximum manganese concentration not greater than 0.002 %.

168.3 *Manganese, Standard Solution A* (1 mL = 0.0008 g Mn)—Transfer an amount of high-purity manganese of known assay, equivalent to 1.6000 g of manganese, weighed to the nearest 0.1 mg, to a 250-mL beaker. Add 20 mL of HNO_3 (1 + 1) and heat gently to dissolve the metal and expel oxides of nitrogen. Cool, transfer to a 2-L volumetric flask, dilute to volume, and mix.

168.4 *Manganese, Standard Solution B* (1 mL = 0.0004 g Mn)—Using a pipet, transfer 50 mL of manganese Solution A (1 mL = 0.0008 g Mn) to a 100-mL volumetric flask, dilute to volume, and mix.

168.5 *Mixed Acids*—Slowly add 100 mL of H_2SO_4 to 525 mL of water while stirring. Cool, add 125 mL of H_3PO_4 and 250 mL of HNO_3, and mix.

168.6 *Potassium Dichromate Solution* (1 mL = 0.001 g Cr)—Dissolve 2.830 g of potassium dichromate ($K_2Cr_2O_7$) in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

168.7 *Silver Nitrate Solution* (8 g/L)—Dissolve 8 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

168.8 *Sodium Arsenite Solution A* (20 g/L)—Dissolve 20 g of sodium arsenite ($NaAsO_2$) in water, and dilute to 1 L.

168.9 *Sodium Arsenite Standard Solution B* (1 mL = 0.0005 g Mn)—Dilute 100 mL of sodium arsenite Solution A (20 g/L) to 1 L, and filter if not clear. Saturate the solution with carbon dioxide. Standardize in accordance with 169.1.3 – 169.1.6.

168.10 *Zinc Oxide Suspension* (165 g/L)—Add 10 g of finely divided zinc oxide (ZnO) to 60 mL of water, and shake thoroughly. Prepare fresh daily as needed.

169. Procedure

169.1 *For Samples Containing Less Than 5 mg of Chromium:*

169.1.1 Select a sample in accordance with the following, weigh it to the nearest 0.5 mg, and transfer to a 500-mL Erlenmeyer flask (Note 43).

Manganese, %	Sample Weight, g
0.1 to 2.0	1.00
1.9 to 2.5	0.60

NOTE 43—If more than 0.020 g of manganese is present, some manganese may precipitate as manganese dioxide during oxidation with ammonium peroxydisulfate, causing low results.

169.1.2 Add 30 mL of mixed acids. Heat until dissolution is complete, adding a few drops of HF if necessary, and boil to expel oxides of nitrogen. Dilute to 250 mL and proceed in accordance with 169.1.4 and 169.1.5.

169.1.3 For standardization, transfer to a 500-mL Erlenmeyer flask approximately the same weight of iron, within 50 mg, as the weight of iron in the sample solution. Add 30 mL of mixed acids. Heat until dissolution is complete, and boil to expel oxides of nitrogen. Using a pipet, transfer a portion of either (or both) manganese Solution A (1 mL = 0.0008 g Mn) or B (1 mL = 0.0004 g Mn) to the iron solution; use the nominal amount that will cause the volume of titrant for standardization and for the sample solution to agree within 2 mL. Dilute to 250 mL and proceed in accordance with 169.1.4 – 169.1.6.

169.1.4 Add 10 mL of $AgNO_3$ solution and 15 mL of $(NH_4)_2S_2O_8$ solution to the sample solution and the standardization solution. Heat the solutions to boiling, and boil briskly for 60 s to 90 s. Cool to 5 °C to 10 °C in an ice bath.

169.1.5 Using a 50-mL buret, titrate each solution rapidly with the sodium arsenite solution (1 mL = 0.0005 g Mn) to a clear, yellow end point that does not change with the addition of more arsenite solution. Calculate the manganese concentration of the sample as directed in Section 170 using the manganese equivalent found in 169.1.6.

169.1.6 Calculate the manganese equivalent of the sodium arsenite solution as follows:

$$M\text{anganese equivalent, g/m}L = A/B \quad (18)$$

where:

A = manganese present in the standardization solution, g, and

B = sodium arsenite solution, mL, required to titrate the manganese in the standardization solution.

169.2 *For Samples Containing 5 to 15 mg of Chromium:*

169.2.1 Proceed in accordance with 169.1.1.

169.2.2 Add 30 mL of mixed acids. Heat until dissolution is complete, adding a few drops of HF if necessary, and boil to expel oxides of nitrogen. Dilute to 250 mL and proceed in accordance with 169.1.4 and 169.1.5.

169.2.3 For standardization, transfer approximately the same weight of iron, within 50 mg, as the weight of iron in the sample solution to a 500-mL Erlenmeyer flask. Add 30 mL of mixed acids. Heat until dissolution is complete, and boil to expel oxides of nitrogen. Using a pipet, transfer a portion of either (or both) manganese Solution A (1 mL = 0.0008 g Mn)

or B (1 mL = 0.0004 g Mn) to the iron solution; use the nominal amount that will cause the volume of titrant for standardization and for the sample solution to agree within 2 mL. Add an amount of potassium dichromate solution (1 mL = 0.001 g Cr) that will provide a chromium content within 20 % of that of the sample solution. Dilute to 250 mL and proceed in accordance with 169.1.4 – 169.1.6.

169.3 *For Samples Containing More Than 15 mg of Chromium*—Proceed in accordance with 169.3.1 if chromium is to be volatilized as chromyl chloride, or as directed in 169.3.2 if it is to be removed by precipitation with zinc oxide.

169.3.1 *Removal of Chromium by Volatilization as Chromyl Chloride:*

NOTE 44—The volatilization of chromium as chromyl chloride may be used for all compositions covered by this test method.

169.3.1.1 Proceed in accordance with 169.1.1.

169.3.1.2 Add 15 mL of HCl and 5 mL of HNO_3. Heat until the sample has been decomposed, adding a few drops of HF if necessary. Add 20 mL of $HClO_4$, heat to fumes, and continue fuming until the chromium is oxidized and the white $HClO_4$ vapors are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl, allowing it to drain down the side of the flask. Make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming until salts begin to separate. Cool, cautiously add 30 mL of the mixed acids, dilute to 250 mL with hot water, and boil for 2 min. Proceed in accordance with 169.1.4 and 169.1.5.

169.3.1.3 For standardization, transfer approximately the same weight of iron, within 50 mg, as the weight of iron in the sample to a 500-mL Erlenmeyer flask. Add 15 mL of HCl and 5 mL of HNO_3. Heat until the sample is decomposed. Using pipet, transfer a portion of either (or both) manganese Solution A (1 mL = 0.0008 g Mn) or B (1 mL = 0.0004 g Mn) to the iron solution; use of the nominal amount that will cause the volume of titrant for standardization and for the sample solution to agree within 2 mL. Add 10 mL of $HClO_4$, heat to fumes, and continue fuming until salts begin to separate. Cool, cautiously add 30 mL of mixed acids, dilute to 250 mL with hot water, and boil for 2 min. Proceed in accordance with 169.1.4 – 169.1.6.

169.3.2 *Removal of Chromium by Precipitation With Zinc Oxide:*

NOTE 45—The zinc oxide procedure is used to separate chromium, iron, titanium, zirconium, tungsten, most of the molybdenum, and other elements from manganese. Cobalt, nickel, and part of the copper accompany manganese in the filtrate. This separation may be used for all compositions covered by this test method.

169.3.2.1 Proceed in accordance with 169.1.1.

169.3.2.2 To decompose the sample, add 25 mL of H_2SO_4 (1 + 5) and, when the reaction ceases, 5 mL HNO_3; or, alternatively, decompose in 60 mL of HNO_3 (1 + 1). Heat gently until the sample and carbides have been decomposed (Note 46), boil to expel oxides of nitrogen, cool, and dilute to 100 mL.

NOTE 46—If the sample is not decomposed by HNO_3 or H_2SO_4, dissolve it in 15 mL of HCl plus 10 mL of HNO_3, adding a few drops of HF if necessary. Heat to decompose, then add 10 mL of $HClO_4$, and heat until chromium has been oxidized and carbides decomposed. Cool, dilute to 100 mL, add enough H_2O_2 to reduce chromium, boil to remove excess peroxide, cool, and proceed as directed in 169.3.2.3.

169.3.2.3 Nearly neutralize the solution with NH_4OH, but do not precipitate hydroxides. 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 47). Allow the precipitate to settle. With the aid of suction, filter the solution through a coarse 15-cm paper supported on a cone. Transfer the filtrate from the suction flask to a 600-mL beaker. Wash the precipitate thoroughly with cold water. Add 30 mL of the mixed acids to the filtrate and reserve the filtrate.

NOTE 47—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.

169.3.2.4 Transfer the filter paper containing the ZnO precipitate to the 500-mL Erlenmeyer flask, and add 25 mL of H_2SO_4 (1 + 5). Macerate the paper and dilute the solution to about 100 mL. Repeat the ZnO separation, proceeding in accordance with 169.3.2.3, and transfer the filtrate from the suction flask to the filtrate reserved in 169.3.2.3. Boil, dilute to 250 mL, and proceed in accordance with 169.1.4 and 169.1.5.

169.3.2.5 For standardization, using a pipet transfer a portion of either (or both) manganese Solution A (1 mL = 0.0008 g Mn) or B (1 mL = 0.0004 g Mn) to 30 mL of mixed acids; use the nominal amount that will cause the volume of titrant for standardization and for the sample solution to agree within 2 mL. Boil to expel oxides of nitrogen, and dilute to 250 mL with water. Proceed in accordance with 169.1.4 – 169.1.6.

170. Calculation

170.1 Calculate the percent of manganese as follows:

$$\text{Manganese, \%} = [(A \times B)/C] \times 100 \quad (19)$$

where:

A = sodium arsenite solution required to titrate the manganese in the sample, mL,
B = manganese equivalent of the sodium arsenite solution as determined in the appropriate standardization solution, and
C = sample used, g.

171. Precision and Bias[7]

171.1 *Precision*—Five laboratories cooperated in this test method and the data for the four test specimens covered by this test method are presented in Table 14.

171.2 *Bias*—Based on the data available from the interlaboratory test of this test method, there is no indication of bias.

PHOSPHORUS BY THE ALKALIMETRIC METHOD

172. Scope

172.1 This test method covers the determination of phosphorus in compositions from 0.02 % to 0.25 %.

TABLE 14 Statistical Information—Manganese

Test Material	Manganese Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
BCS 255/1(0.16)	0.162	0.009	0.012
NIST 72F(0.595)	0.543	0.016	0.017
NIST 13f(0.889)	0.890	0.016	0.016
NIST 100b(1.89)	1.89	0.018	0.049

173. Summary of Test Methods

173.1 Phosphorus is separated as ammonium phosphomolybdate. The precipitate is dissolved in standard NaOH solution, and the excess NaOH is titrated with standard HNO_3.

174. Interferences

174.1 To avoid retardation of the formation of the precipitate and its contamination by vanadium, the latter is reduced to the quadrivalent state and the precipitation is performed at 10 °C to 20 °C.

174.2 To eliminate interference of silicon, HF is added during dissolution of samples containing silicon in compositions greater than 0.5 %.

174.3 The interference of arsenic, which is insignificant at levels as high as 0.1 %, may be avoided by precipitating the phosphorus at 10 °C to 20 °C and increasing the time allotted for the precipitate to form.

175. Apparatus

175.1 *Funnel, Hirsch Porcelain,* 56-mm plate diameter and 94-mm top diameter. Place a 5.5-cm fine qualitative, smooth-surface filter paper over the perforated filter plate. Place an 11-cm fine qualitative, rough-surface filter paper on the funnel, moisten it with KNO_3 solution, and then press it gently into the funnel so that its center lies flat against the first paper. Fold the edge of the paper in a fluted manner and press it against the sides of the funnel. Add enough filter paper pulp to cover the flat center of the filter paper.

175.2 *Funnel, Glass, 60°,* fitted with a 25-mm diameter perforated porcelain filtering disk. Place a 5.5-cm fine paper, over the perforated plate. Place an 11-cm fine paper, on the funnel, moisten it with KNO_3 solution, and then press it gently into the funnel so that its center lies flat against the first paper. Fold the edge of the paper in a fluted manner and press it against the sides of the funnel. Add enough filter paper pulp to cover the flat center of the filter paper.

176. Reagents

176.1 *Ammonium Molybdate Solution (Acidic):*

176.1.1 *Solution No. 1*—Transfer 100 g of molybdic acid (85 % MoO_3) to a 600-mL beaker containing 240 mL of water and mix thoroughly. Add 140 mL of NH_4OH while stirring vigorously. When dissolution is complete, filter through a medium paper, add 60 mL of HNO_3, and cool.

176.1.2 *Solution No. 2*—Add 400 mL of HNO_3 to 960 mL of water in a 2-L beaker and cool.

176.1.3 Add Solution No. 1 to Solution No. 2 while stirring constantly. Add 0.1 g of ammonium phosphate, dibasic ($(NH_4)_2HPO_4$), and let stand at least 24 h before using. Use only the clear supernatant liquid. Filter just prior to use.

176.2 *Ferrous Sulfate Solution* (100 g/L)—Dissolve 100 g of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in 1 L of H_2SO_4 (5 + 95).

176.3 *Nitric Acid, Standard* (1 mL = approximately 0.00013 g P)—Transfer 6.3 mL of HNO_3 to a 1-L volumetric flask containing 500 mL of water. Dilute to volume and mix. Standardize the solution as follows: Using a pipet, transfer 20 mL of NaOH standard solution (1 mL = approximately 0.00013 g P), described in 176.7, to a 125-mL Erlenmeyer flask. Add 3 drops of phenolphthalein indicator solution and titrate with the HNO_3 until 1 drop causes the pink color to disappear. Calculate the phosphorus equivalent as follows:

$$\text{Phosphorus equivalent, g P/mL} = A \times B/C \quad (20)$$

where:

A = NaOH solution, mL,
B = phosphorus equivalent of the NaOH solution, and
C = HNO_3 solution, mL.

176.4 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %).

176.5 *Potassium Nitrate Solution* (10 g/L)—Dissolve 10 g of potassium nitrate (KNO_3) in water, dilute to 1 L, and mix.

176.6 *Potassium Permanganate Solution* (25 g/L)—Dissolve 25 g of potassium permanganate ($KMnO_4$) in water, dilute to 1 L, and mix.

176.7 *Sodium Hydroxide, Standard Solution* (1 mL = approximately 0.00013 g P)—Transfer 4.0 g of sodium hydroxide (NaOH) to a 1-L volumetric flask, and dissolve in freshly boiled water that has been cooled to room temperature. Dilute to volume with the boiled water and mix. Standardize the solution as follows: Transfer to a 300-mL Erlenmeyer flask 0.5000 g of the National Institute of Standards and Technology standard sample of potassium acid phthalate ($KHC_8H_4O_4$) previously dried for 2 h at 105 °C. Add 100 mL of freshly boiled water that has been cooled to room temperature and 3 drops of phenolphthalein indicator solution. Swirl to dissolve the salt. Titrate with the NaOH solution until 1 drop produces a pink color. Calculate the phosphorus equivalent as follows:

$$\text{Phosphorus equivalent, g } P/\text{mL} = A \times 0.001347/B \times 0.2042 \quad (21)$$

where:

A = potassium acid phthalate, g, and
B = NaOH solution, mL.

177. Procedure

177.1 Select and weigh a sample to the nearest 5 mg in accordance with the following:

Phosphorus, %	Sample Weight, g
0.01 to 0.10	2.0
0.10 to 0.25	1.0

Transfer the sample to a 300-mL Erlenmeyer flask.

177.2 Carry a reagent blank through the entire procedure using the same amounts of all reagents, with the sample omitted.

177.3 Add 100 mL of HNO_3 (1 + 3), and if the silicon composition is greater than 0.5 % add 3 to 5 drops of HF. Heat to hasten dissolution. When the sample is decomposed, add $KMnO_4$ solution dropwise, while heating the solution, until a permanent, brown precipitate forms. Boil the solution 3 min.

177.4 Add H_2SO_3 dropwise until the precipitate dissolves, and boil 3 min to expel oxides of nitrogen. Adjust the volume to 100 mL, remove from the hot plate, and allow the solution to cool slightly. Filter, if necessary, through an 11-cm coarse paper into a 300-mL Erlenmeyer flask, and wash the flask and the paper several times with hot water. Discard the precipitate. Evaporate the solution to 100 mL, and cool to room temperature. While swirling the flask, slowly add 20 mL of NH_4OH for a 1.0-g sample, or 17 mL of NH_4OH for a 2.0-g sample, so that no precipitate forms (Note 48). Adjust the temperature to 45 °C.

NOTE 48—The quantities of NH_4OH specified should result in a pH of 0.1 to 0.6 after the addition of the NH_4OH and a pH of 0.2 after the addition of ammonium molybdate solution to the flask. Care must be exercised in the dissolution step to prevent excessive loss of acid. An excessive amount of NH_4OH will precipitate iron as ferric hydroxide. Failure to carefully control the acidity will retard the precipitation of the ammonium phosphomolybdate.

177.5 Add 40 mL of ammonium molybdate solution, stopper the flask, and shake 10 min on a mechanical shaker. If the vanadium concentration is less than 0.1 %, allow the precipitate to settle at least 20 min at room temperature; for samples containing higher concentrations of vanadium, cool the solution to 10 °C to 20 °C, add 5 mL of ferrous sulfate solution and 2 drops to 3 drops of H_2SO_3, and allow the precipitate to settle at least 20 min at 10 °C to 20 °C.

177.6 Filter the solution with the aid of suction using a Hirsch porcelain crucible (175.1) or a glass funnel fitted with a perforated porcelain filtering disk (175.2). Rinse the flask 3 to 5 times with a total volume of approximately 40 mL of KNO_3 solution, transferring all the precipitate to the filter. Wash the filter paper 12 to 15 times with a total volume of approximately 100 mL of KNO_3 solution (Note 49). Discard the filtrate.

NOTE 49—Analysts not having experience with this test method should familiarize themselves with the proper washing technique. Blanks obtained by this test method as written should not be measurable provided the reagents are of the quality specified in Practices E50.

177.7 Return the precipitate and the filter papers to the flask, and add 50 mL to 75 mL of freshly boiled water that has been cooled to room temperature. Shake the flask to break up the filter paper. Using a 25-mL buret, add enough NaOH standard solution to dissolve the precipitate. Stopper the flask and let stand, shaking or swirling the flask occasionally, until a change in color from yellow to white or almost white is noted; then add 2 mL in excess. Add 3 drops of phenolphthalein indicator solution, and shake. Record the buret reading.

177.8 Remove and rinse the stopper. Dilute the solution to 150 mL with freshly boiled water that has been cooled to room temperature, and add 3 drops of phenolphthalein indicator solution. Using a 25-mL buret, titrate the excess NaOH with the standard HNO_3 until 1 drop causes the disappearance of the pink color. Record the buret reading.

178. Calculation

178.1 Calculate the percent of phosphorus as follows:

$$\text{Phosphorus, \%} = (AB - CD) - (EB - FD)/G \times 100 \qquad (22)$$

where:

A = NaOH solution used for the sample, mL, (177.7),
B = phosphorus equivalent of the NaOH solution,
C = HNO_3 solution required by the sample, mL (177.8),
D = phosphorus equivalent of the HNO_3 solution,
E = NaOH solution used for the blank,
F = HNO_3 solution required by the blank, and
G = sample used, g.

179. Precision[11]

179.1 Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 15. Although samples at the lower end of the scope were not tested, the precision data obtained for other types of alloys using the test methods indicated in Table 15 should apply.

NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD

180. Scope

180.1 This test method covers the determination of nickel in compositions from 0.1 % to 5.00 %.

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1063.

TABLE 15 Statistical Information—Phosphorus—Alkalimetric Method

Test Material	Phosphorus Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E353	0.017	0.001	0.006
2. No. 2, E353	0.017	0.004	0.007
3. No. 3, E353	0.024	0.003	0.011
4. No. 4, E353	0.024	0.003	0.009
5. Carbon steel (NIST 19g, 0.046 P)	0.045	0.003	0.009
6. Wrought iron	0.274	0.017	0.017

181. Summary of Test Method

181.1 Nickel dimethylglyoximate is precipitated by adding an alcoholic solution of dimethylglyoxime to a solution of the sample containing ammonium citrate. A second precipitation is performed to purify the precipitate prior to drying and weighing.

182. Interferences

182.1 Cobalt, copper, and manganese are present in the divalent state and consume dimethylglyoxime, making it necessary to add an excess of the precipitant over that required to precipitate nickel.

183. Apparatus

183.1 *Filtering Crucibles,* fritted-glass, 30-mL, medium porosity.

183.2 *pH Meter.*

184. Reagents

184.1 *Ammonium Citrate Solution* (200 g/L)—Dissolve 200 g of diammonium hydrogen citrate [$(NH_4)_2HC_6H_5O_7$] in 600 mL of water. Filter and dilute to 1 L.

184.2 *Dimethylglyoxime Solution in Alcohol* (10 g/L)—Dissolve 10 g of dimethylglyoxime in ethanol, methanol, or No. 30 specially denatured alcohol and dilute to 1 L with alcohol. Filter before using. This solution keeps almost indefinitely.

185. Procedure

185.1 Select and weigh a sample in accordance with the following.

Nickel, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.1 to 1.0	3.00	1.0
1.0 to 5.0	1.00	0.5

185.2 Transfer the sample to a 600-mL beaker. Add 60 mL of HCl (1 + 1) and 10 mL of HNO_3. Heat to dissolve the sample and to expel oxides of nitrogen. Cool the solution and add 30 mL of $HClO_4$. Heat to strong fumes of $HClO_4$ and continue fuming for 5 min.

185.3 Cool, dilute to 100 mL, and filter through an 11-cm coarse paper into a 600-mL beaker. Transfer any insoluble matter to the paper with hot HCl (5 + 95). Wash the beaker and paper alternately with hot HCl (5 + 95) and hot water until iron salts are removed. Finally wash the paper 3 times with 5-mL portions of hot water. Discard the residue.

185.4 Add 100 mL of water and 20 mL of ammonium citrate solution to the filtrate. Using a pH meter, adjust the pH to at least 7.5 with NH_4OH. Acidify the solution with HCl to pH 6.3 ± 0.1.

185.5 Add 10 mL of dimethylglyoxime solution plus an additional 0.4 mL for each milligram of cobalt, copper, manganese, and nickel present.

185.6 Using a pH meter, adjust the pH to 7.4 ± 0.1. Remove and rinse electrodes with water. Heat at 50 °C to 70 °C for 30 min. Let stand for at least 4 h at 20 °C to 25 °C.

185.7 Filter using a 12.5-cm coarse paper. Wash 5 to 7 times with cold water. Transfer the paper and precipitate to the original beaker. Remove any precipitate adhering to the funnel with a small piece of moistened filter paper and place it in the original beaker.

185.8 Add 30 mL of HNO_3 and 15 mL of $HClO_4$, evaporate to strong fumes of $HClO_4$, and continue fuming for 5 min.

185.9 Cool, add 50 mL of water, and filter through an 11-cm coarse paper if necessary. Wash the paper 5 times with HCl (5 + 95) and 3 times with water. Discard the residue.

185.10 Add 10 mL of ammonium citrate solution and 10 mL of HCl. Using a pH meter, adjust the pH to at least 7.5 with NH_4OH. Withdraw the electrodes and rinse them with water, collecting the rinsings in the beaker.

185.11 Add 2 mL of HCl and dilute to 200 mL with water. While stirring, add 10 mL of dimethylglyoxime solution plus an additional 0.4 mL for each milligram of nickel present.

185.12 Using a pH meter, adjust the pH to 7.4 ± 0.1 with NH_4OH. Remove and rinse the electrodes with water. Heat at 50 °C to 70 °C for 30 min, and allow to stand for at least 4 h at 20 °C to 25 °C.

185.13 With the aid of suction, filter using a weighed (Note 50) fritted glass crucible. Wash the beaker and precipitate 6 times with cold water.

NOTE 50—Heat the crucible at 150 °C, and cool in a desiccator before weighing.

185.14 Dry at 150 °C at least 3 h to constant weight. Cool in a desiccator, and weigh.

186. Calculation

186.1 Calculate the percent of nickel as follows:

$$\text{Nickel, \%} = (A - B) \times 0.2032/C \times 100 \quad (23)$$

where:

A = weight of crucible and precipitate, g,
B = weight of crucible, g and
C = sample taken, g.

187. Precision

187.1 Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 16. Although a sample covered by this test method near the lower

TABLE 16 Statistical Information—Nickel—Dimethylglyoxime Gravimetric Method

Test Material	Nickel Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E351	0.115	0.006	0.006
2. Carbon steel (NIST 20f, 0.243 Ni)	0.233	0.017	0.018
3. Low-alloy steel (NIST 32e, 1.19 Ni)	1.18	0.03	0.04
4. Ni-Mo Steel 4 Ni-0.3 Mo (NIST 33d, 3.58 % Ni)	3.57	0.11	0.07

end of the scope was not tested, the data obtained for other types of alloys using the methods indicated in Table 16 should apply.

NICKEL BY THE ION EXCHANGE-ATOMIC ABSORPTION SPECTROMETRY METHOD

188. Scope

188.1 This test method covers the determination of nickel in compositions from 0.005 % to 1.00 %.

189. Summary of Test Method

189.1 Nickel is separated from interfering elements by elution from an anion exchange column using a hydrochloric acid solution. The eluate is aspirated into the air-acetylene flame. Spectral energy at 232.0 nm from a nickel hollow-cathode tube is passed through the flame and the absorbance is measured. The spectrometer is calibrated with solutions of known concentrations of nickel.

190. Concentration Range

190.1 The recommended concentration range is from 0.001 mg to 0.010 mg of nickel per millilitre of solution.

191. Interferences

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

192. Apparatus

192.1 *Atomic Absorption Spectrometer,* capable of resolving the 232.0 nm line, equipped with a nickel hollow-cathode tube whose radiation is modulated with a detector system tuned to the same frequency and with a premix air-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (0.015 mg/mL) produces an absorbance of 0.350 or higher, and a calibration curve whose deviation from linearity is within the limits in accordance with 194.3.

192.2 *Anion-Exchange Column,* approximately 25 mm in diameter and 300 mm long, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. The Jones Reductor, Fig. 5 may be adapted to this test method. A reservoir for the eluants may be added at the top of the column. However, the eluants must be added to the column in accordance with 195.1.3.

193. Reagents

193.1 *Anion Exchange Resin:*

193.1.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and 200 to 400 nominal mesh size.[12] To remove those beads greater than about 180-µm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow at least 30 min for the beads to undergo maximum swelling. Place a No. 80 (180-µm) screen, 150 mm in diameter, over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen using a small stream of water. Discard the beads retained on the screen periodically to avoid undue clogging of the openings. When the bulk of the resin has settled in the 2-L beaker, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19) and stir vigorously, allow the resin to settle for 4 min to 6 min, decant 150 mL to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

193.1.2 Prepare the column as follows: Place a 10 mm to 20-mm layer of glass wool or poly (vinyl chloride) plastic fiber in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 140 mm. Place a 20-mm layer of glass wool or poly (vinyl chloride) plastic fiber at top of resin bed to protect it from being carried into suspension when the solutions are added. Add 100 mL to 125 mL of HCl (3 + 1) to the column and, when the solution level is 10 to 20 mm above the top of the resin bed, close the lower stopcock.

193.2 *Nickel, Standard Solution* (1 mL = 0.1 mg Ni)—Transfer 1 g of nickel (purity: 99 % minimum) to a 400-mL beaker. Add 50 mL of HNO_3 (1 + 1), cover and heat gently until dissolution is complete. Remove the cover and evaporate to dryness slowly to prevent loss by spattering. Cool, rinse sides of beaker with water, add 10 mL HCl, and evaporate to dryness. Perform the rinse and evaporation procedure twice. Cool, add 50 mL of HCl (1 + 1). Warm gently to dissolve salts and dilute to 300 mL with water. Transfer the solution to a 1-L volumetric flask, dilute to volume with water, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask (Note 51). Dilute to volume with water, and mix.

NOTE 51—Prepare the dilute nickel standard solution immediately before preparation of the calibration solution described in 194.1 to maintain proper concentration.

194. Preparation of Calibration Curve

194.1 *Calibration Solutions*—Using pipets, transfer (0, 1, 3, 5, 7, 10, and 15) mL of nickel solution (1 mL = 0.1 mg Ni) to 100-mL volumetric flasks. Add 20 mL of HCl (1 + 1), dilute to volume with water, and mix. Do not use solutions that have stood more than 2 h.

194.2 *Spectrometry:*

194.2.1 With the nickel hollow-cathode tube in position, energized and stabilized, locate the wavelength setting in the vicinity of 232.0 nm that gives the maximum response of the detector system.

194.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the nickel solution with the highest concentration from the series prepared in accordance with 194.1 and adjust the height of the burner, the air and fuel pressures and their flow rates, the aspiration rate of the solution, and the position of the capillary to obtain maximum response.

NOTE 52—Recalibration is required whenever these parameters are changed.

[12] Produced by the Dow Chemical Co., Midland, MI.

194.2.3 Aspirate the nickel solution used in 194.2.2 a sufficient number of times to establish that the absorbance reading is not drifting. Record six readings and calculate the standard deviation, *s*, of the reading as follows:

$$s = (A - B) \times 0.40 \quad (24)$$

where:

A = highest of the six values found, and
B = lowest of the six values found.[9]

194.2.4 Beginning with the solution to which no nickel was added in 194.1, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values recorded in 194.2.3 by more than twice the standard deviation, *s*, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposit in the burner or clogged capillary), correct it, and repeat in accordance with 194.2.1 – 194.2.4.

194.2.5 Proceed immediately in accordance with 194.3.

194.3 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.Calculate the deviation from linearity of the curve as follows:

$$D\text{eviations from linearity} = (C - D)/E \quad (25)$$

where:

C = absorbance value for 0.015 mg Ni/mL,
D = absorbance value for 0.010 mg Ni/mL, and
E = absorbance value for 0.005 mg Ni/mL.

If the calculated value is less than 0.60, correct the indicated malfunction or maladjustment of instrument or hollow-cathode tube and repeat the calibration.

195. Procedure

195.1 *Test Solution:*

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

Nickel, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution After Separation, mL	Aliquot Required, mL	HCl (1 + 1) in Final Dilution, mL	Final Dilution, mL
0.005 to 0.025	1.0	0.1	25	0	5	25
0.020 to 0.10	1.0	0.1	100	0	20	100
0.10 to 0.50	1.0	0.1	100	20	15	100
0.40 to 1.00	1.0	0.1	100	10	20	100

Transfer the sample to a 400-mL beaker.

195.1.2 Add 25 mL HNO_3 (1 + 4). Cover the beaker and warm gently to dissolve. Rinse the sides of the beaker with water. Add 10 drops of HF, 5 mL of HCl, and 15 mL of $HClO_4$. Evaporate to dryness, carefully and with moderate heat to avoid spattering. Cool, rinse sides of beaker with water, add 10 mL of HCl, and evaporate to dryness carefully and with moderate heat. Cool, add 20 mL of HCl (3 + 1), warm gently to dissolve salts, and cool to room temperature.

NOTE 53—If precipitation remains after recommended procedures, filter the solution through glass wool placed in a funnel of the ion exchange column. Add all the rinsings and the eluant through this funnel to the column.

195.1.3 Place a clean 400-mL beaker under the ion-exchange column. Transfer the solution obtained in 195.1.2 to the column and open the lower stopcock. When the solution reaches a level of 10 mm to 20 mm above the resin bed, rinse the original beaker with 5 mL to 6 mL of HCl (3 + 1) and transfer the rinsings to the column. Repeat this at 2-min intervals until the beaker has been rinsed four times. Wash the upper part of the column with HCl (3 + 1) 2 or 3 times and allow the level to drop to 10 mm to 20 mm above the resin bed each time. Maintain the flow rate at not more than 3 mL/min and add HCl (3 + 1) to the column until a total of 200 mL has been collected. Reserve this solution.

195.1.4 Precondition the column for the next test solution as follows: Open the stopcock. Drain the remaining solution in the column 10 mm to 20 mm above the top of the resin. Add in 50-mL increments, HCl (1 + 9) until the iron has been eluted, and the eluate is visibly free of color (Note 54). When the column is free of iron, drain the solution to 10 mm to 20 mm above the top of the resin and close the stopcock. If the column is not to be used immediately, cover and store. If it is to be used immediately, pass 100 mL of HCl (3 + 1) through the column, and proceed in accordance with 193.1.2.

NOTE 54—Approximately 300 mL of HCl (1 + 9) are required.

195.1.5 To the eluate obtained in 195.1.3, add 30 mL of HNO_3 and evaporate to approximately 100 mL. Add 20 mL of HNO_3 and 15 mL of $HClO_4$. Evaporate to dryness and cool. If the nickel content is greater than 0.10 % (195.1.1), add 20 mL HCl (1 + 1) and warm to dissolve salts. Cool to room temperature, and transfer to a 100-mL volumetric flask. Dilute to volume with water, and mix. If no dilution is necessary, add the amount of HCl (1 + 1) listed in 195.1.1, and warm gently to dissolve salts. Cool to room temperature, and transfer to appropriate volumetric flask (195.1.1). Dilute to volume with water, and mix.

195.2 Prepare a reagent blank by treating the same amounts of all reagents in accordance with 195.1.1 – 195.1.4, but omitting the sample. Use reagents from the same lots for the blank and test solution.

195.3 *Spectrometry*—Aspirate and record the absorbance of the reference, calibration, test, and reagent blank solutions.

NOTE 55—After each group of four or fewer test solutions and reagent blank solutions has been aspirated, apply the test with the standard solution in accordance with 194.2.4 depending on the concentration range. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 194.2.2, or by more than 0.01 multiplied by the average of the six values used to calculate *s*, whichever is greater, determine the cause. Correct the deficiency (deposits in burner, clogged capillary, etc.), repeat the calibration procedure, and recheck the readings of the test solutions and reagent blank solution.

196. Calculation

196.1 Convert the absorbance of the test solution and of the reagent blank to milligrams of nickel per millilitre of the final test solution by means of the calibration curve. Calculate the percent of nickel as follows:

$$N\text{ickel, \%} = (A - B) \times C/W \times 10 \quad (26)$$

where:

A = nickel per millilitre of final test solution, mg,
B = nickel per millilitre of final reagent blank solution, mg,
C = final volume of test solution, and
W = weight of sample in final volume of test solution, g.

197. Precision[13]

197.1 Eleven laboratories cooperated in testing this test method and obtained the data summarized in Table 17. Although a sample covered by this test method near the high end of the slope was not tested, the data obtained for other types of alloys using the methods indicated in Table 17 apply.

TIN BY THE SOLVENT EXTRACTION-ATOMIC ABSORPTION SPECTROMETRY METHOD

198. Scope

198.1 This test method covers the determination of tin in the composition range from 0.002 % to 0.10 %.

199. Summary of Test Method

199.1 Tin is extracted from a dilute hydrochloric acid solution of the sample, containing ascorbic acid and potassium iodide, into a solution of trioctylphosphine oxide (TOPO) in methyl isobutyl ketone (MIBK). The MIBK extract is aspirated into the nitrous oxide-acetylene flame. Spectral energy at 286.3 nm from a tin hollow-cathode lamp or tin electrodeless discharge lamp is passed through the flame and the absorbance is measured.

200. Concentration Range

200.1 The recommended concentration range is from 4 g to 40 g of tin per mL in the final 10 millilitre of TOPO-MIBK extract.

201. Interferences

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

202. Apparatus

202.1 *Atomic Absorption Spectrometer,* capable of resolving the 286.3 nm line, equipped with a tin hollow-cathode lamp or tin electrodeless discharge lamp whose radiant energy is modulated, with a detector system tuned to the same frequency and a pre-mix nitrous oxide-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (40 µg per millilitre) produces an absorbance of 0.15 or higher, and a calibration curve whose deviation from linearity is within the limits in accordance with 204.4.

203. Reagents

203.1 *Ascorbic Acid.*

203.2 *Iodide-Ascorbic Acid Solution*—Dissolve 30 g of potassium iodide and 10 g of ascorbic acid in 60 mL of HCl (1 + 5). Dilute to 100 mL with water and mix. Do not use a solution that has stood more than one day.

203.3 *Methyl Isobutyl Ketone (MIBK).*

203.4 *Tin, Standard Solution A* (1 mL = 1.0 mg Sn)—Dissolve 1.000 g of tin (purity: 99.9 % minimum) in 100 mL of HCl. Cool, transfer to a 1-L volumetric flask, dilute to volume with HCl (1 + 2), and mix.

203.5 *Tin, Standard Solution B* (1 mL = 50.0 µg Sn)—Using a pipet, transfer a 10-mL aliquot of Solution A to a 200-mL volumetric flask. Dilute to volume with HCl (1 + 2) and mix.

203.6 *Trioctylphosphine Oxide (TOPO-MIBK) Solution* (50 g/L)—Transfer 12.5 g of TOPO to a 250-mL volumetric flask. Dilute to volume with MIBK and mix until dissolution is complete.

204. Preparation of Calibration Curve

204.1 *Calibration Solutions*—Using pipets, transfer (0, 1, 2, 4, 6, and 8) mL of Solution B (1 mL = 50 µg Sn) to 100-mL volumetric flasks.

NOTE 56—Volumetric flasks with ground glass stoppers must be used.

204.2 *Extraction:*

204.2.1 Add 15 mL of HCl (1 + 1), 3 g of ascorbic acid, and mix. Add 15 mL of iodide-ascorbic acid solution, adjust the volume to approximately 50 mL, and mix.

204.2.2 Using a pipet, add 10 mL of TOPO-MIBK solution, stopper the flask, invert, and shake vigorously several times for 1 min. Allow the phases to separate. Add water to bring the entire organic layer into the neck of the flask. Stopper, invert several times, and allow the phases to separate.

NOTE 57—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

204.3 *Spectrometry:*

204.3.1 With a tin hollow-cathode lamp or electrodeless discharge lamp in position, energized and stabilized, adjust the wavelength setting to the location that gives the maximum detector response in the immediate vicinity of 286.3 nm.

204.3.2 Following the instrument manufacturer's specific directions, ignite the burner using the air-acetylene mode of

[13] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1067.

TABLE 17 Statistical Information—Nickel—Ion Exchange-Atomic Absorption Spectrometry Method

Test Material	Nickel Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Plain carbon steel (NIST 10g, 0.005 Ni)	0.0058	0.002	0.002
2. Plain carbon steel (NIST 152a; 0.056 Ni)	0.055	0.002	0.007
3. No. 3, E351	0.122	0.009	0.015
4. Low-alloy steel (NIST 106b, 0.217 Ni)	0.217	0.012	0.020
5. No. 5, E351	1.07	0.052	0.069

operation. Immediately after ignition, switch over to the nitrous oxide-acetylene mode of operation and allow the burner to reach thermal equilibrium while aspirating water. Cautiously adjust the height of the red cone of the flame to approximately 12 mm by means of the fuel flow-needle valve. Adjust the detector response to zero while aspirating water. Aspirate Solution B (1 mL = 50 µg Sn) and adjust the height of the burner to obtain maximum response from the detector system. Remove the capillary from the solution and allow air to aspirate for 15 s to 30 s. Aspirate MIBK for 30 s, then readjust the detector response to zero, if necessary.

NOTE 58—From this point on, only MIBK solutions should be aspirated until all test and calibration solution measurements have been completed. If the burner slot shows any sign of blockage, shut off the flame in accordance with the instrument manufacturer's approved procedures, clean the slot, and relight in accordance with 204.3.1.

204.3.3 Aspirate the solution with the highest concentration (40 µg Sn per millilitre) from the series prepared in 204.1 a sufficient number of times to establish that the absorbance is not drifting.

NOTE 59—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 60—Due to the small amount of extract available for making this test, the number of readings and the time between readings must be kept to a minimum.

204.3.4 Beginning with the calibration solution to which no tin was added, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration (40 µg Sn per millilitre) differs from the average values obtained in 204.3.3 by more than 0.03 multiplied by the average of the values, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposit in the burner or clogged capillary), correct it, and repeat the procedure in 204.3.1 – 204.3.4.

204.3.5 Proceed immediately in accordance with 205.3.

204.4 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (A - B)/C \quad (27)$$

where:

A = absorbance value for 40 µg Sn/mL,
B = absorbance value for 30 µg Sn/mL, and
C = absorbance value for 10 µg Sn/mL.

If the calculated value is less than 0.60, correct the indicated malfunction or maladjustment of the instrument or lamp and repeat the calibration.

205. Procedure

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

205.2 *Test Solution:*

205.2.1 Select and weigh a sample to the nearest 0.5 mg in accordance with the following:

Tin, %	Sample Weight, g	Dilution, mL	Aliquot, mL	Aliquot Factor
0. 001 to 0.005	3.00	...	...	1
0. 004 to 0.010	2.00	...	...	1
0. 009 to 0.050	1.00	...	...	1
0. 050 to 0.080	1.00	100	50	2
0. 080 to 0.100	1.00	100	20	5

Transfer the sample to a 150-mL poly (tetrafluoroethylene) beaker.

205.2.2 Add 30 mL of HCl (1 + 1) and 5 drops of HF. Cover the beaker with a poly (tetrafluoroethylene) cover and heat at a low temperature (approximately 90 °C) until dissolution is complete.

NOTE 61—For some steels it will be necessary to add H_2O_2 to hasten the dissolution of the sample. For silicon steels, use 10 drops to 12 drops of HF.

205.2.3 Remove the cover with platinum-tipped tongs and cautiously rinse into the beaker with water. Cautiously evaporate the solution at a low temperature (approximately 90 °C) to 15 mL. Rinse the sides of the beaker with water, add 20 mL of HCl (1 + 1), and again evaporate to 15 mL.

205.2.4 Rinse the sides of the beaker with about 5 mL of water and cool. If an aliquot is to be taken (refer to the table in 205.2.1), transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix. Using a pipet, transfer the aliquot to a 150-mL beaker and evaporate at a low temperature to 15 mL. Rinse the sides of the beaker with about 5 mL of water and cool.

205.2.5 Add 3 g of ascorbic acid for a 1-g sample, plus 2 g of ascorbic acid for each additional 1 g of sample. Swirl to dissolve. Add 15 mL of the iodide-ascorbic acid solution.

205.2.6 Transfer the sample to a 100-mL volumetric flask and adjust the volume to approximately 50 mL with water. Using a pipet, transfer 10 mL of TOPO-MIBK solution to the flask, stopper, invert, and shake vigorously several times for 1 min.

205.2.7 Allow the phases to separate. Add water to bring the entire organic layer into the neck of the flask. Stopper, invert several times, and allow the phases to separate.

205.3 *Spectrometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 59) and record the absorbance values. Take three readings on each solution (Note 60). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drift in accordance with 204.3.4 and 204.3.5.

206. Calculation

206.1 Convert the average absorbance of the test and the reagent blank solutions to micrograms of tin per millilitre of the final solution by means of the calibration curve. Calculate the percent of tin as follows:

$$\text{Tin, \%} = [((D - E) \times F)/(G \times 1000)] \quad (28)$$

where:

D = tin per millilitre of the final test solution, µg,
E = tin per millilitre of the final reagent blank solution, µg,
F = aliquot factor (refer to the table in 205.2.1), and
G = sample used, g.

207. Precision

207.1 Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 18.

BORON BY THE DISTILLATION-CURCUMIN SPECTROPHOTOMETRIC METHOD

208. Scope

208.1 This test method covers the determination of boron in compositions from 0.0003 % to 0.006 % using a 2.0-g sample. The scope can be extended to 0.012 % by using a 1.0-g sample and adding 1.0 g of low-boron iron.

209. Summary of Test Method

209.1 Boron is separated by distillation as methyl borate, which is converted to boric acid and reacted with curcumin to form a rose-colored complex. Spectrophotometric measurement is made at approximately 555 nm.

210. Concentration Range

210.1 The recommended concentration ranges are from 0.1 µg to 0.5 µg of boron per 100 mL of solution, using a 5-cm cell; 0.5 µg to 6.0 µg of boron per 100 mL of solution, using a 1-cm cell.

NOTE 62—This test method has been written for cells having a 1-cm and a 5-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

211. Stability of Color

211.1 The color is stable for at least 1 h.

212. Interferences

212.1 Elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1.

213. Apparatus

213.1 *Glassware,* for specimen dissolution and the distillation must be quartz or other "boron-free" glass. Boil the glassware in hydrochloric acid and rinse with water before use. It is recommended that the glassware used for this determination be reserved for this use only.

213.2 *Dissolution Apparatus,* consisting of a 125-mL round-bottom quartz flask fitted with a rubber stopper to a quartz-tube reflux condenser. The air-cooled quartz reflux condenser is a 760-mm long, 3-mm inside diameter, quartz tube.

213.3 *Distillation Apparatus* (Fig. 6), consisting of a 125-mL quartz distillation flask fitted by a two-hole rubber stopper to a water-cooled quartz condensing tube and a quartz methanol addition tube.

213.4 *Water Bath, Controlled Temperature,* capable of maintaining a temperature at 75 ± 2 °C and accommodating 150-mL porcelain evaporating dishes.

213.5 *Platinum Crucible,* 25-mL capacity.

213.6 *Evaporating Dishes,* 125-mL or 150-mL capacity.

213.7 *Spectrophotometer,* equipped with 1-cm and 5-cm cells.

214. Reagents

214.1 *Acetone-Water Solution* (1 + 1)—Dilute 500 mL of acetone to 1 L.

214.2 *Boron-Free Water*—Unless otherwise indicated, the water referred to in this test method is to be treated to remove boron by passing distilled water through a mixed (anion-cation) bed[14] resin dimineralizer.

214.3 *Boron, Standard Solution A* (1 mL = 20 µg B)—Transfer 0.1763 g of sodium borate decahydrate ($Na_2B_4O_7{\cdot}10H_2O$) into a 1-L volumetric flask, dissolve in water, dilute to volume, and mix.

214.4 *Boron, Standard Solution B* (1 mL = 2 µg B)—Using a pipet, transfer 10 mL of Boron Solution A (1 mL = 20 µg B) into a 100-mL volumetric flask, dilute to volume with water and mix. Do not use solutions that have stood for more than 30 days.

214.5 *Curcumin Solution* (1.25 g/L)—Dissolve 0.125 g of curcumin ($C_{21}H_{20}O_6$) in 100 mL of glacial acetic acid (CH_3CO_2H), and mix. Calibration of the spectrophotometer is required each time this solution is prepared.

214.6 *Hydrogen Peroxide* (H_2O_2, 30 %).

214.7 *Iron, Low-Boron.*[15]

214.8 *Methanol, Low-Boron.*

214.9 *Sodium Carbonate* (Na_2CO_3).

214.10 *Sodium Hydroxide Solution* (20 g/L)—Dissolve 20 g of sodium hydroxide (NaOH) in water, and dilute to 1 L. Store in a polyethylene bottle.

[14] Barnstead mixed bed dimineralizer cartridges have been found satisfactory for this purpose.

[15] Johnson-Mathey sponge iron or Spex iron has been found satisfactory for this purpose.

TABLE 18 Statistical Information—Tin—Solvent Extraction-Atomic Absorption Spectrometry Method

Test Material	Tin Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. High-silicon steel (NIST 125b, 0.003 Sn)	0.0034	0.0006	0.0007
2. Carbon steel (NIST 19g, 0.008 Sn)	0.0079	0.0009	0.0014
3. Low-alloy steel (NIST 32e, 0.011 Sn)	0.011	0.001	0.002
4. Carbon steel (NIST 152a, 0.032 Sn)	0.031	0.003	0.004
5. Carbon steel (BCS 454, 0.050 Sn)	0.048	0.008	0.007
6. Low-alloy steel (NIST 363, 0.094 Sn)	0.097	0.011	0.011

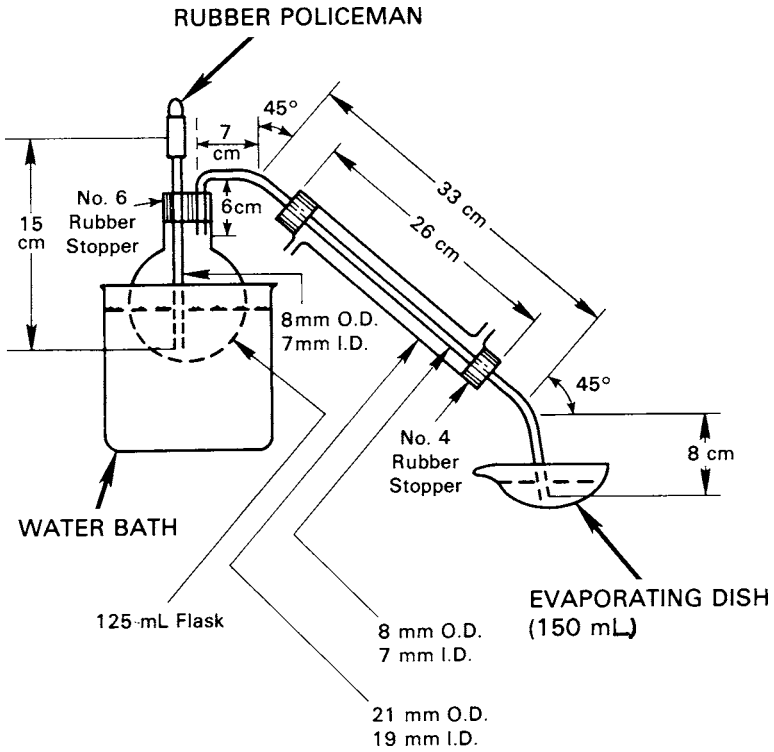


FIG. 6 Distilling Apparatus for Boron in Steel

214.11 *Sulfuric Acid-Acetic Acid Solution* (1 + 1)—While stirring, cautiously add 250 mL of H_2SO_4 to 250 mL of glacial acetic acid.

215. Preparation of Calibration Curve for Compositions from 0.0001 % to 0.0005 % Boron

215.1 *Calibration Solutions:*

215.1.1 Into each of five 125-mL quartz round-bottom dissolution flasks, transfer 2.0 g of low-boron iron and 1.2 g of Na_2CO_3. Using pipets, transfer (1, 2, 3, 4, and 5) mL of boron standard Solution B (1 mL = 2 µg B) into the flasks, respectively.

215.1.2 To each flask add 50 mL of H_2SO_4 (1 + 1) and insert the quartz reflux condenser. Heat below boiling for 30 min and cool. Add 4 mL of H_2O_2 (1 + 4) and continue heating below boiling until dissolution is complete. Cool, disconnect the condenser, and rinse with 2 mL of water into the dissolution flask. Transfer the contents of the dissolution flask into a 100-mL volumetric flask, rinsing with H_2SO_4 (1 + 4). Dilute to volume with H_2SO_4 (1 + 4) and mix.

215.1.3 Using a pipet, transfer a 5-mL aliquot to a 125-mL quartz round-bottom distillation flask. Connect the flask to the condenser and add 30 mL of methanol through the quartz methanol addition tube. Seal the open end of this tube with a rubber policeman. Place the distillation flask in the water bath and place a 150-mL evaporating dish containing 5 mL of NaOH solution at the end of the condenser, making sure that the delivery tip is immersed in the NaOH solution (Fig. 6).

215.1.4 Heat the water bath to 75 °C ± 2 °C and distill until no more than 5 mL of solution remains in the distillation flask. Remove the evaporating dish from under the condenser, and add 10 mL of methanol to the flask through the methanol addition tube. Seal the tube with the rubber policeman, replace the evaporating dish under the condenser, and continue the distillation until no more than 5 mL of solution remains in the flask.

215.1.5 Disconnect the condenser and rinse with 5 mL of methanol, collecting the rinsings in the evaporating dish. Place the evaporating dish in the controlled-temperature water bath and evaporate just to dryness.

NOTE 63—A bath temperature exceeding 80 °C or prolonged heating will cause loss of boron.

215.2 *Reagent Blank*—Transfer 2.0 g of low-boron iron and 1.2 of $NaCO_3$ to a 125-mL quartz round-bottom dissolution flask. Proceed in accordance with 215.1.1 – 215.1.5.

215.3 *Color Development:*

215.3.1 Using a pipet, transfer 3 mL of curcumin solution to the evaporating dish and swirl to dissolve the residue. Using a pipet, add 3 mL of sulfuric-acetic acid solution to each dish and swirl until thoroughly mixed. Allow the solutions to stand for 15 min.

215.3.2 Add 30 mL of acetone-water solution to each dish, mix, and transfer to a 100-mL volumetric flask. Rinse the dish with acetone-water solution, collecting the rinsings in the volumetric flask. Dilute to volume with acetone-water solution and mix.

215.4 *Reference Solution*—Acetone-water solution.

215.5 *Spectrophotometry:*

215.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 5-cm light path and a light band centered at

approximately 555 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

215.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 5-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 555 nm. While maintaining this adjustment, take the spectrophotometric readings of reagent blank solution and the calibration solutions.

215.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.

216. Preparation of Calibration Curve for Compositions from 0.0005 % to 0.006 % Boron

216.1 *Calibration Solutions:*

216.1.1 Into each of five 125-mL quartz round-bottom dissolution flasks transfer 2.0 g of low-boron iron and 1.2 g of $NaCO_3$. Using pipets, transfer (0.5, 1, 2, 4, and 6) mL of boron standard Solution A (1 mL = 20 µg B) to the flasks, respectively.

216.1.2 Proceed in accordance with 215.1.2 – 215.1.5.

216.2 *Reagent Blank*—Proceed in accordance with 215.2.

216.3 *Color Development*—Proceed in accordance with 215.3.

216.4 *Reference Solution*—Acetone-water solution.

216.5 *Spectrophotometry*—Proceed in accordance with 215.5, but use cells having a 1-cm light path.

216.6 *Calibration Curve*—Proceed in accordance with 215.6.

217. Procedure

217.1 *Test Solution:*

217.1.1 Transfer a 2.0-g specimen, weighed to the nearest 1 mg into a 125-mL quartz round-bottom dissolution flask. Add 50 mL of H_2SO_4 (1 + 4), insert a quartz reflux condenser, and heat below boiling for 30 min. Add 4 mL of H_2O_2 (1 + 4) and continue heating below boiling until dissolution is complete. Cool, disconnect the condenser, and rinse with 2 mL of water into the dissolution flask.

217.1.2 Pretreat an 11-cm medium filler paper containing paper pulp by washing with methanol and then with water. Discard the washings. Filter the solution from 217.1.1 into a 100-mL volumetric flask. Wash the paper, pulp, and any insoluble residue ten times with H_2SO_4 (1 + 4), keeping the total volume in the flask including the washings to approximately 50 mL. Reserve the filtrate.

217.1.3 Wash the paper, pulp, and any insoluble residue with two 5-mL portions of water and discard these washings. Sprinkle 0.2 g of Na_2CO_3 over the paper, and transfer it to a 25-mL platinum crucible. Dry the paper, and then heat to 600 °C until carbon is removed. Cool, add 1.0 g Na_2CO_3, and fuse at 1100 °C for 25 min, and cool.

217.1.4 Add H_2SO_4 (1 + 4) dropwise to the fused mass in the crucible until dissolution is complete, keeping the crucible covered between additions. Transfer this solution to the reserved filtrate, rinsing the crucible with H_2SO_4 (1 + 4) into the volumetric flask. Dilute to volume with H_2SO_4 (1 + 4), and mix.

217.1.5 Proceed in accordance with 215.1.3 – 215.1.5.

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

217.3 *Color Development*—Proceed in accordance with 215.3.

217.4 *Reference Solution*—Acetone-water solution.

217.5 *Spectrophotometry*—Proceed in accordance with 215.5.

218. Calculation

218.1 Convert the net photometric reading of the test solution to micrograms of boron by means of the appropriate calibration curve obtained in 215.6 or 216.6. Calculate the percent of boron as follows:

$$\text{Boron, \%} = A \times 0.002/B \quad (29)$$

where:

A = boron found in 100 mL of the final test solution, µg, and
B = sample taken, g.

219. Precision and Bias[16]

219.1 *Precision*—From eight to nine laboratories cooperated in the testing of this test method and obtained the data summarized in Table 19.

219.2 *Bias*—Only one specimen of five tested, has a certified boron content. Because the precision obtained for this specimen (Table 19, No. 5), as measured by R_1 and R_2, Practice E173 is not acceptable to justify measuring boron at this level, the accuracy cannot be determined.

CHROMIUM BY THE ATOMIC ABSORPTION SPECTROMETRY METHOD

220. Scope

220.1 This test method covers the determination of chromium in compositions from 0.006 % to 1.00 %.

[16] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1080.

TABLE 19 Statistical Information—Boron—Distillation-Curcumin Spectrophotometric Method

Test Material	Boron Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Stainless steel BBD (0.0009 B Nominal)	0.0010	0.0002	0.0003
2. Titanium-boron steel (0.0028 B Nominal) BBF	0.0027	0.0003	0.0004
3. Low-alloy steel BBE (0.0055 B Nominal)	0.0057	0.0005	0.0014
4. High-carbon steel (NIST 364, 0.01 B Nominal)	0.0104	0.0009	0.0025
5. Electrolytic iron (NIST 1265; 0.00013)	0.00012	0.00007	0.00013

221. Summary of Test Method

221.1 The sample is dissolved in mineral acids and the residue fused, dissolved, and solution combined. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 357.9 nm from a chromium hollow-cathode lamp is passed through the flame, and the absorbance is measured. The spectrometer is calibrated with solutions of known chromium concentrations.

222. Concentration Range

222.1 The recommended concentration range is from 0.001 mg to 0.015 mg of chromium per millilitre of solution.

223. Interferences

223.1 Because iron acts as a depressant, the calibration solutions must contain approximately the same concentration of iron as the test solutions.

224. Apparatus

224.1 *Atomic Absorption Spectrometer,* capable of resolving the 357.9 nm line, equipped with a chromium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it meets the limits defined in 226.4. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this test method.

225. Reagents

225.1 *Chromium, Standard Solution* (1 mL = 0.1 mg Cr)—Transfer 2.8290 g of potassium dichromate ($K_2Cr_2O_7$) (NIST 136 or equivalent) to an 800-mL borosilicate beaker, add 500 mL of water, and mix. When dissolution is complete, add 5 mL of H_2SO_4 and, while stirring, add 10 mL of H_2O_2 (30 %). Heat at near boiling for 5 min to remove excess H_2O_2. Cool, transfer the solution to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask, dilute to volume, and mix.

225.2 *Iron Low Chromium*—Cr< 0.0001 %.

225.3 *Potassium Carbonate Solution* (50 g/L)—Dissolve 50 g of potassium carbonate (K_2CO_3) in water, and dilute to 1 L. Store the solution in a polyethylene bottle.

226. Preparation of Calibration Curves

226.1 *Calibration Solutions for Compositions 0.005 % to 0.10 %*—To each of seven 250-mL borosilicate beakers, transfer 1.0 g of low-chromium iron weighed to the nearest 1 mg. Add to each beaker 20 mL of HCl and 10 mL of HNO_3 and heat gently until dissolution is complete. Evaporate to dryness on a hot plate and cool. Add 10 mL of HCl and warm to dissolve salts. Dilute to about 50 mL and transfer to 100-mL volumetric flasks. Add 10 mL of K_2CO_3 solution to each of seven flasks. Using pipets, transfer 1 mL, 3 mL, 5 mL, 7 mL, 10 mL, and 15 mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium composition. Dilute to volume and mix.

226.2 *Calibration Solution for Compositions 0.10 % to 1.00 %*—Transfer 2 g of low chromium iron weighed to the nearest 1 mg to a 250-mL borosilicate beaker. Add 20 mL of HCl and 10 mL of HNO_3. Warm as necessary to dissolve the sample. Evaporate just to dryness on a hot plate and cool. Add 20 mL of HCl and warm to dissolve salts. Dilute to about 100 mL and add 20 mL of K_2CO_3 solution. Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Transfer 10-mL aliquots to each of seven 100-mL volumetric flasks and add 9 mL of HCl to each flask. Using pipets, transfer (1, 3, 5, 7, 10, and 15) mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium composition. Dilute to volume and mix.

226.3 *Spectrometry:*

226.3.1 With the chromium hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 357.9 nm line. The wavelength setting in the vicinity of 428.9 nm may be used provided that the instrument meets the performance requirements.

226.3.2 Light the burner, allow it to thermally equilibrate, and adjust the instrument to zero while aspirating water. Aspirate the chromium solution with the highest concentration from the series prepared in accordance with 226.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is required.

226.3.3 Aspirate the chromium solutions used in 226.3.2 to ensure that the absorbance reading is repeatable. Record six readings, and calculate the standard deviation, s, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (30)$$

where:

A = highest of the six values found, and
B = lowest of the six values found.[9]

226.3.4 Using water as a reference solution, and beginning with the solution to which no addition of chromium was made in 226.1 and 226.2, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values calculated in 226.3.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, correct it, and repeat 226.3.1 – 226.3.4.

226.3.5 Proceed immediately in accordance with Section 276.

226.4 *Calibration for Compositions from 0.005 % to 0.10 %*—Follow the instrument manufacturer's instructions for generating the calibration curve. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \quad (31)$$

where:

C = absorbance value for 0.015 mg Cr/mL,
D = absorbance value for 0.010 mg Cr/mL, and

E = absorbance value for 0.005 mg Cr/mL.

If the calculated value is less than 0.60, make the proper adjustment of the instrument or hollow cathode lamp, and repeat the calibration. The absorbance value for C must be 0.200 or higher.

226.5 *Calibration for Compositions from 0.10 % to 1.00 %*—Proceed in accordance with 226.4.

227. Procedure

227.1 *Test Solution:*

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution After Dissolution, mL	Aliquot Required, mL	HCl to Be Added to Aliquot, mL	Final Dilution, mL
0.005 to 0.10	1	0.10	100	0	0	100
0.10 to 1.00	1	0.10	100	10	9	100

Transfer the sample to a 250-mL borosilicate beaker.

227.1.2 Add 20 mL HCl, 10 mL HNO_3, and 5 drops of HF. Heat to dissolve. Remove from the hot plate and dilute to approximately 50 mL. Add a small amount of filter pulp and filter the solution through 11-cm fine filter paper into a 250-mL borosilicate beaker. Wash the paper 5 times with HCl (1 + 99), and reserve the filtrate.

227.1.3 Transfer the paper and contents to a platinum crucible. Dry on a hot plate, and transfer to a muffle furnace that is less than 400 °C. Gradually heat to 600 °C and hold at this temperature for 1 h. Cool, add 0.5 g of K_2CO_3, and carefully fuse over a free flame until a clear melt is obtained (see Note 64). Cool and add 15 mL of water. Add HCl dropwise until reaction ceases. Add 5 drops of HCl in excess and warm on a hot plate, if necessary to obtain a clear solution.

NOTE 64—Fusion of the residue is made in order to include in the sample solution any chromium that might exist in the sample in an acid insoluble form.

227.1.4 Transfer this solution to the filtrate from 227.1.2 and evaporate just to dryness. Add 10 mL HCl and warm to dissolve salts. Transfer quantitatively to a 100-mL volumetric flask, dilute to volume, and mix. For samples with expected chromium compositions less than 0.10 %, proceed in accordance with 227.3. For samples with expected chromium composition greater than 0.10 %, transfer by pipet 10 mL to a 100-mL volumetric flask, add 9 mL of HCl, dilute to volume, and mix.

227.2 Prepare for each composition range a reagent blank by treating the same amount of all reagents in accordance with 227.1.1 – 227.1.4 including the low-chromium iron. Use reagents from the same lots for blank and test solutions.

227.3 *Spectrometry*—Using water as a reference solution, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of four or fewer test solutions and reagent blank solutions has been aspirated, apply the test using the standard solution in accordance with 226.3.4, depending on the composition range. If the value differs from the average of the six values by more than twice the standard deviation, s, found in 226.3.3, or more than 0.01 multiplied by the average of six values used to calculate s, whichever is greater, determine the cause and repeat the calibration and aspiration of test solutions.

228. Calculation

228.1 Convert the absorbance of the test solution and the reagent blank to milligrams of chromium per millilitre of the final test solution by means of the appropriate calibration curve. Calculate the percent chromium as follows:

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (32)$$

where:

A = chromium per millilitre of final test solution, mg,
B = chromium per millilitre of final reagent blank solution, mg,
C = final volume of test solution, and
W = weight of sample in final volume of test solution, g.

229. Precision and Bias[17]

229.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the precision data summarized in Table 20.

229.2 *Bias*—The accuracy can be inferred from the data in Table 20 by comparing the certified values for chromium with the average value obtained by using this test method.

CHROMIUM BY THE PEROXYDISULFATE OXIDATION-TITRATION METHOD

230. Scope

230.1 This test method covers the determination of chromium in compositions from 0.05 % to 3.99 %.

231. Summary of Test Method

231.1 Chromium in an acid solution of the sample is oxidized to the hexavalent state with ammonium peroxydisulfate in the presence of silver nitrate catalyst. The sample is then

[17] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1086.

TABLE 20 Statistical Information—Chromium—Atomic Absorption Method

Test Material	Chromium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. NIST 55e 0.006 Cr	0.0063	0.0014	0.003
2. NIST 125b 0.019 Cr	0.021	0.003	0.003
3. NIST 33d 0.143 Cr	0.149	0.028	0.025
4. NIST 361 0.69 Cr	0.693	0.019	0.024
5. NIST 163 0.982 Cr	0.961	0.036	0.093

titrated with excess ferrous ammonium sulfate to reduce chromium, and the excess is back-titrated with either potassium permanganate or potassium dichromate, depending upon the presence or absence of vanadium.

NOTE 65—In the dichromate titration, the vanadium is not oxidized along with the excess ferrous ions and, therefore, the volume of dichromate added reflects the total of vanadium and chromium and the calculated value for % Cr is high. In the permanganate titration, the V^{IV} is oxidized to V^{V}, thereby compensating for the reduction of vanadium by ferrous sulfate in a previous step.

232. Interferences

232.1 The elements ordinarily present do not interfere if their compositions are less than the maximum limits shown in 1.1.

232.2 Each of the following elements, when present above the indicated limit, imparts color to the solution so that diphenylamine sulfonate indicator cannot be used when $K_2Cr_2O_7$ is chosen as the back-titrant. The limits are: nickel 1.300 g, copper 0.260 g, and tungsten 0.005 g. The effects of the elements are additive. If the numerical value of the following expression does not exceed 1.300, the indicator may be used.

$$(2.6A + 0.05B + 0.01C) \times D \quad (33)$$

where:

A = tungsten in the sample, %,
B = copper in the sample, %,
C = nickel in the sample, %, and
D = sample weight, g.

When the value exceeds 1.300, the end point must be determined potentiometrically if $K_2Cr_2O_7$ is the back-titrant.

233. Apparatus

233.1 *Apparatus for Potentiometric Titrations*—pH meter with a saturated calomel reference and platinum indicator electrode.

234. Reagents

234.1 *Ammonium Peroxydisulfate Solution*—Dissolve 15 g of ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] in water and dilute to 100 mL. Do not use solutions that have stood for more than 24 h.

234.2 *Ferrous Ammonium Sulfate, Standard Solution* (0.05 N)—Dissolve 20 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) in 500 mL of cold H_2SO_4 (5 + 95) and dilute to 1 L with H_2SO_4 (5 + 95). Standardize the solution in accordance with 235.1, 235.2, or 235.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

234.3 *Potassium Dichromate, Standard Solution* (0.05 N)—Dissolve 2.4518 g of NIST 136c standard potassium dichromate ($K_2Cr_2O_7$) or equivalent primary standard grade in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

234.4 *Potassium Permanganate Solution* (25 g/L)—Dissolve 25 g of reagent grade $KMnO_4$ in 200 mL of water, dilute to 1 L, and mix.

234.5 *Potassium Permanganate, Standard Solution* (0.05 N):

234.5.1 *Preparation*—Dissolve 1.6 g of potassium permanganate ($KMnO_4$) in 1 L of water. Let stand in the dark for 2 weeks. Filter, without washing, through a Gooch crucible or a fine porosity fritted-glass crucible. Avoid contact with rubber or other organic material. Store in a dark-colored glass-stoppered bottle.

234.5.2 *Standardization*—Dry a portion of the NIST 40h or equivalent primary standard grade sample of sodium oxalate at 105 °C. Transfer 0.1500 g of the sodium oxalate to a 600-mL beaker. Add 250 mL of H_2SO_4 (5 + 95), previously boiled for 10 min to 15 min and then cooled to 27 °C ± 3 °C, and stir until the oxalate has dissolved. Add 39 mL to 40 mL of the $KMnO_4$ solution, at a rate of 25 mL/min to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s). Heat to 55 °C to 60 °C and complete the titration by adding $KMnO_4$ solution until a faint pink color persists for 30 s. Add the last 0.5 to 1 mL dropwise, allowing each drop to become decolorized before adding the next drop. To determine the blank: Titrate 250 mL of H_2SO_4 (5 + 95), treated as above, with $KMnO_4$ solution to a faint pink color. The blank correction is usually equivalent to 0.03 mL × 0.05 mL.

234.6 *Silver Nitrate Solution* (8 g/L)—Dissolve 8 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

234.7 *Sodium Diphenylamine Sulfonate Indicator Solution* (2.0 g/L):

234.7.1 *Preparation from Barium Diphenylamine Sulfonate*—Dissolve 0.32 g of barium diphenylamine sulfonate in 100 mL of hot water. Add 0.5 g of sodium sulfate (Na_2SO_4), stir, and filter through a fine paper to remove the $BaSO_4$. Store in a dark-colored bottle.

234.7.2 *Preparation from Sodium Diphenylamine Sulfonate*—Dissolve 0.20 g of sodium diphenylamine sulfonate in 100 mL of water. Store in a dark-colored bottle.

234.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 *M*)—Dissolve 1.485 g of 1,10-phenanthroline monohydrate in 100 mL of ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$).

234.9 *Ferrous Sulfate Solution* (0.025 *M*)—Dissolve 6.95 g of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in 500 mL of water and dilute to 1 L.

235. Standardization of Ferrous Ammonium Sulfate Solution

235.1 *Against Potassium Permanganate Solution:*

235.1.1 Transfer 180 mL of water, 12 mL of H_2SO_4 (1 + 1), and 5 mL of H_3PO_4 into a 500-mL Erlenmeyer flask. Add 20 mL of $Fe(NH_4)_2(SO_4)_2$ solution (234.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 1 drop to 2 drops of 1,10 phenanthroline indicator solution. Using a 25-mL buret, titrate the ferrous ions with 0.05 *N* $KMnO_4$ standard solution (234.5) while swirling the flask. As the end point is approached, add $KMnO_4$ dropwise. Continue until the pink color changes to clear green and persists for at least 60 s.

235.1.2 Calculate the normality of the $Fe(NH_4)_2(SO_4)_2$ solution as follows:

$$\text{Normality} = AB/C \quad (34)$$

where:

A = normality of $KMnO_4$ solution (234.5),
B = $KMnO_4$ solution, mL, and
C = $Fe(NH_4)_2(SO_4)_2$ solution, mL.

235.2 *Against Potassium Dichromate Solution Using Diphenylamine Sulfonate End Point:*

235.2.1 Transfer 180 mL of water, 12 mL of H_2SO_4 (1 + 1), and 5 mL of H_3PO_4 into a 500-mL Erlenmeyer flask. Add 20 mL of $Fe(NH_4)_2(SO_4)_2$ (234.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using a 25-mL buret, titrate the ferrous ions with 0.05 *N* $K_2Cr_2O_7$ solution, while swirling the flask. As the end point is approached, add the $K_2Cr_2O_7$ titrant dropwise. Continue until a blue color appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL. Refill the burets, add the same volume of $Fe(NH_4)_2(SO_4)_2$ solution as before and again titrate with 0.05 *N* $K_2Cr_2O_7$ solution to the blue end point. Record the buret reading. Subtract this volume of 0.05 *N* $K_2Cr_2O_7$ solution from the volume recorded for the first titration. Record the difference as the indicator blank.

235.2.2 Calculate the normality of the $Fe(NH_4)_2(SO_4)_2$ solution as follows:

$$\text{Normality} = (0.05(A - B))/C \quad (35)$$

where:

A = 0.05 *N* $K_2Cr_2O_7$ solution used in the first titration, mL,
B = millilitres equivalent to the indicator blank, and
C = $Fe(NH_4)_2(SO_4)_2$ solution used in the first titration, mL.

235.3 *Against Potassium Dichromate Using Potentiometric End Point:*

235.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 *N* $K_2Cr_2O_7$ solution into a 600-mL beaker. Reserve the remaining 0.05 *N* $K_2Cr_2O_7$ solution in the buret for the back-titration. Add 150 mL of water, 10 mL of H_2SO_4 (1 + 1), and 5 mL of H_3PO_4. Insert the saturated calomel reference electrode and the platinum indicator electrode into the beaker and connect them to the potentiometer apparatus. While stirring the solution, add $Fe(NH_4)_2(SO_4)_2$ until the dichromate ion yellow color disappears and then add a slight excess. Record the volume of the $Fe(NH_4)_2(SO_4)_2$ solution to the nearest 0.01 mL. Back-titrate with the remaining 0.05 *N* $K_2Cr_2O_7$ solution by adding the solution in 0.1-mL increments as the end point is approached. Record the voltage when equilibrium is reached after each 0.1-mL increment. Inspect the data for the maximum voltage change per 0.1-mL increment. Determine the voltage change for the 0.1-mL increments before and after this maximum change. Determine the two differences between the three voltage readings corresponding to the volume (0.1-mL) increment before the maximum, the maximum, and after the maximum. This is a very close approximation of the second derivative of the volume versus change in voltage curve corresponding to the maximum inflection if this curve were plotted. Sum the two voltage differences. Determine the ratio of the first of these two differences to the sum and multiply 0.1 mL by this ratio to obtain the volume to be added to the smaller volume between the two incremental additions that the maximum change in voltage occurred. See the following example:

Volume of 0.05 *N* $K_2Cr_2O_7$ Back Titrant, mL	Voltage, mV	Δ Voltage, mV	Difference Before and After Maximum
20.80	555		
20.90	570	50	50
21.00	620	100	20
21.10	720	80	
21.20	800		
21.30	835		
21.40	854		

Maximum voltage change occurred between 21.00 mL and 21.10 mL of $K_2Cr_2O_7$ solution. The changes in voltage were 50 mV before the maximum, 100 mV at the maximum, and 80 mV after the maximum. The two differences between the maximum, corresponding to before and after the maximum, were 50 mV and 20 mV, respectively. Their sum equals 70 and the ratio of the first to the sum equals 50/70. Thus 50/70 multiplied by 0.1 mL must be *added* to the smaller volume between the two increments where the maximum change in voltage occurred. The end-point is 21.07 mL.

235.3.2 Calculate the normality of the $Fe(NH_4)_2(SO_4)_2$ solution as follows:

$$\text{Normality} = 0.05\,A/B \quad (36)$$

where:

A = 0.05 *N* $K_2Cr_2O_7$ solution, mL, and
B = $Fe(NH_4)_2(SO_4)_2$ solution, mL.

236. Procedure

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.05 to 0.50	3.5	2
0.40 to 1.0	2.0	1
0.80 to 1.6	1.25	0.5
1.5 to 3.5	0.5	0.3
3.3 to 3.99	0.35	0.2

Transfer the sample to a 600-mL beaker.

236.2 Add 80 mL of H_2SO_4 (1 + 5) and 5 mL of H_3PO_4. Cover the beaker with a ribbed cover glass and heat at 85 °C to 100 °C until the sample is decomposed. Add sufficient HNO_3 in small increments to oxidize the iron. Boil 2 min to expel oxides of nitrogen.

236.3 Dilute the solution to 150 mL, add paper pulp, and filter through an 11-cm fine paper into a 500-mL Erlenmeyer flask or a 600-mL beaker if the potentiometric titration procedure is to be used. Wash the residue 10 to 12 times with warm water, and reserve the filtrate.

236.4 Transfer the paper and residue to a platinum crucible, char the paper, and ignite at 850 °C to 900 °C for 15 min. Cool, add sufficient H_2SO_4 (1 + 1) to moisten the residue, and then add 3 mL to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue with a minimum amount of either fused sodium hydrogen sulfate (sodium pyrosulfate-$Na_2S_2O_7$) or potassium pyrosulfate ($K_2S_2O_7$). Cool the crucible, place in a 250-mL beaker, and dissolve the melt in 20 mL of H_2SO_4 (1 + 10).

Remove the crucible, rinse with water, transfer the solution to the reserved filtrate (236.3), and dilute to 200 mL.

236.5 Add 5 mL of $AgNO_3$ solution and 20 mL of $(NH_4)_2S_2O_8$ solution. If a beaker is used, cover it with a ribbed cover glass. Boil the solution 8 min to 10 min, maintaining the volume at 200 mL by additions of hot water. If the color due to permanganate ions does not develop, or develops but does not persist, add 2 drops of $KMnO_4$ solution (234.4), 5 mL more of $AgNO_3$ solution, and 20 mL more of $(NH_4)_2S_2O_8$ solution, and boil for an additional 8 min to 10 min. Add hot water to maintain the volume at 200 mL during this operation and the operations that follow in 236.6.

236.6 Reduce the permanganate ions as follows: Add 5 mL of HCl (1 + 3) and continue boiling for 10 min after the disappearance of permanganate color. If the permanganate ions have not been completely reduced or if a precipitate of MnO_2 is present, add 2 mL of HCl (1 + 3) and boil again for 10 min. Repeat the addition of HCl and boiling until all manganese is present as colorless manganous ions. Cool to room temperature and dilute to 200 mL. If vanadium is present or its absence has not been confirmed, proceed in accordance with 236.7. If vanadium is absent and the criteria of 232.2 are met, proceed in accordance with 236.8. If vanadium is absent and the criteria of 232.2 are not met, or if the potentiometric titration is preferred and vanadium is absent, proceed in accordance with 236.9.

236.7 *Titration With Potassium Permanganate*—While swirling the flask, add 1 drop to 2 drops of 1,10 phenanthroline indicator solution and then add sufficient $Fe(NH_4)_2(SO_4)_2$ solution to effect a change in color from clear green to pink. Add 1 mL to 2 mL more and record the buret reading to the nearest 0.01 mL. Using a 25-mL buret, back-titrate the excess ferrous ions with 0.05 *N* $KMnO_4$ standard solution. Add $KMnO_4$ dropwise as the end point is approached. Continue the titration until the pink color has changed to clear green which persists for 60 s. Record the buret reading to the nearest 0.01 mL.

236.8 *Titration with Potassium Dichromate to the Diphenylamine Sulfonate End Point*—While swirling the flask, add $Fe(NH_4)_2(SO_4)_2$ solution from a 25-mL buret until the disappearance of the yellow color. Then add 1 mL to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using another 25-mL buret, back-titrate the excess ferrous ions with 0.05 *N* $K_2Cr_2O_7$ standard solution. Add the $K_2Cr_2O_7$ solution dropwise as the end point is approached. Continue the titration until a blue color appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL.

236.9 *Titration with Potassium Dichromate and Potentiometric End Point Detection*—Stir the sample solution in the 600-mL beaker with a magnetic stirrer and insert the saturated calomel reference and platinum indicator electrodes. With the electrodes connected to the potentiometer apparatus, add from a 25-mL buret the $Fe(NH_4)_2(SO_4)_2$ solution while stirring until the yellow color disappears. Add 1 mL to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Using another 25-mL buret, add 0.05 *N* $K_2Cr_2O_7$ standard solution in 0.1-mL increments, recording the voltage after equilibrium is reached for each increment. Inspect the data for the maximum voltage change between increments of the standard dichromate solution (see 235.3). Determine the voltage change for the increments before and after the maximum change and interpolate the end point to the nearest 0.01 mL in accordance with 235.3.

237. Calculation

237.1 If $KMnO_4$ was used, calculate the percent of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (37)$$

where:

A = $Fe(NH_4)_2(SO_4)_2$ solution, mL,
B = normality of $Fe(NH_4)_2(SO_4)_2$ solution,
C = $KMnO_4$ solution used, mL,
D = normality of the $KMnO_4$ solution, and
E = sample taken, g.

237.2 If $K_2Cr_2O_7$ was used, calculate the percent of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (38)$$

where:

A = $Fe(NH_4)_2(SO_4)_2$ solution,
B = normality of $Fe(NH_4)_2(SO_4)_2$ solution,
C = $K_2Cr_2O_7$ solution,
D = normality of $K_2Cr_2O_7$ solution, and
E = sample taken, g.

238. Precision and Bias[18]

238.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 21. Although a sample at the low end of the scope was not tested, the precision data for other types of alloys using the test methods indicated in Table 21 should apply.

238.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be

[18] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1091.

TABLE 21 Statistical Information—Chromium—Peroxydisulfate Oxidation-Titration Method

Test Material	Chromium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E351	0.044	0.008	0.024
2. Carbon Steel (NIST 155, 0.485 Cr)	0.481	0.015	0.053
3. Low-Alloy Steel (NIST 30f, 0.95 Cr)	0.95	0.024	0.050
4. Nitralloy G (NIST 106b, 1.18 Cr)	1.18	0.033	0.048
5. No. 3, E352	3.68	0.16	0.48

judged, however, by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing (see Table 21).

VANADIUM BY THE ATOMIC ABSORPTION SPECTROMETRY METHOD

239. Scope

239.1 This test method covers the determination of vanadium in compositions from 0.006 % to 0.15 %.

240. Summary of Test Method

240.1 The sample is dissolved in hydrochloric, nitric, and perchloric acids. An aluminum solution is added as a spectrochemical buffer. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 269.4 nm from a vanadium hollow cathode lamp is passed through the flame, and the absorbance is measured. This absorbance is compared with the absorbance of a series of standard calibration solutions.

241. Concentration Range

241.1 The recommended concentration range is from 0.002 mg to 0.016 mg vanadium per millilitre of solution.

242. Interferences

242.1 Iron interferes by acting as a depressant. This interference is overcome by the addition of aluminum chloride, which acts as a spectrochemical buffer. Titanium and tungsten interferes when present in compositions greater than 0.5 % and 1.0 %, respectively.

243. Apparatus

243.1 *Atomic Absorption Spectrometer,* capable of resolving the 318.4-nm line, equipped with a vanadium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it is suitable for use in accordance with Guide E1024.

244. Reagents

244.1 *Aluminum Chloride Solution* (1 mL = 20 mg A1)—Dissolve 90 g of aluminum chloride ($AlCl_3 \cdot 6H_2O$) in approximately 300 mL of water, add 10 mL of HCl, and dilute to 500 mL.

244.2 *Vanadium, Standard Solution* (1 mL = 0.2 mg V)—Dissolve 0.200 g of vanadium (purity: 99.9 % minimum) in 20-mL aqua regia (three volumes of HCl to one volume of HNO_3). Evaporate to near dryness and add 10 mL of HCl. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

NOTE 66—As an alternative to vanadium metal, ammonium metavanadate may be used to prepare the standard vanadium solution by drying several grams of ammonium metavanadate (NH_4VO_3) minimum purity 99.9 %, in an air oven at 105 °C to 110 °C for at least 1 h and cool to room temperature in a desiccator. Weigh 0.4592 g of the dried product into a 600-mL beaker, add 400 mL of hot water, and gently simmer to dissolve. Cool, transfer to a 1000-mL volumetric flask, dilute to volume, and mix (1 mL = 0.20 mg V).

245. Preparation of Calibration Curve

245.1 *Calibration Solutions*—To each of five, 250-mL borosilicate beakers, add 10 mL of $HClO_4$. Using a microburet, transfer (0.0, 1.0, 2.0, 4.5, and 8.0) mL of vanadium standard solution to each beaker, respectively. Cover with a watch glass, heat, and evaporate to fumes. Continue heating until solutions are near dryness (Note 67). Cool, dissolve the salts with 10 mL of HCl and 20 mL of water. Filter through a medium-porosity filter paper into a 100-mL volumetric flask and wash well with warm HCl (2 + 100). Cool, add 10 mL of $AlCl_3$ solution (244.1), dilute to volume, and mix.

NOTE 67—The remaining amount of $HClO_4$ must be at a minimum.

245.2 *Spectrometry:*

245.2.1 With the vanadium hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 318.4-nm line.

245.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the vanadium solution with the highest concentration from the series prepared in accordance with 245.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is necessary.

245.2.3 Aspirate the vanadium solution used in 245.2.2 to ensure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (39)$$

where:

A = highest absorbance of the six values found, and
B = lowest absorbance of the six values found.

245.2.4 Using water as a reference, and beginning with the solution to which no addition of vanadium was made in 245.1, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values calculated in 245.2.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 245.2.1 – 245.2.4.

245.2.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve.Test for linearity in accordance with Guide E1024.

246. Procedure

246.1 *Test Solution:*

246.1.1 Transfer 1.0 g of sample, weighed to the nearest 1 mg, to a 250-mL borosilicate beaker.

246.1.2 Add 20 mL of HCl, 4 mL of HNO_3, and cover with a cover glass. Heat until dissolution is complete. Add 10 mL of $HClO_4$ and evaporate to fumes. Continue heating until solutions are near dryness (Note 67). Cool, dissolve the salts with 10 mL of HCl and 20 mL of water. Filter through a medium-porosity filter paper into a 100-mL volumetric flask, and wash well with warm HCl (2 + 100). Cool, add 10 mL of $AlCl_3$ solution (244.1), dilute to volume, and mix.

246.1.3 Prepare a reagent blank by using a 250-mL borosilicate beaker and proceeding in accordance with 246.1.2. Use reagents from the same lots as those used for the sample solution.

246.2 *Spectrometry*—Using water as a reference, aspirate and record the absorbance of the calibration, sample, and reagent blank solutions. After each group of four or fewer samples and reagent blank solutions has been aspirated, apply the test using the standard solution in accordance with 245.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 245.2.3, or more than 0.01 multiplied by the average of six values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration, sample, and reagent blank measurements.

247. Calculation

247.1 Convert the absorbance of the sample solution and the reagent blank to milligrams of vanadium per millilitre of the final dilution volume by means of the calibration curve. Calculate the percent of vanadium as follows:

$$V\text{anadium, \%} = ((A - B) \times 10)/C \qquad (40)$$

where:

A = vanadium per millilitre of the final sample solution, mg,
B = vanadium per millilitre of the final reagent blank solution, mg, and
C = weight of sample, g.

248. Precision and Bias

248.1 *Precision*—Twenty-three laboratories participated in testing this test method under the auspices of WG-9 of ISO Committee TC 17/SC 1 and obtained the data summarized in Table 22. All testing meets the requirements of Practice E173.

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

CERIUM AND LANTHANUM BY THE DIRECT CURRENT PLASMA ATOMIC EMISSION SPECTROMETRY METHOD

249. Scope

249.1 This test method covers the determination of cerium in compositions from 0.003 % to 0.50 % and lanthanum in compositions from 0.001 % to 0.30 %.

250. Summary of Test Method

250.1 The sample is dissolved in mineral acids and evaporated to perchloric acid fumes. The diluted sample solution is measured using a direct current plasma atomic emission spectrometer. Wavelengths of 456.24 nm for cerium and 408.67 nm for lanthanum are selected. The spectrometer is calibrated with solutions of known concentrations of cerium and lanthanum in the presence of iron and programmed to read out in milligrams per litre of cerium and lanthanum.

251. Concentration Range

251.1 The recommended concentration range is from 0.3 mg/L to 50 mg/L of cerium and from 0.1 mg/L to 30 mg/L of lanthanum.

252. Interferences

252.1 Spectral interference is minimized by matching matrices of calibration and sample solutions and by carefully peaking the wavelength.

252.2 It is very important that the 456.24-nm wavelength be used for Ce determinations. There are several other Ce wavelengths of comparable intensity, but these are all subject to spectral interferences. For example:

Wavelength, nm	Interference
393.109	Fe
394.215	Mo, Fe
394.275	Mo, Co, Mn (Ca and Al cause a baseline shift)
394.314	Fe
394.350	(not intense enough to use)
394.389	Al
399.924	Nb, Ti, V, Zr
401.239	Cr
413.380	Fe
418.660	Fe
418.732	Zr
Wavelength, nm	Interference
429.667	Zr, Cr, Ni, Mo
446.021	Nb, Zr, V
456.236	Ti (only if 100 times greater than Ce)

253. Apparatus

253.1 An atomic emission instrument equipped with a direct current plasma excitation source, photomultiplier assembly, nebulizer system, and dedicated microprocessor (Note 68) and capable of emitting spectral energy at 456.24 nm and 408.67 nm. The instrument is calibrated and programmed in accordance with the manufacturer's instructions. The recording system is calibrated in milligrams per litre of solution.

NOTE 68—Instruments without a microprocessor can be programmed manually according to their capabilities.

254. Reagents

254.1 *Cerium Standard Solution* (1 mL = 1.0 mg Ce)—Dry cerium ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ (purity: 99.9 %

TABLE 22 Statistical Information—Vanadium—Atomic Absorption Spectrometry Method

Test Material	Vanadium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
Low-Alloy Steel (JSS 152-8, 0.100 V)	0.107	0.008	0.014
No. 1, E351	0.008	0.002	0.003
No. 1, E352	0.032	0.002	0.004
No. 1, E353	0.038	0.003	0.005
No. 2, E352	0.161	0.007	0.011

minimum) (Note 69) at 82 °C to 85 °C for 4 h to 6 h and store in a desiccator over anhydrous magnesium perchlorate desiccant. Dissolve 3.9121 g of the dried $(NH_4)_2Ce(NO_3)_6$ in 300 mL of HNO_3 (1 + 10). Transfer to a 1-L volumetric flask, dilute to volume with HNO_3 (1 + 50), and mix.

NOTE 69—Also listed as ammonium hexanitrato cerate.

254.2 *Iron,* cerium and lanthanum free.

NOTE 70—NIST SRM 365 or equivalent material may be used.

254.3 *Lanthanum, Standard Solution* (1 mL = 1.0 mg La)—Ignite the lanthanum oxide (La_2O_3) (purity: 99.9 % minimum) at 1000 °C for 1 h and store in a desiccator over anhydrous magnesium perchlorate desiccant. Dissolve 1.1728 g of the ignited La_2O_3 in 500 mL of HNO_3 (1 + 10). Transfer to a 1-L volumetric flask, dilute to volume with HNO_3 (1 + 50), and mix.

254.4 *Cerium and Lanthanum, Composite Standard Solution* (1 mL = 0.1 mg Ce and 0.1 mg La)—Using a pipet, transfer 10.0 mL of cerium standard solution (1 mL = 1.0 mg Ce) and 10.0 mL of lanthanum standard solution (1 mL = 1.0 mg La) to a 100-mL volumetric flask. Dilute to volume with HNO_3 (1 + 50) and mix.

254.5 *Cerium Solution for Wavelength Optimization*—Transfer approximately 10 mL of cerium standard solution (1 mL = 1.0 mg Ce) prepared in 275.1 to a 100-mL beaker. Dilute to approximately 75 mL with water and mix. This solution does not need to be accurately prepared since it is used only to select the optimum wavelength for cerium spectral energy near 456.24 nm.

254.6 *Lanthanum Solution for Wavelength Optimization*—Transfer approximately 10 mL of lanthanum standard solution (1 mL = 1.0 mg La) prepared in 275.3 to a 100-mL beaker. Dilute to approximately 75 mL and mix. This solution does not need to be accurately prepared since it is used only to select the optimum wavelength for lanthanum spectral energy at 408.67 nm.

255. Procedure

255.1 *Calibration Solutions:*

255.1.1 *Calibration Solution A* (0.10 % upper limit; 10 mg Ce/L and 10 mg La/L)—To a 250-mL beaker (Note 71), add 1.0 g of iron (254.2), and 10.0 mL of cerium and lanthanum composite standard solution (1 mL = 0.1 mg Ce and 0.1 mg La) as prepared in 254.4. Add 15 mL of HNO_3 (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until dissolution is complete. Add 15 mL of $HClO_4$, cover, and heat to perchloric acid fumes. Cool, rinse cover and sides of beaker with water, add 10 mL of HNO_3 (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. Cool, transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix.

NOTE 71—The use of poly(tetrafluoroethylene) beakers and covers are required. If borosilicate glass is used, varying amounts of Ca may be dissolved out of the glass, shifting the background and causing erratic readings.

255.1.2 *Calibration Solution B* (0.50 % upper limit for Ce and 0.30 % upper limit for La; 50 mg Ce/L and 30 mg La/L)—To a 250-mL beaker (Note 71), add 1.0 g of iron (254.2) and 5.0 mL of Ce standard solution (1 mL = 1.0 mg Ce) prepared as in 303.1 and 3.0 mL of La standard solution (1 mL = 1.0 mg La) as prepared in 254.3. Add 15 mL of HNO_3 (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until dissolution is complete. Add 15 mL of $HClO_4$, cover, and heat to perchloric acid fumes. Cool, rinse cover and sides of beaker with water, add 10 mL of HNO_3 (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. Cool, transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix.

255.1.3 *Matrix Blank Solution—Both Concentration Ranges*—To a 250-mL beaker (Note 71), add 1.0 g of iron (254.2). Add 15 mL of HNO_3 (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until dissolution is complete. Add 15 mL of $HClO_4$, cover, and heat to perchloric acid fumes. Cool, rinse cover and sides of beaker with water, add 10 mL of HNO_3 (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. Cool, transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix.

255.2 *Test Solution*—Transfer a 1.0-g sample weighed to the nearest 1.0 mg to a 250-mL poly(tetrafluoroethylene) beaker (Note 71). Add 15 mL of HNO_3 (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until dissolution is complete. Add 15 mL of $HClO_4$, cover, and heat to perchloric acid fumes. Cool and rinse cover and sides of beaker with water. Add 10 mL of HNO_3 (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. If necessary filter the solution through high-porosity filter paper into a 100-mL volumetric flask. Cool, dilute to volume with water, and mix.

255.3 *Preparation of Instrument*—Follow the instrument manufacturer's instructions for startup and wavelength selection.

255.3.1 *Cerium*—Using the wavelength optimization solution in accordance with 254.5, select the cerium 456.24-nm wavelength. Further optimize the instrument with the high calibration solution in accordance with the manufacturer's instructions.

255.3.2 *Lanthanum*—Using the wavelength optimization solution in accordance with 254.6, select the lanthanum 408.67-nm wavelength. Further optimize the instrument with the high calibration solution in accordance with the manufacturer's instructions.

255.4 *Measurement:*

255.4.1 *Calibration Solutions*—Enter the value for the appropriate calibration solution (milligrams per litre) and also the value for the matrix blank into the computer. Auto Range (A/R) while introducing the appropriate calibration solution into the plasma with the instrument set to average 3 readings at 10 s each. Introduce the matrix blank into the plasma and complete the auto range sequence. (**Warning—***Observe instrument during calibration cycle* when instrument is calibrated for a

maximum of 50 mg Ce/L (or 30 mg La/L). If a maximum count is reached and then falls off before the calibration cycle is completed, this indicates a possible saturation of the detector. The results will be in error. This situation may be remedied by reducing the photomultiplier tube voltage, decreasing the slit width, or in extreme cases locating an alternate emission line or diluting sample and standards. This note may not apply to all instruments.)

255.4.2 *Test Solution*—To ensure that the instrument is in calibration, measure the calibration solution as a test solution. If the reading differs by more than 2 % from the established value, recalibrate and repeat. Introduce a series of five (or fewer) test solutions into the plasma with the instrument set to average three readings at 10 s each. Check the calibration by measuring the calibration solution as a test solution. If the reading differs by less than 2 % from the established value, continue with another series of five (or fewer) test solutions. After each series of test solutions, check the calibration by measuring the calibration solution as a test solution. If the reading for the calibration solution differs by more than 2 % from the established value, recalibrate the instrument and remeasure the test solutions.

NOTE 72—To ensure close calibration tolerances, a series of test solutions can be measured by recalibrating before each test sample.

256. Calculation

256.1 Convert the instrument readings (in milligrams per litre) to % analyte in the sample as follows:

$$Cerium, \% = \frac{A \times B}{C \times 10} \quad (41)$$

where:

A = cerium in test solution, mg/L,
B = volume of final test solution (304.2), L, and
C = weight of sample, g.

$$Lanthanum, \% = \frac{D \times B}{C \times 10} \quad (42)$$

where:

D = lanthanum in test solution, mg/L.

257. Precision and Bias[19]

257.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 23 and Table 24.

257.2 *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.

TOTAL TITANIUM BY THE DIANTIPYRYLMETHANE SPECTROPHOTOMETRIC METHOD

258. Scope

258.1 This test method covers the determination of total titanium in compositions from 0.025 % to 0.30 %.

259. Summary of Test Method

259.1 Dissolution of the sample is followed by reduction and complexation of interfering elements. The titanium 4,4'-diantipyrylmethane complex is formed and determined spectrophotometrically. The spectrophotometric measurement is made at approximately 390 nm.

260. Concentration Range

260.1 The recommended concentration range is from 0.006 mg to 0.140 mg of titanium per 50 mL of solution. A 2-cm cell should be used for concentrations of 0.006 mg to 0.070 mg of titanium. A 1-cm cell should be used for concentrations of 0.070 mg to 0.140 mg of titanium.

261. Stability of Color

261.1 The color takes 90 min to develop at ambient temperature and then is stable for up to 12 h.

[19] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1042.

TABLE 23 Statistical Information—Cerium—Direct Current Plasma Atomic Emission Spectrometry Method

Test Material	Cerium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Low Alloy (NIST 362, 0.0019 Ce)	0.0027	0.0002	0.0005
2. Low Alloy (NIST 361, 0.0040 Ce)	0.0041	0.0003	0.0006
3. Cast Iron	0.0059	0.0002	0.0004
4. R. E. Cast Iron (Leco 206, 0.011 Ce)	0.011	0.0005	0.0008
5. R. E. Cast Iron (Leco 207, 0.016 Ce)	0.016	0.0005	0.0013
6. Low Alloy (NIST 1286)	0.018	0.0004	0.0008
7. R. E. Cast Iron (Leco 208, 0.018 Ce)	0.018	0.0004	0.0010
8. R. E. Cast Iron (Leco 209, 0.026 Ce)	0.025	0.0009	0.0027
9. Ductile Iron (NIST 1140)	0.086	0.0015	0.0033
10. Low Alloy	0.16	0.0049	0.0066
11. Cast Iron	0.28	0.0067	0.0154
12. Cast Iron	0.38	0.0079	0.0183

TABLE 24 Statistical Information—Lanthanum—D-C Plasma Optical Emission Method

Test Material	Lanthanum Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Low Alloy (NIST 362, 0.001 La)	0.0008	0.0001	0.0004
2. Low Alloy (NIST 361, 0.001 La)	0.0012	0.0001	0.0004
3. Cast Iron	0.0028	0.0002	0.0006
4. R. E. Cast Iron (Leco 206)	0.0037	0.0002	0.0005
5. R. E. Cast Iron (Leco 207)	0.0032	0.0002	0.0006
6. Low Alloy (NIST 1286)	0.0083	0.0003	0.0008
7. R. E. Cast Iron (Leco 208)	0.0057	0.0002	0.0007
8. R. E. Cast Iron (Leco 209)	0.0075	0.0004	0.0012
9. Ductile Iron (NIST 1140)	0.024	0.0007	0.0027
10. Low Alloy	0.098	0.0033	0.0108
11. Cast Iron	0.16	0.0038	0.0142
12. Cast Iron	0.20	0.0055	0.0152

262. Interferences

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

263. Apparatus

263.1 *Glassware*—To prevent contamination of the sample, all glassware must be cleaned with hot HCl (1 + 1) before use.

264. Reagents

264.1 *Ascorbic Acid Solution* (100 g/L)—Dissolve 25 g of ascorbic acid in water and dilute to 250 mL. Prepare as needed.

264.2 *Diantipyrylmethane (DAPM)* (20 g/L)—Dissolve 5 g of 4,4'-diantipyrylmethane monohydrate ($C_{23}H_{24}N_4O_2{\cdot}H_2O$) in HCl (1 + 9) and dilute to 250 mL with the dilute hydrochloric acid. Prepare as needed.

264.3 *Potassium Hydrogen Sulfate-Fused* (a mixture of $K_2S_2O_7$ and $KHSO_4$).

264.4 *Tartaric Acid Solution* (100 g/L)—Dissolve 50 g of tartaric acid in water and dilute to 500 mL.

264.5 *Titanium Sulfate Standard Solution* (1 mL = 0.010 mg Ti)—Transfer 0.1000 g of titanium metal (purity: 99.9 % minimum) weighed to within ± 0.2 mg to a 1-L volumetric flask. Add 50 mL of H_2SO_4 (1 + 3) and dissolve at less than 150 °C. Oxidize the titanium by adding HNO_3 dropwise (Note 73). Cool, dilute to volume with H_2SO_4 (1 + 9), and mix. Using a pipet, transfer 10 mL to a 100-mL volumetric flask, add 10 mL of tartaric acid solution, dilute to volume, and mix. Do not use a solution that has stood more than one day.

NOTE 73—An excess of HNO_3 should be avoided. Two drops to three drops of HNO_3 should be sufficient to oxidize the titanium sulfate solution and discharge the blue color.

265. Preparation of Calibration Curve

265.1 Prepare a new calibration curve for each new lot of DAPM.

265.2 *Calibration Solutions*—Using pipets, transfer (0.5, 1, 2, 4, 6, 8, 10, 12, and 14) mL of titanium solution (1 mL = 0.010 mg Ti) to 50-mL volumetric flasks.

NOTE 74—Take spectrophotometric readings of the calibration solutions containing (0.5, 1, 2, 4, and 6) mL of titanium solution using a 2-cm light path. Use a 1-cm light path for the remaining solutions.

265.3 *Reference Solution*—Water.

265.4 *Reagent Blank*—Transfer 10 mL of water to a 50-mL volumetric flask and proceed in accordance with 265.5.

265.5 *Color Development*—Add 3.0 mL of HCl (1 + 1) and 5 mL of ascorbic acid solution and allow to stand for 10 min. Add 10 mL of DAPM solution, dilute to volume with water, mix, and allow the solution to stand for at least 90 min.

265.6 *Spectrophotometry:*

265.6.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with either a 1-cm light path or a 2-cm light path and a light band centered at approximately 390 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions and the reagent blank solutions versus the reference solution.

265.6.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm or 2-cm light path, and adjust the spectrophotometer using a light band centered at approximately 390 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank solutions.

265.7 *Calibration Curve*—Subtract the reagent blank reading from each of the calibration solution readings. Plot the blank-corrected spectrophotometric readings of the calibration solutions against milligrams of titanium per 50 mL of solution. Prepare separate curves for 1-cm and 2-cm light path cells.

266. Procedure

266.1 *Test Solution:*

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

Titanium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Final Volume, mL	Aliquot Volume, mL	Cell Size, cm
0.02 to 0.07	1.00	1	100	10.00	2
0.07 to 0.14	1.00	1	100	10.00	1
0.14 to 0.30	0.40	0.4	100	10.00	1

Transfer the sample to a 250-mL beaker.

266.1.2 Add 20 mL of HCl and digest at a low temperature until dissolution is complete. Add 5 mL of HNO_3 and evaporate the solution to dryness (Note 75). Cool, add 5 mL of HCl to the glass-covered beaker and dissolve the iron salts at 90 °C to 100 °C and then add 15 mL of water.

NOTE 75—The use of a coarse screen of 3-mm (⅛-in.) wire, or triangles

on the hot plate, permits more rapid evaporation without the danger of spattering.

266.1.3 Filter through an 11-cm medium-porosity filter paper containing paper pulp into a 100-mL volumetric flask in accordance with 266.1.1 and rinse the beaker and filter paper three times each with hot water. Remove the iron salts by washing the paper with 10 mL of HCl (1 + 1) and hot water. Volume in the flask at this point should not exceed 70 mL.

266.1.4 Transfer the paper to a platinum crucible, dry the paper and residue, and then heat in a muffle furnace at about 700 °C until the carbon is removed. Cool and add a few drops of H_2SO_4 (1 + 1) followed by 2 mL of HF. Evaporate to dryness, and then heat at a gradually increasing rate until the H_2SO_4 is removed. Cool, add 2 g of fused potassium pyrosulfate, fuse over a gas burner, and heat until a clear melt is obtained. Add 10 mL of tartaric acid solution to the cooled melt, heat at 90 °C to 100 °C, and when the melt is dissolved, add this solution to the reserved filtrate in the volumetric flask (266.1.3). Dilute to volume and mix.

266.1.5 Using a pipet, transfer a 10-mL portion to a 50-mL volumetric flask and treat in accordance with 265.5.1 using 1 mL of HCl (1 + 1).

266.2 *Sample Blank Solution*—Using a pipet, transfer a second 10-mL portion of the test solution to a 50-mL volumetric flask and treat in accordance with 266.1.5 and 265.5, omitting the addition of DAPM.

266.3 *Reagent Blank Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with the sample omitted (see 266.1.1 – 266.1.5).

266.4 *Reference Solutions*—Water and the sample blank solution, in accordance with 266.5.

266.5 *Spectrophotometry*—Take the spectrophotometric reading of the reagent blank solution versus water and of the test solution versus the sample blank solutions in accordance with 265.6.

267. Calculation

267.1 Convert the spectrophotometric reading of the test solution to milligrams of titanium by means of the appropriate calibration curve. Calculate the percent of titanium as follows:

$$\text{Titanium, \%} = (A - B)/(C \times 100) \times 100 \quad (43)$$

where:

A = titanium found in the final color development solution, mg,
B = titanium found in the reagent blank, mg, and
C = original sample weight, g, as determined in 266.1.1.

268. Precision and Bias

268.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 25.

268.2 *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.

MANGANESE BY THE ATOMIC ABSORPTION SPECTROMETRY METHOD

269. Scope

269.1 This test method covers the determination of manganese in compositions from 0.005 % to 2.0 %.

270. Summary of Test Method

270.1 The sample is dissolved in a mixture of hydrochloric and nitric acids, filtered and aspirated into an air-acetylene flame. The absorbance of light energy at 279.5 nm from a manganese hollow cathode lamp is compared with the absorbance of a series of standard calibration solutions.

271. Concentration Range

271.1 The recommended concentration range is from 0.0005 mg to 0.010 mg manganese per millilitre of solution.

272. Interferences

272.1 Iron is not a spectral interference but may affect the aspiration rate by contribution to the solution viscosity. For this reason, iron is added to the calibration solutions.

273. Apparatus

273.1 *Atomic Absorption Spectrometer,* equipped with a monochromatic radiation source such as a manganese hollow cathode lamp, a monochromator to isolate the 279.5-nm resonance line, an atomization source such as a burner, and a readout device. The recommended flame is a lean air-acetylene flame. Determine that the instrument is suitable for use in accordance with Guide E1024.

274. Reagents

274.1 *Manganese, Standard Solution A* (1 mL = 1.0 mg Mn)—Weigh 1.000 g of electrolytic manganese (purity: 99.9 % minimum) into a 250-mL beaker. Add 20 mL of HNO_3 (1 + 1), cover with a watchglass, and heat on a hot plate until dissolved. Transfer to a 1-L volumetric flask. Dilute to volume with HCl (1 + 99) and mix.

274.2 *Manganese, Standard Solution B* (1 mL = 0.10 mg Mn)—Using a pipet, transfer 10 mL of Solution A to a 100-mL volumetric flask. Dilute to volume and mix. Prepare immediately before preparation of calibration standards.

274.3 *Iron Solution* (1 mL = 10 mg Fe)—Weigh 1.000 g of manganese-free iron powder into a 250-mL beaker. Add 10 mL

TABLE 25 Statistical Information—Titanium—Diantipyrylmethane Spectrophotometric Method

Test Material	Titanium Found, %	Repeatability, % (R_1, E173)	Reproducibility, % (R_2, E173)
1. Low Alloy (NIST 19g, 0.027 Ti)	0.028	0.0013	0.0043
2. Low Alloy (NIST 170a, 0.281 Ti)	0.282	0.0097	0.0228

of HCl (1 + 1) and 3 mL of HNO_3 (1 + 1), cover with a watchglass, and heat on a hot plate until dissolved. Transfer to a 100-mL volumetric flask, dilute to volume, and mix.

275. Preparation of Calibration Curves

275.1 *Calibration Solutions:*

275.1.1 *Manganese Compositions Between 0.005 % and 0.10 %*—Weigh 1.000 g manganese-free iron powder into each of six 250-mL beakers. Add 10 mL of HCl (1 + 1) and 3 mL of HNO_3 (1 + 1), cover with a watchglass, and heat on a hot plate until dissolved. Transfer each solution to a 100-mL volumetric flask. Transfer by pipet (0, 1, 3, 5, 7, and 10) mL of each Standard Manganese Solution B into the series of flasks. Dilute each to volume and mix.

275.1.2 *Manganese Compositions Between 0.10 % and 1.0 %*—To prepare 100 mL of calibration solutions, pipet (0, 1, 3, 5, 7, and 10) mL of Standard Manganese Solution B into six 100-mL volumetric flasks. Add 10 mL of iron solution and 5 mL of HCl (1 + 1). Dilute to volume and mix.

275.1.3 *Manganese Compositions Between 1.0 % and 2.0 %*—Pipet (0, 1, 3, 5, 7, and 10) mL of Standard Manganese Solution B into six 100-mL volumetric flasks. Add 5 mL of iron solution and 5 mL of HCl (1 + 1). Dilute to volume and mix.

275.2 *Reference Solution*—The 0-mL solution in 275.1.1 – 275.1.3 is the reference solution.

275.3 *Spectrometry:*

275.3.1 Optimize the instrument response by correct positioning of hollow cathode lamp, burner, and isolation of 279.5-nm resonance line. Allow enough warmup time with the burner and hollow cathode lamp on. Use a lean air-acetylene flame.

275.3.2 Aspirate deionized water and zero the instrument. Aspirate the highest manganese standard from the series prepared in accordance with 275.1.1. Adjust the burner, air and acetylene pressures, and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is necessary.

275.3.3 Aspirate the manganese solutions with the highest concentrations from the series prepared as directed in 275.1.1 – 275.1.3. Record six absorbance readings for each of these three calibration solutions and calculate the standard deviation, *s*, using the following formula:[9]

$$s = (A - B) \times 0.40 \quad (44)$$

where:

A = highest absorbance value from the six readings, and
B = lowest absorbance value from the six readings.

275.4 Beginning with the solution to which no addition of manganese was made in 275.1.1, 275.1.2, and 275.1.3, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values recorded in 275.3.3 by more than twice the standard deviation or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 275.3.1 – 275.3.3.

275.5 Plot the average absorbance values against milligrams of manganese per millilitre for each series of solutions. Test for linearity in accordance with Guide E1024.

276. Procedure

276.1 *Test Solution:*

276.1.1 Use the following sample sizes for the different composition ranges.

Manganese, %	Sample Weight, g
0.005 to 0.10	1.000
0.10 to 1.0	1.000
1.0 to 2.0	0.500

Weigh the suggested sample size to the nearest tenth of a milligram into a 250-mL beaker. Add 10 mL of HCl (1 + 1) and 3 mL of HNO_3 (1 + 1), cover with a watchglass, and heat on a hot plate at low heat until dissolved. For difficult to dissolve samples, add a few drops of HF. Filter, if necessary, and transfer to a 100-mL volumetric flask. Dilute to volume and mix.

276.1.2 For samples containing 0.005 % to 0.10 % Mn, use the test solution as prepared in 276.1.1.

276.1.3 For samples containing more than 0.10 % Mn, pipet 10 mL of the test solution as prepared in 304.1.1 into a 100-mL volumetric flask. Add 5 mL of HCl (1 + 1), dilute to volume, and mix.

276.2 *Spectrometry*—Aspirate the reference solution and zero the instrument with this solution. Aspirate and record absorbance readings for the other five calibration solutions and the test solution. Aspirate the reference solution after every third calibration or test solution to check stability of base line or instrument drift and rezero if necessary. Calculate standard deviation in accordance with 275.3.3 for every third solution aspirated. Repeat calibration and aspiration of test solutions if the absorbance value differs from the average of six values by more than twice the standard deviation or by more than 0.01 multiplied by the average of the six values used to calculate *s*, whichever is greater.

277. Calculation

277.1 Determine the milligrams of manganese per millilitre of test solution using the appropriate calibration curve from 275.4. Calculate the percent of manganese in the sample as follows:

For Mn composition of 0.005 % to 0.10 %:

$$M\text{anganese, \%} = (C \times 10/D) \quad (45)$$

For Mn composition of 0.10 to 2.0 %:

$$M\text{anganese, \%} = (C \times 100/D) \quad (46)$$

where:

C = manganese, mg/mL of final solution, and
D = weight of sample, g.

278. Precision and Bias[20]

278.1 *Precision*—Eight laboratories cooperated in testing this test method and obtained the precision data summarized in Table 26.

[20] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1047.

TABLE 26 Statistical Information—Manganese—Atomic Absorption Spectrometry Method

Test Material	Manganese Certified, %	Manganese Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. NIST 365	0.0056	0.0059	0.0007	0.0013
2. Brammer AA	0.021	0.0248	0.001	0.002
3. NIST 179	0.094	0.0925	0.004	0.005
4. NIST 364	0.255	0.250	0.012	0.023
5. NIST 11 H	0.51	0.502	0.020	0.046
6. BCS 159/3	0.77	0.775	0.019	0.045
7. NIST 362	1.04	1.040	0.021	0.081
8. NIST 363	1.50	1.485	0.026	0.067
9. NIST 100b	1.89	1.888	0.052	0.064

278.2 *Bias*—The accuracy of this test method can be inferred from the data in Table 26 by comparing the certified values for manganese with the average value obtained.

COPPER BY THE ATOMIC ABSORPTION SPECTROMETRY METHOD

279. Scope

279.1 This test method covers the determination of copper in compositions from 0.004 % to 0.5 %.

280. Summary of Test Method

280.1 The sample is dissolved in mineral acids. Insolubles present are removed by filtration. The sample solution is aspirated into an air-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 324.7 nm from a copper hollow cathode lamp is passed through the flame, and the absorbance is measured. This absorbance is compared with the absorbance of a series of standard calibration solutions.

281. Concentration Range

281.1 The recommended concentration range is from 0.0005 mg to 0.005 mg of copper per millilitre in the final 100-mL dilution.

282. Interferences

282.1 Iron interferes by acting as a depressant. This interference can be minimized by using calibration solutions which contain approximately the same concentration of iron as the test solutions.

283. Apparatus

283.1 *Atomic Absorption Spectrometer,* capable of resolving the 324.7-nm line, equipped with a copper hollow cathode lamp, and a laminar flow air-acetylene burner. The performance of the instrument must be such that it is suitable for use in accordance with Guide E1024.

284. Reagents

284.1 *Copper Metal*—Purity: 99.95 %.

284.2 *Copper, Standard Solution A* (1 mL = 1.0 mg Cu)—Transfer 1.000 g of copper metal to a 400-mL beaker. Add 25 mL of HNO_3 (1 + 4) and cover with a watchglass. When the copper metal is dissolved, evaporate on a low-temperature hot plate until crystallization begins. Dissolve the residue in water, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

284.3 *Copper, Standard Solution B* (1 mL = 0.02 mg Cu)—Transfer a 20.0-mL aliquot of Standard Solution A to a 1-L volumetric flask, dilute to volume, and mix.

284.4 *Hydrochloric-Nitric-Perchloric Acid Mixture*—In a 600-mL beaker, combine 60 mL of HCl, 165 mL of HNO_3, and 225 mL of $HClO_4$ (Note 76).

NOTE 76—**Warning:** Prepare just before use; do not store. Dispose of any excess.

284.5 *Iron Solution* (1 mL = 20.0 mg Fe)—Transfer 10.0 g of high-purity iron (copper content < 0.0005 %) to a 1-L beaker and cover with a watchglass. Add in small amounts, 400 mL of freshly prepared hydrochloric-nitric-perchloric acid mixture and heat gently to dissolve. When dissolution is complete, evaporate until the appearance of dense white perchloric acid fumes. Fume strongly for at least 1 min after the white fumes are refluxing on the walls of the beaker. Cool, add 100 mL of water, and heat gently to dissolve the perchlorate salts. Cool to room temperature and transfer to a 500-mL volumetric flask. Dilute to volume and mix.

285. Preparation of Calibration Curves

285.1 *Calibration Solutions:*

285.1.1 *Copper Compositions from 0.004 % to 0.1 %*—To each of seven 100-mL volumetric flasks, add a 25-mL aliquot of the iron solution. Using a buret, add (0, 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0) mL of Copper Standard Solution B. Dilute to volume and mix.

285.1.2 *Copper Compositions Between 0.1 % to 0.5 %*—To each of seven, 100-mL volumetric flasks, add a 5-mL aliquot of the iron solution. Using a buret, add (0, 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0) mL of Copper Standard Solution B. Dilute to volume and mix.

285.2 *Spectrometry:*

285.2.1 With the copper hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 324.7-nm line.

285.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the copper solution with the highest concentration from the series prepared in accordance with 285.1 or 285.1.2, and adjust the burner, acetylene flow, and air flow

rates to obtain maximum response. Whenever one or more of these parameters is changed, recalibration is necessary.

285.2.3 Aspirate the copper solution used in 285.2.2 to ensure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, *s*, or the readings as follows:

$$s = (A - B) \times 0.40 \quad (47)$$

where:

A = highest absorbance of the six values found, and
B = lowest absorbance of the six values found.[9]

285.2.4 Using water as a zero absorbance reference, and beginning with the solution to which no addition of copper was made in 285.1.1 or 285.1.2, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values calculated in 285.2.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 285.2.1 – 285.2.4.

285.2.5 *Calibration Curve for Compositions from 0.004 % to 0.10 % Copper*—Follow the manufacturer's instructions for generating the calibration curve. Test for linearity in accordance with Guide E1024.

285.2.6 *Calibration Curve for Compositions from 0.1 % to 0.5 % Copper*—Proceed in accordance with 285.2.5.

286. Procedure

286.1 *Test Solution:*

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

Copper, %	Sample weight, %	Tolerance in sample weight, mg	Dilution, mL	Aliquot, mL	Dilution factor
0.004 to 0.10	0.5	0.1	100	0	1
0.10 to 0.50	0.5	0.1	100	20	5

Transfer the sample to a 250-mL borosilicate beaker.

286.1.2 Add in small amounts, 20 mL of freshly prepared hydrochloric-nitric-perchloric acid mixture, and cover with a watchglass. Heat until dissolution is complete. Evaporate to dense white fumes. Continue fuming for at least 1 min after the white fumes are refluxing on the walls of the beaker (Note 77).

NOTE 77—For samples not readily soluble in the hydrochloric-nitric-perchloric acid mixture, dissolve in 10 mL of a freshly prepared HCl-HNO_3 mixture (3 parts HCl, 1 part HNO_3, and 2 parts water) before adding the 20 mL of hydrochloric-nitric-perchloric acid mixture.

286.1.3 Allow sample to cool, add 25 mL of water, and the heat gently to dissolve salts. Allow to cool again and quantitatively transfer to a 100-mL volumetric flask. Dilute to volume and mix.

286.1.4 Filter through a dry medium-porosity filter paper to remove any insolubles that might be present. Collect the filtrate in a dry beaker after discarding the first 10 mL to 15 mL.

286.2 For each concentration range prepare a reagent blank by treating the same amount of all reagents as directed in 286.1.2 – 286.1.4 but omitting the sample reagents from the same lots for blank and test solutions (Note 78).

NOTE 78—If it is necessary to dilute the test sample, the reagent blank must be diluted the same way.

286.3 *Spectrometry*—Using deionized water as a zero absorbance reference, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of four or fewer test and reagent blank solutions has been aspirated, apply the precision test using the copper solution with the highest concentration described in 285.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 285.2.3, or by more than 0.01 multiplied by the average of the six values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration, the sample, and reagent blank measurements.

287. Calculation

287.1 Convert the absorbance of the test solution and the reagent blank solution to milligrams of copper per millilitre of the final dilution volume by means of the calibration curve. Calculate the percent copper as follows:

$$\text{Copper, \%} = \frac{(C - D) \times E}{F \times 10} \quad (48)$$

where:

C = mg of copper/mL of the final test solution,
D = mg of copper/mL of the final reagent blank solution,
E = dilution factor, and
F = weight of sample, g.

288. Precision and Bias[21]

288.1 *Precision*—Eight laboratories participated in testing this test method under the auspicies of ISO Committee TC 17/SC 1, and obtained the data summarized in Table 27.

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

[21] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1054.

TABLE 27 Statistical Information—Copper—Atomic Absorption Spectrometry Method

Test Material	Copper Found, %	Repeatability, *R1*	Reproducibility, *R2*
1. Plain Carbon Steel (BCS 434, 0.017 Cu)	0.017	0.0011	0.0018
2. Low-Alloy Steel (BCS 407, 0.43 Cu)	0.434	0.0280	0.0554

CALCIUM BY THE DIRECT-CURRENT ARGON PLASMA ATOMIC EMISSION SPECTROMETRY METHOD

289. Scope

289.1 This test method covers the determination of calcium in compositions from 0.0005 % to 0.010 %.

290. Summary of Test Methods

290.1 The sample is dissolved in mineral acids. The diluted sample solution is analyzed using a direct current plasma atomic emission spectrometer at 393.37 nm. The spectrometer is calibrated with a solution of known concentration of calcium in the presence of iron and programmed to read out in milligrams per litre of calcium.

291. Concentration Range

291.1 The recommended concentration range is from 0.05 mg to 1.0 mg calcium per litre of solution.

292. Interferences

292.1 Spectral interference is minimized by matching the matrices of calibration and sample solutions and by carefully peaking the wavelength.

NOTE 79—**Caution:** Exercise caution in selecting reagents to ensure freedom from calcium contamination. Use all reagents from the same lots for calibration and sample preparation.

293. Apparatus

293.1 *Atomic Emission Instrument,* equipped with a direct current plasma excitation source, photomultiplier assembly, nebulizer system and dedicated microprocessor (Note 80), and capable of detecting and quantifying spectral energy emitted at 393.37 nm. The instrument is calibrated and programmed in accordance with the manufacturer's instructions.

NOTE 80—Instruments without a microprocessor can be programmed manually according to their capabilities.

294. Reagents (Note 81)

294.1 *Calcium, Standard Solution A* (1 mL = 1.0 mg Ca)—Dry a portion of calcium carbonate ($CaCO_3$) (purity: 99.9 % minimum) in a drying oven at 110 °C for 1 h and cool in a desiccator. Weigh 2.500 g of the dried material into a 600-mL beaker and dissolve in 300 mL of HNO_3 (1 + 10). Transfer the solution to a 1-L volumetric flask, dilute to volume with HNO_3 (1 + 50), and mix.

294.2 *Calcium, Standard Solution B* (1 mL = 0.1 mg Ca)—Using a pipet, transfer 10.0 mL of Calcium Standard Solution A to a 100-mL volumetric flask. Dilute to volume with HNO_3 (1 + 50) and mix.

294.3 *Calcium Solution for Wavelength Optimization*—Transfer approximately 10 mL of Calcium Standard Solution A to a 100-mL beaker. Dilute to approximately 75 mL with water and mix. This solution does not need to be accurately prepared since it is used only to optimize the calcium spectral energy emitted at 393.37 nm.

294.4 *Iron, Calcium Free* (Note 81).

294.5 *Water*—Reagent water conforming to Type I of Specification D1193.

NOTE 81—Because calcium contamination is common in reagent grade acids, it is essential to use acids from the same lots for calibration and sample preparation.

NOTE 82—NIST SRM365 or equivalent material may be used.

295. Procedure

295.1 *Calibration Solutions:*

295.1.1 *Calibration Solution* (0.01 % Ca upper limit; 1 mg Ca/L)—Add 1.0 g of calcium-free iron to a 250-mL polytetrafluoroethylene beaker. Add 20 mL of HNO_3 (1 + 3). After the reaction subsides, add 5 mL of HCl and 2 mL of HF. Heat at low temperature until dissolution is complete. Cool. Add by means of a pipet 1.0 mL of Calcium Standard Solution B. Transfer the solution to a 100-mL polypropylene volumetric flask. Dilute to volume with water and mix.

295.1.2 *Matrix Blank Solution*—Add 1.0 g of calcium-free iron to a 250-mL polytetrafluoroethylene beaker. Add 20 mL of HNO_3 (1 + 3). After the reaction subsides, add 5 mL of HCl and 2 mL of HF. After dissolution is complete, cool and transfer the solution to a 100-mL polypropylene volumetric flask. Dilute to volume with water and mix.

295.2 *Test Solution:*

295.2.1 Transfer a 1.0-g sample weighed to the nearest 1.0 mg to a 250-mL polytetrafluoroethylene beaker. Add 20 mL of HNO_3 (1 + 3). After the reaction subsides, add 5 mL of HCl and 2 mL of HF. Cover and heat at low temperature until dissolution is complete. Cool and rinse cover and sides of beaker with water. Dilute to approximately 50 mL with water and filter the solution if necessary through a high-porosity filter paper, using a polypropylene funnel, into a 100-mL polypropylene volumetric flask, washing the paper thoroughly with water, and collecting all washings. Dilute to volume with water and mix.

295.3 *Preparation of Instrument:*

295.3.1 Follow the instrument manufacturer's instructions for startup and operation.

295.3.2 Further optimize the instrument with the high calibration solution in accordance with manufacturer's instructions.

295.4 *Measurement:*

295.4.1 *Calibration Solution*—Enter the value for the 1.0-mg/L calibration solution and also the value for the matrix blank (*O*) into the computer. Auto range (A/R) while introducing the calibration solution into the plasma with the instrument set to average three readings at 10 s each. Introduce the matrix blank into the plasma and complete the auto range sequence. (Note 82).

295.4.2 *Test Solution*—To ensure that the instrument is in calibration, measure the calibration solution as a test solution. If the reading differs by more than 2 % from the established value, recalibrate and repeat. Introduce a series of five (or fewer) test solutions into the plasma with the instrument set to average three readings at 10 s each. Check the calibration by measuring the calibration solution as a test solution. If the reading differs by less than 2 % from the established value, continue with another series of five (or fewer) test solutions.

After each series of test solutions, check the calibration by measuring the calibration solution as a test solution. If the reading for the calibration solution differs by more than 2 %, recalibrate the instrument and remeasure the test solutions (Note 83).

NOTE 83—**Caution:** Observe the instrument during the calibration cycle when the instrument is calibrated for a maximum of 1 mg Ca/L. If a maximum count is reached and then falls off before the calibration cycle is completed, this indicates a possible saturation of the detector. The results will be in error. This situation may be remedied by reducing the photomultiplier tube voltage, decreasing the slit width, or in extreme cases locating an alternate emission line or diluting sample and standards. This note may not apply to all instruments.

NOTE 84—To ensure close calibration tolerances, a series of test solutions can be measured by recalibrating before each test solution.

296. Calculation

296.1 Convert the instrument readings (in milligrams per litre) to percent calcium in the sample as follows:

$$\text{Calcium, \%} = \frac{A \times B}{C \times 10} \quad (49)$$

where:

A = mg of calcium/L of test solution,
B = volume of final test solution, L, and
C = weight of sample, g.

297. Precision and Bias

297.1 *Precision:*

297.1.1 Six laboratories cooperated in testing this test method and obtained the data summarized in Table 28.

297.1.2 The samples used for this calcium method did not test to the same level as the maximum scope of 0.010 %. However, experience with calibration solutions of various known quantities of calcium demonstrated that calcium can be attainable up to 0.010 %.

297.2 *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.

BISMUTH BY THE ATOMIC ABSORPTION SPECTROMETRY METHOD

298. Scope

298.1 This test method covers the determination of bismuth in compositions from 0.02 % to 0.25 % in low-alloy steel.

299. Summary of Test Method

299.1 The sample is dissolved in mineral acids and any silicon present is volatilized. Insolubles present are removed by filtration. The sample solution is aspirated directly into the air-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 223.1 nm from a bismuth hollow-cathode lamp is passed through the flame and the absorbance is measured. The spectrometer is calibrated with solutions of known bismuth concentrations.

300. Concentration Range

300.1 The recommended concentration range is from 0.001 mg to 0.015 mg of bismuth per mL of solution.

301. Interferences

301.1 The elements ordinarily present in low-alloy steel do not interfere.

302. Apparatus

302.1 *Atomic Absorption Spectrometer,* capable of resolving the 223.1-nm line, equipped with a bismuth hollow-cathode lamp and a laminar flow air-acetylene burner.

303. Reagents

303.1 *Bismuth Metal*—99.99 % minimum purity (Note 85).

303.2 *Bismuth Standard Solution* (1 mL = 1.0 mg Bi)—Dissolve 1.0000 g ± 0.1 mg of bismuth metal in a minimum volume of HNO_3 (1 + 1). Transfer the solution to a 1-L volumetric flask, dilute to volume with HNO_3 (2 + 98) and mix (Note 85).

303.3 *Iron Background Solution*—Weigh 20 ± 0.1 g of electrolytic iron with low-residual element content and transfer it to a 1-L beaker. Add 125 mL of water, 125 mL of HNO_3 in five 25-mL incremental portions, and 50 mL of HCl. When all of the iron is dissolved, add 250 mL of $HClO_4$ and evaporate

TABLE 28 Statistical Information—Calcium, Direct-Current Argon Plasma Optical Emission Spectroscopy Method

Test Material	Calcium Found, %	Repeatability, (R_1, E173)	Reproducibility, (R_2, E173)
1. Low-Alloy Steel (J SS 169-3, 0.0006 Ca)	0.0007	0.0002	0.0002
2. Low-Alloy Steel (J SS 171-3, 0.0013 Ca)	0.0013	0.0002	0.0003
3. Mild Steel	0.0019	0.0004	0.0005
4. Low-Alloy Steel (J SS 168-3, 0.0025 Ca)	0.0025	0.0001	0.0006
5. Low-Alloy Steel (J SS 170-3, 0.0032 Ca)	0.0032	0.0003	0.0008
6. Mild Steel	0.0052	0.0004	0.0008
7. Mild Steel	0.0086	0.0005	0.0009

to strong white fumes. Cool, transfer the solution to a 500-mL volumetric flask, dilute to volume, and mix.

NOTE 85—**Warning:** Bismuth is a toxic metal. Careful practices should be exercised in preparing the calibration solutions and dissolving the samples.

304. Preparation of Calibration Curve

304.1 *Calibration Solutions*—Pipet 50 mL of the iron background solution into each of four 100-mL volumetric flasks. Then pipet (0, 3, 9, and 15) mL of the bismuth standard solution into each of the four flasks, respectively. Dilute to the mark and mix (Note 85).

304.2 *Spectrometry:*

304.2.1 With the bismuth hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize detector response in the immediate vicinity of 223.1 nm (Note 86).

NOTE 86—Bismuth has resonance lines at 222.8 nm and 223.1 nm. Ordinarily, for most instruments both lines will pass the slit aperture and their net response will be measured.

304.2.2 Light the burner, allow it to thermally equilibrate, and adjust the instrument to zero while aspirating water. Aspirate the bismuth solution with the highest concentration from the series prepared in 304.1, and adjust the burner height and fuel and oxidant pressure and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is required.

304.2.3 Aspirate the bismuth solution used in 304.2.2 to ensure that the absorbance reading is repeatable. Record six readings, and calculate an estimate of the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (50)$$

where:

A = highest of the six values found, and
B = lowest of the six values found.[9]

304.2.4 Using water as a reference solution, and beginning with the solution to which no addition of bismuth was made in 304.1, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of the six values recorded in 304.2.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, correct it, and repeat 304.2.1 – 304.2.4.

304.2.5 Proceed immediately as directed in 304.3.

304.2.6 *Calibration*—Follow the manufacturer's instructions for directly generating the calibration curve. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \quad (51)$$

where:

C = absorbance value for 0.15 mg Bi/mL,
D = absorbance value for 0.09 mg Bi/mL, and
E = absorbance value for 0.03 mg Bi/mL.

304.2.7 If the calculated value is less than 0.60, correct the adjustment of the instrument or hollow-cathode lamp, and repeat the calibration. The absorbance value for C must be 0.200 or higher; if it is not, correct the adjustment of the instrument or hollow-cathode lamp, and repeat the calibration.

305. Procedure

305.1 *Test Solution:*

305.1.1 Transfer a 2-g sample (Note 87), weighed to the nearest 0.1 mg, to a 250-mL beaker. Add 20 mL of water, then add with caution 25 mL of HNO_3 (1 + 1) and 5 mL of HCl (1 + 1). Cover and apply low heat as required until the reaction subsides.

305.1.2 Add 25 mL of $HClO_4$, bring to a boil, and add 3 to 5 drops of HF. Evaporate to strong white fumes and continue fuming for 3 min to 5 min. Cool, transfer to a 100-mL volumetric flask, dilute to the mark, and mix.

305.1.3 If insolubles are present, filter approximately 10 mL of the diluted sample solution through a dry 11-cm low-porosity filter paper and use the filtrate for the measurement.

NOTE 87—Bismuth in high compositions is known to be heterogeneously distributed in steel. A sample should be carefully obtained that represents the actual content of the bismuth in the steel.

305.2 Prepare a reagent blank using the same amounts of all reagents in accordance with 305.1.1 – 305.1.3, but omitting the sample. Use reagents from the same lot for blank and test solutions.

305.3 *Spectrometry*—Using water as a reference solution, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of four or fewer reagent blank and test solutions has been aspirated, apply the test using the standard solution in accordance with 304.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 304.2.3 or more than 0.01 multiplied by the average of six values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration and aspiration of test solutions.

306. Calculation

306.1 Convert the absorbance of the test solution and the reagent blank solution to milligrams of bismuth per millilitre of the final dilution volume by means of the calibration curve. Calculate the percent bismuth as follows:

$$\text{Bismuth, \%} = \frac{(F - G) \times H}{I \times 10} \quad (52)$$

where:

F = mg of bismuth per mL of final test solution,
G = mg of bismuth per mL of final reagent blank solution,
H = final volume of test solution, mL, and
I = weight of sample in final volume of test solution, g.

307. Precision and Bias

307.1 *Precision*—Six laboratories cooperated in testing this test method and obtained the precision data summarized in Table 29.

307.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be

TABLE 29 Statistical Information—Bismuth—Atomic Absorption Spectrometry Method

Test Material	Bismuth Found, %	Repeatability, (R_1, E173)	Reproducibility, (R_2, E173)
1. Low-alloy steel (NIST 362)	0.0069	0.0039	0.0087
2. Low-alloy steel	0.0192	0.0025	0.0080
3. Low-alloy steel	0.0587	0.0029	0.0113
4. Low-alloy steel	0.1125	0.0041	0.0217
5. Low-alloy steel	0.157	0.010	0.025
6. Low-alloy steel	0.235	0.0138	0.045

judged by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing (Note 88).

NOTE 88—Although this test method was tested to only 0.25 %, most commercial instruments are believed capable of analyzing samples containing bismuth up to 0.75 %.

TOTAL OR ACID-SOLUBLE ALUMINUM BY THE ATOMIC ABSORPTION SPECTROMETRY METHOD

308. Scope

308.1 This test method covers the determination of total aluminum or acid-soluble aluminum in compositions from 0.005 % to 0.20 %.

308.2 For this test method, acid-soluble aluminum is defined as the aluminum soluble in the dissolving acids of this procedure.

308.3 This test method is not applicable to silicon steels.

309. Summary of Test Method

309.1 The sample is dissolved in a mixture of HCl and HNO_3. Insolubles present are removed by filtration and fused with a boric acid (H_3BO_3)-potassium carbonate (K_2CO_3) mixture. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 309.3 nm from an aluminum hollow-cathode lamp is passed through the flame, and the absorbance is measured. This absorbance is compared with the absorbance of a series of standard calibration solutions.

310. Concentration Range

310.1 The recommended concentration range is from 0.001 mg to 0.04 mg of aluminum per millilitre in the final 100-mL dilution.

311. Interferences

311.1 In the nitrous oxide-acetylene flame aluminum is partially ionized. This ionization is suppressed by the addition of potassium ions. Iron also interferes by acting as a depressant. This interference is minimized by using calibration solutions which contain approximately the same concentration of iron as the test solutions.

312. Apparatus

312.1 *Atomic Absorption Spectrometer,* capable of resolving the 309.3-nm line, equipped with an aluminum hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it is suitable for use in accordance with Guide E1024.

312.2 *Filter Media,* 0.45-µm cellulose nitrate filter.

312.3 *Filter Funnel,* a two-piece acid-resistant filter funnel with a support screen between the funnel body and stem, designed for the vacuum filtration of liquids. The stem of the funnel is fitted with a rubber stopper for insertion into an opening of the vacuum vessel.

312.4 *Vacuum Vessels:*

312.4.1 Vacuum vessel of 500-mL capacity.

312.4.2 Vacuum vessel large enough to contain a 100-mL volumetric flask with an opening to allow for the insertion of the rubber stopper of the filter funnel stem.

313. Reagents

313.1 *Acid Mixture*—Combine three volumes of HCl, one volume of HNO_3, and two volumes of water.

NOTE 89—**Warning:** Prepare just before use; do not store. Dispose of any excess.

313.2 *Aluminum, Stock Solution* (1 mL = 2.0 mg Al)—Transfer 2.000 g of aluminum metal (purity: 99.9 % minimum) to a 250-mL beaker, add 40 mL of HCl and 10 mL of HNO_3 to the beaker, and cover with a watchglass. Heat until dissolution is complete and boil to eliminate oxides of nitrogen. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

313.3 *Aluminum, Standard Solution A* (1 mL = 0.20 mg Al)—Transfer a 20.0-mL aliquot of the stock solution to a 1-L volumetric flask, dilute to volume, and mix.

313.4 *Aluminum, Standard Solution B* (1 mL = 0.02 mg Al)—Transfer a 20.0-mL aliquot of Standard Solution A to a 200-mL volumetric flask, dilute to volume, and mix.

313.5 *Fusion Mixture*—Combine one part by mass of H_3BO_3 and one part by mass of K_2CO_3. Mix well.

313.6 *Fusion Mixture Solution* (5 mL = 1.0 g of fusion mixture)—Dissolve 20.0 g of fusion mixture in water and dilute to 100 mL.

313.7 *Pure Iron*—Containing less than 0.0001 % aluminum, or of known low-aluminum content.

314. Preparation of Calibration Curves

314.1 *Calibration Solutions for Compositions of 0.005 % to 0.010 % Aluminum*—To each of five, 250-mL beakers, add 2.00 g ± 0.001 g of pure iron. Cover the beakers with a watchglass and add to each in small portions, 40 mL of the acid mixture. Heat until the dissolution of the iron is complete. Heat to

boiling to eliminate oxides of nitrogen. Cool and transfer the solutions into each of five 100-mL volumetric flasks. Using a burette, add (0, 2.5, 5.0, 7.5, and 10.0) mL of Aluminum Standard Solution B to each volumetric flask respectively. Add 5.0 mL of fusion mixture solution to each volumetric flask and cool. Swirl and let stand to allow all the carbon dioxide produced to escape, then dilute to volume and mix.

314.2 *Calibration Solutions for Compositions of 0.020 % to 0.20 % Aluminum*—To each of five, 250-mL beakers, add 2.00 g ± 0.01 g of pure iron. Cover the beakers with a watchglass and add to each, in small portions, 40 mL of the acid mixture. Heat until the dissolution of the iron is complete. Heat to boiling to eliminate oxides of nitrogen. Cool and transfer the solutions into each of five 100-mL volumetric flasks. Using a burette, add (0, 5.0, 10.0, 15.0, and 20.0) mL of Aluminum Standard Solution A to each volumetric flask, respectively. Add 5.0 mL of the fusion mixture solution to each volumetric flask and cool. Swirl and let stand to allow the carbon dioxide produced to escape. Dilute to volume and mix.

314.3 *Spectrometry:*

314.3.1 With the aluminum hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 309.3-nm line.

314.3.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the aluminum solution with the highest concentration from the series prepared in accordance with 314.1 or 314.2, and adjust the burner, nitrous-oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is necessary.

314.3.3 Aspirate the aluminum solution used in 314.3.2 to ensure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (53)$$

where:

A = highest of six values found, and
B = lowest of the six values found.[9]

314.3.4 Using water as a zero absorbance reference, and beginning with the solution to which no addition of aluminum was made in 314.1 or 314.2, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration used in 314.1 or 314.2 differs from the average of the six values obtained in 314.3.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 314.3.1 – 314.3.4.

314.3.5 *Calibration Curve for Compositions of 0.005 % to 0.010 % Aluminum*—Follow the manufacturer's instructions for generating the calibration curve. Test for linearity as described in Guide E1024.

314.3.6 *Calibration Curve for Compositions of 0.010 % to 0.20 % Aluminum*—Proceed in accordance with 314.3.5.

315. Procedure

315.1 *Test Solution:*

315.1.1 Transfer 2.0 g of test material, weighed to the nearest 0.1 mg into a 250-mL borosilicate beaker.

315.1.2 Add, in small amounts, 40 mL of the acid mixture and cover the beaker with a watchglass. Heat until dissolution is complete. Heat to boiling to remove the oxides of nitrogen, and then cool.

315.2 *Filtration of Test Solution:*

315.2.1 Place a filter on the support screen of a filter funnel. Moisten the filter with water and connect the body and stem of the funnel. Insert the stopper of the filter funnel stem into a vacuum vessel 312.4.1 or 312.4.2. Apply gentle vacuum to the vacuum vessel and filter the solution. Wash the funnel sides and residue alternately with warm HCl (2 + 100) and warm water until no trace of the yellow iron color remains. Stop the vacuum gently.

315.2.2 When a 500-mL capacity flask is used as the vacuum vessel (312.4.1):

315.2.2.1 If the volume of the filtrate and the washings is less than approximately 70 mL, transfer the solution quantitatively to a 100-mL volumetric flask, and proceed to 315.3 or 315.4;

315.2.2.2 If the volume of the filtrate and the washings is greater than approximately 70 mL, transfer the solution to a 250-mL borosilicate beaker, reduce the volume of the solution to approximately 70 mL by evaporation, cool, transfer quantitatively to a 100-mL volumetric flask, and proceed to 315.3 or 315.4.

315.2.3 When a 100-mL volumetric flask is contained in the vacuum vessel (312.4.2):

315.2.3.1 If the volume of the filtrate and the washings is less than approximately 70 mL, proceed to 315.3 or 315.4;

315.2.3.2 If the volume of the filtrate and the washings is greater than approximately 70 mL, transfer the solution to a 250-mL borosilicate beaker, reduce the volume of the solution to approximately 70 mL by evaporation, cool, transfer again quantitatively to the original 100-mL volumetric flask, and proceed to 315.3 or 315.4.

315.3 *Preparation of the Test Solution for the Determination of Acid-Soluble Aluminum:*

315.3.1 Add 5.0 mL of the fusion mixture solution to the filtrate contained in the 100-mL volumetric flask from 315.2 and cool. Swirl and let stand to allow the carbon dioxide produced to escape. Dilute to volume and mix. Retain this solution for the determination of acid-soluble aluminum.

NOTE 90—The insoluble residue and cellulose nitrate filter are discarded in this case.

315.4 *Preparation of the Test Solution for the Determination of Total Aluminum:*

315.4.1 Transfer the filter containing the insoluble residue into a 30-mL platinum crucible. Char the filter at low heat and ignite slowly to 1000 °C. Cool and add several drops of water, several drops of H_2SO_4, and 5.0 mL of HF. Evaporate to dryness and again ignite slowly to 1000 °C. Cool and add 1.0 g of the fusion mixture, and fuse the contents of the crucible in a muffle furnace at 1000 °C for 15 min. Cool and add 1 mL to

2 mL of HCl (1 + 1) and 8 mL of water into the crucible. Heat gently to dissolve the fusion products. Cool, quantitatively transfer the solution to the 100-mL volumetric flask resulting from in either 315.2.2 or 315.2.3. Dilute to the mark and mix. Retain this solution for the total aluminum determination.

315.5 Prepare separate acid-soluble or total aluminum reagent blanks, or both, by treating the same amount of all reagents as directed in 315.1 – 315.3 or 315.4, but omitting the sample. Use reagents from the same lots for blank and test solutions.

315.6 *Spectrometry*—Using deionized water as a zero absorbance reference, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of four or fewer test and reagent blank solutions has been aspirated, apply the precision test in accordance with 314.3.4 (using the calibration solution with the highest aluminum concentration). If the value differs from the average of the six values by more than twice the standard deviation, *s*, in accordance with 314.3.3, or by more than 0.01 multiplied by the average of the six values used to calculate *s* whichever is greater, determine the cause and repeat the calibration, sample, and reagent blank measurements.

316. Calculation

316.1 Convert the absorbance of the test solution and the reagent blank solution to milligrams of aluminum per millilitre of the final dilution volume by means of the calibration curve. Calculate the percent aluminum as follows:

$$\text{Aluminum, \%} = \frac{(A - B) \times C}{W \times 10} \quad (54)$$

where:

A = mg of aluminum/mL of final test solution,
B = mg of aluminum/mL of final reagent blank solution,
C = final volume of test solution, and
W = weight of sample in final volume of test solution, g.

317. Precision and Bias

317.1 *Precision*—Twenty-eight laboratories participated in testing the test method described in this document under the auspices of ISO Committee TC 17/SC-1 and obtained the data summarized in Table 30.[22]

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

NICKEL BY THE ATOMIC ABSORPTION SPECTROMETRY METHOD

318. Scope

318.1 This test method covers the determination of nickel in compositions from 0.003 % to 0.5 %.

319. Summary of Test Method

319.1 The sample is dissolved in a mixture of perchloric and nitric acids and then taken to fumes of perchloric acid.

[22] The data given on the first item in Table 30 is for information only. The statistical data available on this test method has been judged sufficient to support the lower scope of 0.005 %.

TABLE 30 Statistical Information—Aluminum—Atomic Absorption Spectrometry Method

Test Material	Aluminum Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
	Total Aluminum		
Carbon steel (BAM 038-1, 0.002 Al)	0.0020	0.0013	0.0019
Carbon steel (BCS 456/1, 0.009 Al)	0.0094	0.0015	0.0020
Carbon steel (BAM 035-1, 0.026 Al)	0.0258	0.0029	0.0037
Carbon steel (NIST 65d, 0.059 Al)	0.0584	0.0028	0.0059
Carbon steel (BCS 457/1, 0.11 Al)	0.1090	0.0042	0.0087
Carbon steel (IPT 39, 0.169 Al)	0.1718	0.0054	0.0114
	Acid Soluble Aluminum		
Carbon steel[A] (BAM 038-1)	0.0012	0.0004	0.0014
Carbon steel[A] (BCS 456/1)	0.0079	0.0009	0.0018
Carbon steel[A] (BAM 035-1)	0.0217	0.0018	0.0043
Carbon steel[A] (NIST 65d)	0.0525	0.0025	0.0058
Carbon steel[A] (BCS 457/1)	0.1024	0.0051	0.0106
Carbon steel[A] (IPT 39)	0.1659	0.0084	0.0157

[A] The acid-soluble values for these reference materials, using this particular acid mixture, have not been previously reported or certified.

Insolubles that are present are removed by filtration. The sample solution is aspirated into an air-acetylene flame of an atomic absorption spectrophotometer. Spectral energy at approximately 352.5 nm from a nickel hollow-cathode lamp is passed through the flame, and the absorbance is measured. This absorbance is compared with the absorbance of a series of standard calibration solutions.

NOTE 91—With some instruments, it may not be possible to obtain enough sensitivity at the 352.5-nm line for compositions of nickel near the low end of the scope. In such cases it is recommended that the 232.0-nm line be used.

320. Concentration Range

320.1 The recommended concentration range is from 0.0003 mg to 0.05 mg of nickel per millilitre in the final 100-mL dilution.

321. Interferences

321.1 Iron interferes by acting as a depressant. This interference is minimized by using calibration solutions which contain approximately the same concentration of iron as the test solutions.

322. Apparatus

322.1 *Atomic Absorption Spectrometer,* capable of resolving the 352.5-nm or 232.0-nm lines, equipped with a nickel hollow-cathode lamp and a laminar flow air-acetylene burner. The performance of the instrument must be such that it is suitable for use in accordance with Guide E1024.

323. Reagents

323.1 *Acid Mixture*—Combine 100 mL of HNO_3 with 800 mL of $HClO_4$. Mix well and dilute to 1 L. Prepare fresh; do not store.

323.2 *Iron Solution* (1 mL = 40 mg Fe)—Transfer 10 g ± 0.1 g of high-purity iron (nickel content <0.0005 %) to a 800-mL beaker. Add in small amounts, 100 mL of a HCl-HNO_3 mixture (three volumes HCl, one volume HNO_3, and two volumes of water), cover the beaker with a watchglass, and heat gently to dissolve.

323.2.1 When dissolution is complete, add 150 mL of the acid mixture (see 323.1) and evaporate until the appearance of dense white perchloric acid fumes. Fume strongly for at least 1 min after the white fumes are refluxing on the walls of the beaker. Cool, add 100 mL of water, and heat gently to dissolve the perchlorate salts. Cool to room temperature and transfer to a 250-mL volumetric flask. Dilute to volume and mix.

323.3 *Nickel, Stock Solution* (1 mL = 1 mg Ni)—Transfer 0.500 g of nickel metal (purity: 99.9 % minimum) to a 250-mL beaker, add 25 mL of HNO_3 (1 + 1) to the beaker, and cover with a watchglass. Heat until dissolution is complete and boil to expel oxides of nitrogen. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix.

323.4 *Nickel, Standard Solution A* (1 mL = 0.04 mg Ni)—Pipet a 10-mL aliquot of the stock solution to a 250-mL volumetric flask, dilute to volume, and mix.

324. Preparation of Calibration Curves

324.1 *Calibration Solutions for Compositions 0.003 % to 0.1 %*—To each of seven, 100-mL volumetric flasks, add a 25-mL aliquot of the iron solution (see 323.1). Using a buret, add (0, 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0) mL of Nickel Standard Solution A. Dilute to volume and mix.

NOTE 92—While it is recognized that the lowest calibration solution to which nickel has been added represents a composition five times higher than the low end of the scope, the fact that the zero nickel calibration solution is employed in the fit of the curve supports this approach and the linearity in this portion of the curve has been checked and verified.

324.2 *Calibration Solutions for Compositions 0.1 % to 0.5 % Nickel*—To each of seven, 100-mL volumetric flasks, add a 5-mL aliquot of the iron solution. Using a buret, add (0, 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0) mL of Nickel Standard Solution A. Dilute to volume and mix.

324.3 *Spectrometry:*

NOTE 93—While calibration is described separately here, the calibration test, and reagent blank solutions are, in fact, measured at the same time, in accordance with 374.3.

324.3.1 With the nickel hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 352.5-nm line (Note 91).

324.3.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the nickel solution with the highest concentration from the series prepared in accordance with 324.1 or 324.2, and adjust the burner, acetylene, and air flow rates to obtain maximum response. Whenever one or more of these parameters is changed, recalibration is necessary.

324.3.3 Aspirate the nickel solution used in 324.3.2 to ensure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (55)$$

where:

A = highest of six values found, and
B = lowest of the six values found.[9]

324.3.4 Using water as a zero reference, and beginning with the solution to which no addition of nickel was made in 324.1 or 324.2, aspirate each calibration solution in ascending order of concentration and record its absorbance. If the value of the solution with the highest concentration used in 324.1 or 324.2 differs from the average of the six values obtained in 324.3.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 324.3.1 – 324.3.4.

324.3.5 *Calibration Curve for Compositions of 0.003 % to 0.10 % Nickel*—Follow the manufacturer's instructions for generating the calibration curve. Test for linearity in accordance with Guide E1024.

324.3.6 *Calibration Curve for Compositions of 0.10 % to 0.5 % Nickel*—Proceed in accordance with 324.3.5.

TABLE 31 Statistical Information—Nickel—Atomic Absorption Spectrometry Method

Test Material	Nickel Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
Plain carbon steel (BCS 431, 0.069 Ni)	0.066	0.0020	0.0029
High-purity iron (BCS 260/4, 0.003 Ni)	0.003	0.0012	0.0013
24 % Cr steel (BCS 341, 0.56 Ni)	0.576	0.028	0.042

325. Procedure

325.1 *Test Solution:*

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

Estimated % Ni	Sample Weight, g	Tolerance in Sample Weight, mg
0.003–0.1	1.0	0.1
0.1–0.5	0.2	0.1

Transfer the solution to a 250-mL beaker.

325.1.2 Add, in small portions, 15 mL of the acid mixture (see 323.1) and cover with a watchglass. Heat until dissolution is complete (Note 94). Evaporate to dense white fumes. Continue fuming for at least one minute after the white fumes are refluxing on the walls of the beaker.

NOTE 94—For samples that will not readily dissolve in the acid mixture, first dissolve the sample in 10 mL of a HCl-HNO_3 mixture (three volumes HCl, one volume HNO_3, and two volumes of water) before adding the 15 mL of acid mixture.

325.1.3 Allow the sample to cool, add 25 mL of water, and heat gently to dissolve perchlorate salts. Allow to cool again and transfer to a 100-mL volumetric flask. Dilute to volume and mix.

325.1.4 Filter through a dry medium-porosity filter paper to remove any insolubles that are present. Collect the filtrate in a dry beaker after discarding the first 10 mL to 15 mL.

325.2 Prepare for each concentration range a reagent blank by treating the same amount of all reagents, including iron, in accordance with 325.1.2 – 325.1.4. Use reagents from the same lots for blank and test solutions.

325.3 *Spectrometry*—Using deionized water as a zero absorbance reference, aspirate and record the absorbance of the calibration and test and reagent blank solutions. After each group of four or fewer test and reagent blank solutions has been aspirated, apply the precision test in accordance with 324.3.4 (using the calibration solution with the highest nickel concentration). If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 324.3.3, or by more than 0.01 multiplied by the average of the six values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration, test, and reagent blank measurements.

326. Calculation

326.1 Convert the absorbance of the test sample solution and the reagent blank solution to milligrams of nickel per millilitre of the final dilution volume by means of the appropriate calibration curve. Calculate the percent nickel as follows:

$$\text{Nickel, \%} = \frac{(A - B) \times C}{W \times 10} \quad (56)$$

where:

A = mg of nickel/mL of final test solution,
B = mg of nickel/mL of final reagent blank solution,
C = final volume of test solution, mL, and
W = weight of sample in final volume of test solution, g.

327. Precision and Bias[23]

327.1 *Precision*—Seven laboratories participated in testing the test method described in this document under the auspices of ISO Committee TC 17/SC-1 and obtained the data summarized in Table 31.

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

328. Keywords

328.1 aluminum; antimony; bismuth; boron; calcium; carbon; carbon steel; cerium; chromium; cobalt; copper; ingot iron; lead; low-alloy steel; manganese; molybdenum; nickel; phosphorus; silicon; silicon electrical steel; tin; titanium; vanadium

[23] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1062.