Designation: E351 – 13

Standard Test Methods for Chemical Analysis of Cast Iron—All Types[1]

This standard is issued under the fixed designation E351; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope

1.1 These test methods cover the chemical analysis of pig iron, gray cast iron (including alloy and austenitic), white cast iron, malleable cast iron, and ductile (nodular) iron having chemical compositions within the following limits:

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

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

1.3 Procedures for the determination of carbon and sulfur not included in these test methods can be found in Test Methods E1019.

1.4 Some of the composition ranges given in 1.1 are too broad to be covered by a single method and therefore this standard contains multiple methods for some elements. The user must select the proper method by matching the information given in the Scope and Interference sections of each method with the composition of the alloy to be analyzed.

1.5 The values stated in SI units are to be regarded as standard.

[1] These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferroalloys.

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1.6 *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 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]

E350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron

E352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels

E353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys

E380 Practice for Use of the International System of Units (SI) (the Modernized Metric System) (Withdrawn 1997)[3]

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]

E1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition

2.2 *Other Document:*[4]

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

3. Terminology

3.1 For definitions of terms used in these test methods, refer to Terminology E135.

4. Significance and Use

4.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with compositional specifications, particularly those under the jurisdiction of ASTM Committee A04 on Iron Castings. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide E882.

5. Apparatus, Reagents, and Instrumental Practices

5.1 *Apparatus*—Specialized apparatus requirements are listed in the Apparatus section in each method.

5.2 *Reagents:*

5.2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as conforming to Type I or Type II of Specification D1193. Type III or IV may be used if they effect no measurable change in the blank or sample.

5.3 *Spectrophotometric Practice*—Spectrophotometric practice prescribed in these test methods shall conform to Practice E60.

6. Hazards

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

7. Sampling

7.1 For procedures 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 in accordance with Practice E173 (withdrawn 1997) or ISO 5725. The Reproducibility R2 of E173 corresponds to the Reproducibility Index R of E1601. The Repeatability R1 of E173 corresponds to the Repeatability Index r of E1601.

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

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

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

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

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

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

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

10. Summary of Method

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

11. Concentration Range

11.1 The recommended concentration range is 0.15 mg to 0.8 mg of manganese per 50 mL of solution, using a 1-cm cell (Note 1) and a spectrophotometer with a band width of 10 nm or less.

NOTE 1—This method has been written for cells having a 1-cm light path and a narrow-band instrument. The concentration range depends upon band width and spectral region used as well as cell optical path length. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

12. Stability of Color

12.1 The color is stable for at least 24 h.

13. Interferences

13.1 The elements ordinarily present do not interfere. $HClO_4$ treatment, which is used in the procedure, yields solutions which can be highly colored due to the presence of Cr (VI) ions. Although these ions and other colored ions in the sample solution undergo no further change in color quality upon treatment with metaperiodate ion, the following precautions must be observed when filter spectrophotometers are used: Select a filter with maximum transmittance between 545 nm and 565 nm. The filter must transmit not more than 5 % of its maximum at a wavelength shorter than 530 nm. The band width of the filter should be less than 30 nm when measured at 50 % of its maximum transmittance. Similar restrictions apply with respect to the wavelength region employed when other wide-band instruments are used.

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

14. Reagents

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

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

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

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

15. Preparation of Calibration Curve

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

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

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

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

15.4 *Spectrophotometry:*

15.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using the Reference Solution (15.2) in absorption cells with a 1-cm light path and using a light band centered at 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:

Maganese, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL
0.01 to 0.5	0.80	0.5	100
0.45 to 1.0	0.35	0.3	100
0.85 to 2.0	0.80	0.5	500

Transfer it to a 300-mL Erlenmeyer flask.

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

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

16.1.5 Using a pipet, transfer 20 mL aliquots, to two 50-mL borosilicate glass volumetric flasks. Treat one portion as directed in 16.3. Treat the other portion as directed in 16.4.1.

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

16.3 *Color Development*—Proceed as directed in 15.3.

16.4 *Reference Solutions:*

16.4.1 *Background Color Solution*—To one of the sample aliquots in a 50-mL volumetric flask, add 100 mL of HNO_3-H_3PO_4 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 as directed in 16.4.1 and use as reference solution for Background Color Solutions.

16.5 *Spectrophotometry*—Establish the cell corrections with the Reagent Blank Reference solution to be used as a reference solution for Background Color solutions. Take the spectrophotometric readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference Solutions as directed in 15.4.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Spectrophotometric Method

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

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 percentage of manganese as follows:

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

where:

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

18. Precision and Bias

18.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 1. Although a sample covered by this method with manganese composition of approximately 2.0 % was not available, the precision data for this composition should be similar to those obtained for material 5.

18.2 *Bias*—No information on the accuracy of this method is known. The accuracy of this 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 method covers the determination of phosphorus in compositions from 0.02 % to 0.90 %.

20. Summary of Method

20.1 The sample is dissolved in mixed acids and the solution is fumed with $HClO_4$. Ammonium molybdate is added to react with the phosphorus to form the heteropoly phosphomolybdate. This species is then reduced with hydrazine sulfate to form the molybdenum blue complex. Spectrophotometric measurement is made at 650 nm or 825 nm, depending upon the concentration.

21. Concentration Range

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

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

22. Stability of Color

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

23. Interferences

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

24. Apparatus

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

25. Reagents

25.1 *Ammonium Molybdate Solution* (20 g/L)—Cautiously, while stirring and cooling, add 300 mL of H_2SO_4 to 500 mL of water and cool. Add 20 g of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}·4H_2O$), 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 mL, 10 mL, 15 mL, 25 mL, and 50 mL of Phosphorus Standard Solution B (1 mL = 0.01 mg P) to 100-mL volumetric flasks. Add 20 mL of $HClO_4$, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 100-mL borosilicate glass volumetric flask. Proceed 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 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 30 mL of Phosphorus Standard Solution C (1 mL = 0.10 mg P) to 100-mL volumetric flasks. Add 20 mL of $HClO_4$, 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 Select and weigh a sample in accordance with the following:

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

Transfer it to a 250-mL Erlenmeyer flask.

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

28.1.2.1 Add 15 mL of a freshly prepared mixture of 1 volume of 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 white fumes and then, without delay, fume strongly enough to cause the white fumes to clear the neck of the flask, and continue at this rate for 1 min.

28.1.2.2 Cool the solution, add 60 mL of $HClO_4$ (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.

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

28.1.3.1 Crush the material in an iron mortar and weigh only particles passing through a No. 50 (300-µm) sieve. Transfer the weighed sample to a 250-mL Erlenmeyer flask. Add 15 mL of HNO_3 and 5 mL of HBr. Heat until dissolution is complete. Add 10 mL of $HClO_4$, evaporate to copious white fumes; then, without delay, fume strongly enough to cause the white fumes to clear the neck of the flask, and continue at this rate for 1 min.

28.1.3.2 Cool the solution, add 60 mL of $HClO_4$ (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 28.1.2.2 or 28.1.3.2, 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 28.1.2.2 or 28.1.3.2. 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.

TABLE 2 Statistical Information—Phosphorus

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

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 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 2.

SULFUR BY THE GRAVIMETRIC METHOD

This test method, which consisted of Sections 30 through 36, was discontinued in 1988.

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

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

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

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

47. Summary of Test Method

47.1 After dissolution of the sample, silicic acid is dehydrated by fuming with H_2SO_4 or $HClO_4$. The solution is filtered, and the impure silica is ignited and weighed. The silica is then volatilized with HF. The residue is ignited and weighed; the loss in weight represents silica.

48. Interferences

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

49. Reagents

49.1 The analyst should 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 5) to each of two 400-mL beakers. To one of the beakers transfer an additional 50 mL of $HClO_4$. Using a pipet, transfer 20 mL of Na_2SiO_3 solution (1 mL = 1.00 mg Si) to each of the beakers. Evaporate the solutions to fumes and heat for 15 min to 20 min at such a rate that $HClO_4$ refluxes on the sides of the beakers. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C).

NOTE 5—The 15-mL addition of $HClO_4$ can be from the same lot as the one to be tested. Once a lot has been established as having less than 0.0002 % silicon, it should preferably be used for the 15-mL addition in all subsequent tests of other lots of acid.

49.2.3 Add paper pulp and filter immediately, using 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.

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

50. Procedure

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

Silicon, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dehydrating Acid, mL H_2SO_4 (1 + 4)	Dehydrating Acid, mL $HClO_4$
0.10 to 1.00	4.0	4	150	60
1.00 to 2.00	3.0	3	100	50
2.00 to 4.00	2.0	2	100	40
4.00 to 6.00	1.0	1	100	40

Transfer it to a 400-mL beaker or a 300-mL porcelain casserole.

50.2 If the sample type is other than white iron, proceed as directed in 50.3; treat samples of white iron as directed in 50.2.1.

50.2.1 Crush the material in an iron mortar and use only particles passing through a No. 100 (150-µm) sieve. Add 30 mL of HNO_3 and 10 mL of HBr. When the dissolution reaction becomes passive, decant the bulk of the solution to a 400-mL beaker and crush the remaining insoluble matter in the original beaker with a glass rod. Add 20 mL of HNO_3 and 10 mL of HBr, and heat gently until dissolution is complete. Combine the two portions of the solution and add the amount of H_2SO_4 or $HClO_4$ specified in 50.1.

50.2.2 *Sulfuric Acid Dehydration:*

50.2.2.1 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.

50.2.3 *Perchloric Acid Dehydration:*

50.2.3.1 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.

50.3 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 the $HClO_4$ dehydration method 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.

50.4 Add 15 mL of HNO_3 to the filtrate, stir, and evaporate in accordance with either 50.2.2 or 50.2.3, depending upon the dehydrating acid used. Filter immediately, using a low-ash, 9-cm-100-porosity filter paper, and wash in accordance with 50.3.

50.5 Transfer the paper and precipitate to the reserved platinum crucible. Dry the papers and then heat the crucible at

TABLE 3 Statistical Information—Silicon

Test Specimen	Silicon Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
$HClO_4$ Dehydration			
1. Cast iron 1.2Ni-0.3Cr-0.8 Mo (NIST 107b, 1.35 Si)	1.36	0.02	0.02
2. Cast iron (NIST 4i, 1.45 Si)	1.45	0.04	0.05
3. Cast iron 1.07Ni-0.32Cr (NIST 82a, 2.07 Si)	2.08	0.04	0.05
4. Cast iron (NIST 5k, 2.08 Si)	2.08	0.03	0.05
5. Cast iron, high (0.79) phosphorus (NIST 7g, 2.41 Si)	2.40	0.04	0.07
6. White cast iron (NIST 1176, 3.19 Si)	3.20	0.03	0.10
H_2SO_4 Dehydration			
1. Cast iron 1.2Ni-0.3Cr-0.8Mo (NIST 107b, 1.35 Si)	1.36	0.02	0.03
2. Cast iron (NIST 4i, 1.45 Si)	1.45	0.04	0.06
3. Cast iron 1.07Ni-0.32Cr (NIST 82a, 2.07 Si)	2.08	0.04	0.04
4. Cast iron (NIST 5k, 2.08 Si)	2.08	0.04	0.05
5. Cast iron, high (0.79) phosphorus (NIST 7g, 2.41 Si)	2.41	0.03	0.05

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.

50.6 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

52.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 3. Although samples covered by this method with silicon compositions near the extreme limits of the scope were not available for testing, the precision data obtained for low-alloy steels by Test Methods E350 should apply at the lower limit.

COBALT BY THE ION-EXCHANGE-POTENTIOMETRIC TITRATION METHOD

53. Scope

53.1 This test method covers the determination of cobalt in compositions from 2.0 % to 4.5 %.

54. Summary of Method

54.1 Cobalt is separated from interfering elements by selective elution from an anion-exchange column using HCl. The cobalt is oxidized to the trivalent state with ferricyanide, and the excess ferricyanide is titrated potentiometrically with cobalt solution.

55. Interferences

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

56. Apparatus

56.1 *Ion-Exchange Column,* approximately 25 mm in diameter and 300 mm in length, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. A Jones Reductor, may be adapted to this method. A reservoir for the eluants may be added at the top of the column.

56.2 *pH meter,* with a platinum and a saturated calomel electrode.

57. Reagents

57.1 *Ammonium Citrate Solution* (200 g/l)—Dissolve 200 g of di–ammonium hydrogen citrate in water and dilute to 1 L.

57.2 *Cobalt, Standard Solution* (1mL = 1.5 mg of Co).

57.2.1 *Preparation*—Dry a weighing bottle in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer 3.945 g of cobalt sulfate ($CoSO_4$)[25] 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 desiccator, stopper the bottle, and weigh. The difference in weight is the 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 20 mL of HNO_3, and heat to dissolve the salts. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

57.2.2 *Standardization*—Calculate the cobalt concentration as follows:

$$\text{Cobalt, mg/mL} = \text{weight of } CoSO_4, \text{ g}, \times 0.38026 \quad (5)$$

57.3 *Ion-Exchange Resin:*[6]

57.3.1 Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a nominal crosslinkage of 8 %, and 200-nominal to 400-nominal mesh size. 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 sufficient time (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, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 min to 6 min, decant 150 mL to 175 mL of the

[6] Available from the Dow Chemical Co., Midland, MI.

suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

57.3.2 Prepare the column as follows: Place a 10-mm to 20-mm layer of glass wool or polyvinyl 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 polyvinyl chloride plastic fiber at the top of the resin bed to protect it from being carried into suspension when the solutions are added. While passing a minimum of 35 mL of HCl (7 + 5) through the column, with the hydrostatic head 100 mm above the top of the resin bed, adjust the flow rate to not more than 3.0 mL per min. Drain to 10 mm to 20 mm above the top of the resin bed and then close the lower stopcock.

NOTE 6—The maximum limits of 0.125 g of cobalt and 0.500 g in the sample solution take into account the exchange capacity of the resin, the physical dimensions of the column, and the volume of eluants.

57.4 *Potassium Ferricyanide, Standard Solution* (1 mL = 3.0 mg of Co):

57.4.1 Dissolve 16.68 g of potassium ferricyanide ($K_3Fe(CN)_6$) in water and dilute to 1 L. Store the solution in a dark-colored bottle. Standardize the solution each day before use as follows: Transfer from a 50-mL buret approximately 20 mL of $K_3Fe(CN)_6$ solution to a 400-mL beaker. Record the buret reading to the nearest 0.01 mL. Add 25 mL of water, 10 mL of ammonium citrate solution, and 25 mL of NH_4OH. Cool to 5 °C to 10 °C, and maintain this temperature during the titration. Transfer the beaker to the potentiometric titration apparatus. While stirring, titrate the $K_3Fe(CN)_6$ with the cobalt solution (1 mL = 1.5 mg Co) using a 50-mL buret. Titrate at a fairly rapid rate until the end point is approached, and then add the titrant in 1-drop increments through the end point. After the addition of each increment, record the buret reading and voltage when equilibrium is reached. Estimate the buret reading at the end point to the nearest 0.01 mL by interpolation.

57.4.2 Calculate the cobalt equivalent as follows (Note 7):

$$\text{Cobalt equivalent, mg/mL} = (A \times B)/C \quad (6)$$

where:

A = cobalt standard solution required to titrate the potassium ferricyanide solution, mL,
B = cobalt standard solution, mg/mL, and
C = potassium ferricyanide solution, mL.

NOTE 7—Duplicate or triplicate values should be obtained for the cobalt equivalent. The values obtained should check within 1 part per thousand to 2 parts per thousand.

58. Procedure

58.1 Transfer a 0.50-g sample, weighed to the nearest 0.1 mg, to a 150-mL beaker. Add 20 mL of a mixture of 5 parts of HCl and 1 part of HNO_3 (Note 8). Cover the beaker and digest at 60 °C to 70 °C until the sample is decomposed. Rinse and remove the cover. Place a ribbed cover glass on the beaker, and evaporate the solution nearly to dryness, but do not bake. Cool, add 20 mL of HCl (7 + 5), and digest at 60 °C to 70 °C until salts are dissolved (approximately 10 min).

NOTE 8—Other ratios and concentrations of acids, with or without the addition of 1 mL to 2 mL of HF, are used for the decomposition of special grades of alloys.

58.2 Cool to room temperature and transfer the solution to the ion-exchange column. Place a beaker under the column and open the lower stopcock. When the solution reaches a level 10 mm to 20 mm above the resin bed, rinse the original beaker with 5 mL to 6 mL of HCl (7 + 5) 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 (7 + 5) 2 times 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 3.0 mL/min and add HCl (7 + 5) to the column until a total of 175 mL to 185 mL of solution (sample solution and washings) containing mainly chromium, manganese, and nickel is collected (Note 9). When the solution in the column reaches a level 10 mm to 20 mm above the resin bed, discard the eluate and then use a 400-mL beaker for the collection of the cobalt eluate.

NOTE 9—To prevent any loss of cobalt, the leading edge of the cobalt band must not be allowed to proceed any farther than 25 mm from the bottom of the resin. Normally, when the cobalt has reached this point in the column, the chromium, manganese, and nickel have been removed. Elution can be stopped at this point, although the total volume collected may be less than 175 mL.

58.3 Add HCl (1 + 2) to the column and collect 165 mL to 175 mL of the solution while maintaining the 3.0 mL/min flow rate. Reserve the solution. If the sample solution did not contain more than 0.200 g of iron, substitute a 250-mL beaker and precondition the column for the next sample as follows: Drain the remaining solution in the column to 10 mm to 20 mm above the resin bed, pass 35 mL to 50 mL of HCl (7 + 5) through the column until 10 mm to 20 mm of the solution remains above the resin bed, then close the lower stopcock. If the sample solution contained more than 0.200 g of iron, or if the column is not to be used again within 3 h, discard the resin and recharge the column as directed in 57.3.

58.4 Add 30 mL of HNO_3 and 15 mL of $HClO_4$ to the solution from 58.3 and evaporate to fumes of $HClO_4$. Cool, add 25 mL to 35 mL of water, boil for 1 min to 2 min, cool, and add 10 mL of ammonium citrate solution.

58.5 Using a 50-mL buret, transfer to a 400-mL beaker a sufficient volume of $K_3Fe(CN)_6$ solution to oxidize the cobalt and to provide an excess of about 5 mL to 8 mL. Record the buret reading to the nearest 0.01 mL. Add 50 mL of NH_4OH and cool to 5 °C to 10 °C. Transfer the beaker to the potentiometric titration apparatus and maintain the 5 °C to 10 °C temperature during the titration.

58.6 While stirring, add the sample solution to the solution from 58.5, rinse the beaker with water, and add the rinsings to the solution (Note 10). Using a 50-mL buret, titrate the excess

TABLE 4 Statistical Information—Cobalt

Test Specimen	Cobalt Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E352	1.86	0.05	0.12
2. No. 2, E352	4.82	0.08	0.11

$K_3Fe(CN)_6$ with the cobalt solution (1 mL = 1.5 mg Co), at a fairly rapid rate until the end point is approached, and then add the titrant in 1-drop increments through the end point. After the addition of each increment, record the buret reading and voltage when equilibrium is reached. Estimate the buret reading at the end point to the nearest 0.01 mL by interpolation.

NOTE 10—For a successful titration, the sample solution must be added to the excess $K_3Fe(CN)_6$ solution.

59. Calculation

59.1 Calculate the percentage of cobalt as follows:

$$\text{Cobalt, \%} = [(AB - CD)/E] \times 100 \quad (7)$$

where:

A = standard potassium ferricyanide solution, mL,
B = cobalt equivalent of the standard potassium ferricyanide solution,
C = cobalt standard solution, mL,
D = concentration of cobalt standard solution, mg/mL, and
E = sample used, mg.

60. Precision

60.1 Although samples covered by this method were not available for testing, the precision data obtained for other types of alloys, using the method indicated in Table 4, should apply.

COBALT BY THE NITROSO-R-SALT SPECTROPHOTOMETRIC METHOD

61. Scope

61.1 This method covers the determination of cobalt in compositions from 0.01 % to 4.50 %.

62. Summary of Method

62.1 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 HNO_3 stabilizes the cobalt complex and also destroys certain interfering complexes. Spectrophotometric measurement is made at approximately 520 nm.

63. Concentration Range

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

NOTE 11—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.

64. Stability of Color

64.1 The color is stable for at least 3 h.

65. Interferences

65.1 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 HNO_3.

66. Reagents

66.1 *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 ($CoSO_4$)[7] 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 concentration (in milligrams of cobalt per millilitre) of the final solution is the exact weight of $CoSO_4$ taken multiplied by 0.076046.

66.2 *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.

66.3 *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.

66.4 *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.

67. Preparation of Calibration Curve

67.1 *Calibration Solutions*—Using pipets, transfer 2 mL, 5 mL, 10 mL, 15 mL, 20 mL, 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 acordance with 67.3.

67.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed in accordance with 67.3.

67.3 *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.

67.4 *Spectrophotometry:*

67.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction with water using absorption cells with a 1-cm light

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

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 (67.2).

67.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (67.2) to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 520 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

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

68. Procedure

68.1 *Test Solution:*

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

Cobalt, %	Sample Weight, g	Tolerance in Sample Weight, mg	Volume of Sample Solution, mL
0.01 to 0.30	0.500	0.2	100
0.25 to 1.00	0.375	0.2	250
0.90 to 3.00	0.125	0.1	250
2.80 to 5.00	0.150	0.1	500

Transfer it to a 100-mL, 250-mL, or 500-mL borosilicate glass volumetric flask.

68.1.2 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. Add 50 mL to 55 mL of water and cool.

68.1.3 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 12). 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 68.3.

NOTE 12—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.

68.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed in accordance with 68.3.

68.3 *Color Development*—Proceed in accordance with 67.3.

68.4 *Spectrophotometry*—Take the spectrophotometric reading of the test solution in accordance with 67.4.

TABLE 5 Statistical Information—Cobalt

Test Specimen	Cobalt Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E350	0.011	0.005	0.007
2. No. 2, E352	1.87	0.09	0.13
3. No. 3, E352	4.94	0.08	0.17

69. Calculation

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

$$\text{Cobalt},\% = A/(B \times 10) \quad (8)$$

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.

70. Precision

70.1 Although samples covered by this method were not available for testing, the precision data obtained for other types of alloys, using the methods indicated in Table 5, should apply.

MAGNESIUM BY THE ATOMIC ABSORPTION METHOD

71. Scope

71.1 This method covers the determination of magnesium in compositions from 0.002 % to 1.10 %.

72. Summary of Method

72.1 A HCl solution of the sample is aspirated into the air-acetylene flame. The radiation from a magnesium hollow cathode tube at 285.2 nm is passed through the flame, and the attenuation is measured. The spectrometer is calibrated with solutions of known concentrations of magnesium in the presence of iron. The appropriate concentrations of the calibration solutions, iron solution, and test solutions are determined on the basis of the sensitivity of the instrument.

73. Concentration Range

73.1 The concentration range (nominal, 0.01 mg/100 mL to 0.06 mg/100 mL) is dependent upon the sensitivity of the instrument; the sensitivity is determined as a numerical factor that is used to adjust the concentrations employed. The recommended upper limit is one that gives a reading of approximately 0.400 absorbance, or its equivalent.

74. Interferences

74.1 Inteferences by such elements as phosphorus and aluminum are overcome by providing a high concentration of strontium. The interference of iron, mainly due to its effect on the flow rate of the solution into the burner, is overcome by providing approximately the same concentration of iron in the calibration solutions and in the test solutions.

75. Apparatus

75.1 An atomic absorption spectrometer capable of resolving the 285.2 nm line, equipped with a magnesium hollow cathode tube whose radiation is modulated, with a detector system tuned to the same frequency, and with a premix burner that uses air and acetylene. To determine the sensitivity factor of the instrument, proceed as directed in 75.1.1 through 75.1.4.

75.1.1 Transfer 15 mg ± 0.5 mg of magnesium, weighed to the nearest 0.1 mg, to a 250-mL borosilicate glass volumetric

flask. Add 20 mL of HCl (1 + 1). When dissolution is complete, cool, dilute to volume, and mix. Using a pipet, transfer 10 mL to a 1-L volumetric flask, add 10 mL of HCl, dilute to volume, and mix. Store the solution in a polyethylene bottle. Do not use a solution that is more than two weeks old.

75.1.2 With the hollow cathode tube in position, energized and stabilized, locate the wavelength setting in the vicinity of 285.2 nm that gives the maximum response of the detector system.

75.1.3 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero with water. Aspirate the magnesium solution, adjust the height of the burner, the air and fuel pressures and their flow rates, and the aspiration rate of the solution to obtain maximum response. Record the absorbance of the magnesium solution.

75.1.4 Calculate the sensitivity factor as follows, and round the value to the nearest 0.05:

$$\text{Sensitivity factor, } F = (0.400 \times A)/(15 \times B) \quad (9)$$

where:

A = magnesium weighed, mg, and
B = absorbance value found in 75.1.3.

76. Reagents

76.1 *Iron Solution* ((10 × *F*)g/L)—Select a lot of iron containing not more than 0.0005 % magnesium (Note 13). Transfer (5 × *F*)g (75.1.4), weighed to the nearest 10 mg, to a 400-mL beaker, add 6 mL of HCl (1 + 1) for each 1 g of iron plus 25 mL of HCl (1 + 1) and 10 mL of HNO_3. Cover the beaker, and, when the vigorous reaction subsides, digest until action ceases. Substitute a ribbed cover glass, evaporate to dryness, and bake at moderate heat for 5 min. Add 25 mL of HCl and heat gently until salts are dissolved. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix.

NOTE 13—The suitability of the iron and the strontium chloride (76.4) in combination may be determined by evaluating the correction required to derive net absorbance values in 77.4. To accomplish this, read from the calibration curve, plotted as directed in 77.4, the milligrams of magnesium per 100 mL of the solution to which no magnesium was added. If the value does not exceed 0.0005 % of (mg Fe + mg Sr), both reagents may be assumed to be suitable. If the value exceeds that limit, apply the procedures in the Appendix to screen lots of iron and strontium chloride individually to find one suitable for use.

76.2 *Magnesium, Standard Solution A* (1 mL = (0.2 × *F*)mg Mg)—Transfer (0.200 × *F*)*g* (75.1.4) of magnesium (purity: 99.9 % minimum) to a 1-L borosilicate glass volumetric flask. Add 20 mL of HCl (1 + 1). When dissolution is complete, cool, dilute to volume, and mix. Store in a polyethylene bottle.

76.3 *Magnesium, Standard Solution B* (1 mL = (0.002 × *F*)mg Mg)—Using a pipet, transfer 10 mL of magnesium solution A to a 1-L volumetric flask, add 10 mL of HCl, dilute to volume, and mix. Store in a polyethylene bottle. Do not use a solution that is more than two weeks old.

76.4 *Strontium Solution* ((33 × *F*)*g* Sr/L)—Select a lot of strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) containing not more than 0.0002 % magnesium (approximately 0.0005 % with respect to Sr) (Note 13). Transfer (100 × *F*)*g* (75.1.4) to a 1-L volumetric flask, dissolve in 800 mL of water, dilute to volume, and mix.

77. Preparation of Calibration Curves

77.1 *Calibration Solutions for Compositions from 0.002 % to 0.03%*—Using pipets, transfer 0 mL, 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 30 mL of magnesium standard solution B to 100-mL volumetric flasks; add 20 mL of iron solution and 5 mL of strontium solution. Dilute to volume, and mix. Store in polyethylene bottles. Do not use solutions that are more than two weeks old.

NOTE 14—Prepare the test solution (78.1) and the reagent blank solution (78.2), and have them ready to aspirate immediately after aspirating the calibration solutions.

77.2 *Calibration Solutions for Compositions from 0.025 % to 0.10 %*—Proceed as directed in 77.1 adding 6 mL of iron solution instead of 20 mL (see Note 14).

77.3 *Spectrometry for Compositions from 0.002 % to 0.03 %:*

77.3.1 With the magnesium hollow cathode tube in position, energized and stabilized, locate the wavelength setting in the vicinity of 285.2 nm that gives the maximum response of the detector system.

77.3.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the magnesium solution with the highest concentration from the series prepared as directed in 77.1, 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 15). If the absorbance is less than 0.350 or greater than 0.450, recalculate the sensitivity factor by dividing 0.400 by the observed absorbance and multiplying by the factor previously used. Substitute the value for the one found in 75.1.4, and repeat the preparation of reagents and calibration solutions to conform to this factor.

NOTE 15—Recalibration is required whenever these parameters are changed.

77.3.3 Aspirate the magnesium solution used in 77.3.2 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:

$$s = (A - B) \times 0.40 \quad (10)$$

where:

A = the highest of the six values found, and
B = the lowest of the six values found.[8]

77.3.4 Beginning with the solution to which no magnesium was added in 77.1, 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 77.3.3 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

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

example, deposits in the burner or clogged capillary), correct it, and repeat the steps as directed in 77.3.1 – 77.3.4.

77.3.5 Proceed immediately as directed in 78.3.

77.4 *Calibration Curve for Compositions from 0.002 % to 0.03%*—Subtract the absorbance value found for the solution to which no magnesium was added from the value recorded for each of the other solutions. Plot the net absorbance values against milligrams of magnesium per 100 mL.

77.5 *Spectrometry for Compositions from 0.025 % to 0.10 %:*

77.5.1 Proceed as directed in 77.3.1 – 77.3.4 with the solutions prepared as directed in 77.2.

77.5.2 Proceed immediately as directed in 78.3.

77.6 *Calibration Curve for Compositions from 0.025 % to 0.10 %*—Proceed as directed in 77.4.

78. Procedure

78.1 *Test Solution:*

78.1.1 Transfer $(1.00 \times F)g$ (75.1.4) of sample, weighed to the nearest 1 mg, to a 250-mL beaker.

78.1.2 If the sample type is other than white iron, add 6 mL of HCl (1 + 1) per gram of sample plus 10 mL of HCl (1 + 1) and 5 mL of HNO_3. Cover the beaker and heat as required until action ceases. Substitute a ribbed cover glass, evaporate the solution to dryness, and bake at moderate heat for 5 min. Treat samples of white iron as directed in 78.1.2.1.

78.1.2.1 Crush the material in an iron mortar and use only particles passing through a No. 100 (150-µm) sieve. Transfer the sample to a 250-mL beaker. Cover the beaker and add 10 mL of HNO_3 and 10 mL of HBr. Heat cautiously to dissolve the sample. Substitute a ribbed cover glass, evaporate the solution to a syrupy consistency, add 10 mL of HCl, and evaporate to dryness. Proceed as directed in 78.1.3.

78.1.3 Add 10 mL of HCl and heat gently until salts are dissolved. Add 50 mL of water and digest for 5 min. Cool, transfer to a 250-mL volumetric flask, dilute to volume, and mix. Filter a portion through a dry, coarse paper, discarding the first 10 mL to 15 mL. Collect approximately 100 mL in a dry beaker. Using a pipet, transfer 50 mL if the expected magnesium composition is 0.002 % to 0.030 %, or 15 mL if the magnesium composition is 0.025 % to 0.10 %, to a 100-mL volumetric flask, add 5 mL of strontium solution, dilute to volume, and mix. If the solution is to be retained more than 8 h before proceeding as directed in 78.3, transfer it to a polyethylene bottle. Do not use a solution that is more than two weeks old.

78.2 *Reagent Blank:*

78.2.1 Prepare a reagent blank by treating the amounts of all reagents, with sample omitted, as directed in 78.1.2 and 78.1.3, and taken from the same lots used to prepare the test solution.

78.2.2 Prepare a calibration solution to be used to evaluate the reagent blank (iron absent) by diluting 2.0 mL of magnesium standard solution B to 100 mL in a volumetric flask. Store in a polyethylene bottle. Do not use a solution that is more than two weeks old.

TABLE 6 Statistical Information—Magnesium

Test Specimen	Magnesium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Cast iron (NIST 4i, 0.002 Mg, min)[A]	0.0022	0.0003	0.0006
2. Cast iron (NIST 4i, 0.005 Mg, min)[A]	0.0052	0.0004	0.0005
3. Nodular cast iron (B.C.S. No. SS41, 0.012 Mg)	0.0125	0.0011	0.0023
4. Nodular cast iron (B.C.S. No. SS42, 0.024 Mg)	0.0225	0.0012	0.0014
5. Nodular cast iron	0.0304[B]	0.0008	0.0029
6. Nodular cast iron	0.0307	0.0010	0.0017
7. Nodular cast iron (B.C.S. No. SS43, 0.039 Mg)	0.0395	0.0014	0.0034
8. Nodular cast iron (B.C.S. No. SS44, 0.053 Mg)	0.0522	0.0019	0.0029
9. Ductile cast iron, Ni 20 (NIST 341, 0.068 Mg)	0.0691	0.0035	0.0036
10. Nodular cast iron (B.C.S. No. SS45, 0.078 Mg)	0.0785	0.0027	0.0033
11. Nodular cast iron[C] (NIST 4i + B.C.S. No. SS45 (mixed), 0.10 Mg, min)	0.0993	0.0050	0.0046

[A] Synthetic samples prepared by adding appropriate amounts of magnesium solution B (76.3) to NIST 4i (Mg found to be less than 0.0001 by method described in the Appendix) and then proceeding with dissolution.
[B] Same sample; data based on calibration curves in 69.4 and 76.6, respectively.
[C] NIST 4i/B.C.S. No. SS45 (0.128 Mg) = 0.781/0.219.

78.3 *Spectrometry*—Aspirate the test solution, and record the absorbance; aspirate the reagent blank solution (78.2.1) and the associated calibration solution (78.2.2) and record the absorbance values.

NOTE 16—After each group of four or fewer test solutions and reagent blank solutions has been aspirated, apply the test with the standard solution as directed in 77.3.4, 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 77.3.4, or by more than 0.01 multiplied by the average of the six values used to calculate *s*, whichever is greater, determine the cause, for example, deposits in the burner or clogged capillary. Correct the deficiency, repeat the calibration procedure, and recheck the readings of the test solutions and reagent blank solution.

79. Calculation

79.1 Convert the absorbance value of the test solution to milligrams of magnesium per 100 mL of the final test solution using the appropriate calibration curve (77.4 and 77.6).

79.2 Calculate the correction to be applied for the reagent blank as follows:

$$\text{Milligrams of magnesium in 100 mL of the final reagent blank solution} = \left[(0.004\,A)/B\right] \times F \quad (11)$$

where:

A = absorbance found for solution prepared as directed in 78.2.1, and

B = absorbance found for solution prepared as directed in 78.2.2.

79.3 Calculate the percentage of magnesium as follows:

$$\text{Magnesium, \%} = (A - B)/(C \times 100) \quad (12)$$

where:

A = magnesium found in 100 mL of the final test solution (79.1), mg,

B = magnesium found in 100 mL of the final reagent blank solution (79.2), mg, and
C = sample represented in 100 mL of the final test solution, g.

80. Precision

80.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 6. The sensitivity factors of the instruments used ranged from 1.0 to 1.2; six laboratories reported *s* values of 0.001 or less, while the highest was 0.003. (Test specimens designated "B.C.S." (British Chemical Standards) are issued in rod form by the Bureau of Analyzed Samples.)

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81. Scope

81.1 This method covers the determination of copper in compositions from 0.03 % to 7.50 %.

82. Summary of Method

82.1 Copper 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 (Note 17). Chloride ions are removed from the filtrate, and copper, as the metal, is deposited on a platinum cathode.

NOTE 17—This method describes the preliminary separations for the determination of tin by the sulfide-iodatimetric titration method.

83. Interferences

83.1 Ammonium salts may cause the copper deposit to be spongy and subject to air oxidation while drying in the oven. If this occurs the copper should be dissolved from the platinum cathode and redeposited (Note 20).

84. Apparatus

84.1 *Electrodes*—Platinum electrodes of the stationary type are recommended as described in 84.2 and 84.3, but strict adherence to the exact size and shape of the electrodes is not mandatory. When agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes, generally available, may be employed. The surface of the platinum electrodes should be smooth, clean, and bright to promote uniform deposition and good adherence. Sandblasting is not recommended.

84.2 *Cathodes*—Platinum cathodes may be formed either from plain or perforated sheets or from wire gauze, and may be either open or closed cylinders. Gauze cathodes are recommended, and shall be made preferably from 50-mesh gauze woven from wire approximately 0.21 mm (0.0085 in.) in diameter. The cathode should be stiffened by doubling the gauze for about 3 mm at the top and the bottom of the cylinder or by reinforcing the gauze at the top and bottom with a platinum band or ring. The cylinder should be approximately 30 mm in diameter and 50 mm in height. The stem should be made from a platinum alloy wire such as platinum-iridium, platinum-rhodium, or platinum-ruthenium, having a diameter of approximately 1.30 mm. It should be flattened and welded the entire length of the gauze. The over-all height of the cathode should be approximately 130 mm. A cathode of these dimensions will have a surface area of 135 cm^2 exclusive of the stem.

84.3 *Anodes*—Platinum anodes may be of the spiral type when anodic deposits are not being determined, or if the deposits are small (as in the electrolytic determination of lead when it is present in amounts not over 0.2 %). When used in analyses where both cathodic and anodic plates are to be determined, the anodes should be of wire gauze. Spiral anodes should be made from 1.00-mm or larger platinum wire formed into a spiral of seven turns having a height of approximately 50 mm and a diameter of 12 mm, the over-all height being approximately 130 mm. A spiral anode of this description will have a surface area of 9 cm^2. Platinum gauze anodes should be made of the same material and of the same general design as platinum gauze cathodes. The anode cylinder should be approximately 12 mm in diameter and 50 mm in height and the over-all height of the anode should be approximately 130 mm. A gauze anode of these dimensions will have a surface area of 54 cm^2. Both areas are exclusive of the stem.

85. Reagents

85.1 *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).

85.2 *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).

85.3 *Sulfamic Acid* ($H(NH_2)SO_3$).

86. Procedure

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

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.03 to 1.0	10	10
1.0 to 2.5	5	5
2.5 to 5.0	2	2
5.0 to 7.5	1	1

Transfer it to a 1-L Erlenmeyer flask (see 86.2.1 for white iron).

86.2 If the sample type is other than white iron, proceed as directed in 86.3.1 through 86.3.22; treat samples of white iron as directed in 86.2.1 and 86.2.2.

86.2.1 Crush the material in an iron mortar and weigh only particles passing through a No. 100 (150-µm) sieve. Add 30 mL of HNO_3 and 10 mL of HBr. Heat cautiously to start dissolution of the sample. When the reaction becomes passive, add HF dropwise until dissolution is complete.

86.2.2 Evaporate the solution to a syrupy consistency and cool. Add 115 mL of HCl (1 + 2) and heat until salts are dissolved. Boil the solution 2 min to 3 min.

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

86.2.4 If the solution contains insoluble matter, add paper pulp, digest 15 min to 20 min, and then filter through medium filter paper into a 1-L Erlenmeyer flask. Suction may be used if necessary. Wash the filter 4 times or 5 times with water. Reserve the filtrate. Proceed as directed in 86.2.4.1 or 86.2.4.2 according to preference, bearing in mind that the latter procedure may be the easier to apply when copious amounts of insoluble matter are encountered.

86.2.4.1 Transfer the paper and precipitate to the original flask, add 20 mL of HNO_3 and 10 mL of $HClO_4$, heat moderately to oxidize organic matter, and finally heat to mild fumes of $HClO_4$. Cool the solution, add 1 mL to 2 mL of HF, and repeat the fuming.

86.2.4.2 Transfer the paper and precipitate to a platimum crucible. Dry the paper and heat at 600 °C until the carbon is removed. Finally ignite for 30 min at 1100 °C. Cool, add 3 drops of HNO_3 and 1 mL to 2 mL of HF, and evaporate to dryness. Add 10 mL of HNO_3 (1 + 1) and digest at 90 °C to 100 °C for 5 min. Transfer the contents of the crucible to the original flsk, add 10 mL of $HClO_4$, and heat to mild fumes of $HClO_4$.

86.2.5 Cool the solution from 86.2.4.1 or 86.2.4.2, add 100 mL of water and digest at or near boiling for about 45 min.

86.2.6 If tungsten is present, as indicated by the presence of a bright yellow precipitate of tungstic acid, add a slight excess of NH_4OH and 20 g of tartaric acid. When the tartaric acid has dissolved, again add a slight excess of NH_4OH and digest near the boiling point until dissolution is complete, or nearly so.

86.2.7 Add 5 mL of H_2SO_4 and heat at 85 °C to 95 °C for 30 min. If insoluble matter persists, repeat the steps as directed in 86.2.4.1 through 86.2.7. When dissolution is complete, combine the solution with the filtrate reserved in 86.2.4.

86.2.8 If the volume is less than 600 mL, dilute the solution approximately to that volume and treat with H_2S; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 h to 15 h.

86.2.9 Add paper pulp and filter using a fine filter paper. Wash the filter thoroughly with ammonium sulfate-hydrogen sulfide wash solution. Discard the filtrate.

86.2.10 Transfer the filter paper and precipitate to the original flask, add 12 mL of H_2SO_4,and heat to char the paper. Add 20 mL of HNO_3 and evaporate to fumes to destroy organic matter. Add HNO_3 in 1-mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

86.2.11 Cool the solution, rinse the sides of the flask, and repeat the fuming to ensure the complete removal of HNO_3.

86.2.12 Cool, add 100 mL of water, and boil to dissolve the soluble salts. Add 15 mL of HCl, and digest for about 10 min.

86.2.13 Filter through a coarse filter paper into a 400-mL beaker. Wash the filter alternately with hot water and hot HCl (1 + 99). Discard the filter paper.

86.2.14 Add 10 mL of $FeCl_3$ solution to the filtrate. Add just enough NH_4OH (1 + 1) to precipitate the iron, tin, and chromium and to complex the copper (indicated by the formation of a blue color), and then add 1 mL to 2 mL in excess. Add paper pulp, and heat the solution to boiling to coagulate the precipitate. Filter the hot solution through a coarse filter paper, and wash alternately five times each with hot NH_4OH (1 + 99) and water into an 800-mL beaker. Reserve the filter and filtrate. Dissolve the precipitate by washing the filter alternately with hot HCl (1 + 1) and hot water, and reserve the filter paper. Precipitate the iron, tin, and chromium as before. Wash the reserved filter paper three times with hot NH_4OH (1 + 99) and then filter the hot solution into the 800-mL beaker reserved from the first filtration; wash alternately five times each with hot NH_4OH (1 + 99) and water.

NOTE 18—If tin is to be determined by using the same sample, reserve the precipitate and proceed as directed in 94.18 through 94.21.

86.2.15 Acidify the combined filtrates with HNO_3, and evaporate at low heat until salts begin to appear. Remove the beaker from the hot plate and while the solution is still hot add 5 mL of HNO_3. When the reaction has subsided, add another 5 mL of HNO_3 and again wait until the reaction subsides. Continue adding 5-mL increments of HNO_3 in this manner until there is no further reaction with the chloride ions. Cover the beaker with a ribbed cover glass and warm gently until the vigorous evolution of gas ceases. Evaporate to fumes of SO_3. Cool, add 25 mL of water, and heat to dissolve the salts. Cool, transfer to a 250-mL beaker, add 3 mL of HNO_3, and dilute to 175 mL.

86.2.16 With the electrolyzing current off, position the anode and the accurately weighed cathode in the solution so that the gauze is completely immersed. Cover the beaker with a split cover glass.

86.2.17 Stir the solution with an automatic stirrer; start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1 A/dm^2. Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 to 3 A/dm^2 (Note 19). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 19—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm^2, and 2 h to 3 h should be allowed for complete deposition.

86.2.18 Add about 0.5 g of sulfamic acid, rinse the underside of the cover glass and the inside walls of the beaker, and continue the electrolysis for 10 min to 15 min to ensure complete deposition of the copper.

86.2.19 Slowly withdraw the electrodes (or lower the beaker) with the current still flowing, and rinse them with a stream of water from a wash bottle. Return the voltage to zero, and turn off the switch.

86.2.20 Remove the cathode, rinse it thoroughly with water and then with acetone or ethanol. Dry it in an oven at 105 °C to 110 °C for 2 min to 3 min.

NOTE 20—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of HNO_3 and 5 mL of H_2SO_4 in 175 mL of water contained in a 300-mL tail-form beaker. Reverse the polarity of the electrodes, and electrolyze with a current density of 3 A/dm^2 until the copper has been removed from

the original electrode. Reverse the polarity and redeposit the copper on the original electrode as directed in 86.2.16 and 86.2.17. Proceed as directed in 86.2.18 and 86.2.19.

86.2.21 Allow the electrode to cool to room temperature undesiccated, and weigh.

NOTE 21—To prepare the electrode for reuse, immerse it in HNO_3 (1 + 1) to dissolve the deposit of copper, rinse thoroughly with water and then with acetone or ethanol. Dry in an oven, cool to room temperature, and weigh.

86.3 If the sample type is other than white iron, proceed as directed in 86.3.1 through 86.3.22.

86.3.1 Add 115 mL of HCl (1 + 2) plus an additional 9 mL of HCl (1 + 2) and 1 mL of HNO_3 for each gram of sample. Heat until dissolution is complete, and then boil the solution for 2 min to 3 min. If the solution is clear, proceed as directed in 86.3.2 and 86.3.9 through 86.3.22.

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

86.3.3 If the solution contains insoluble matter, add paper pulp, digest 15 min to 20 min, and then filter through medium filter paper into a 1-L Erlenmeyer flask. Suction may be used if necessary. Wash the filter 4 times or 5 times with water. Reserve the filtrate. Proceed as directed in 86.3.4 or 86.3.5 according to preference, bearing in mind that the latter procedure may be the easier to apply when copius amounts of insoluble matter are encountered.

86.3.4 Transfer the paper and precipitate to the original flask, add 20 mL of HNO_3 and 10 mL of $HClO_4$, heat moderately to oxidize organic matter, and finally heat to mild fumes of $HClO_4$. Cool the solution, add 1 mL to 2 mL of HF, and repeat the fuming.

86.3.5 Transfer the paper and precipitate to a platinum crucible. Dry the paper and heat at 600 ºC until the carbon is removed. Finally, ignite for 30 min at 1100 ºC. Cool, add 3 drops of HNO_3 and 1 mL to 2 mL of HF, and evaporate to dryness. Add 10 mL of HNO_3 (1 + 1) and digest at 90 ºC to 100 ºC for 5 min. Transfer the contents of the crucible to the original flask, add 10 mL of $HClO_4$, and heat to mild fumes of $HClO_4$.

86.3.6 Cool the solution from 86.3.4 or 86.3.5, add 100 mL of water and digest at or near boiling for about 45 min.

86.3.7 If tungsten is present, as indicated by the presence of a bright yellow precipitate of tungstic acid, add a slight excess of NH_4OH and 20 g of tartaric acid. When the tartaric acid has dissolved, again add a slight excess of NH_4OH and digest near the boiling point until dissolution is complete, or nearly so.

86.3.8 Add 5 mL of H_2SO_4 and heat at 85 ºC to 95 ºC for 30 min. If insoluble matter persists, repeat the steps as directed in 94.4 through 94.7. When dissolution is complete, combine the solution with the filtrate reserved in 94.4.

86.3.9 If the volume is less than 600 mL, dilute the solution approximately to that volume and treat with H_2S; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 h to 15 h.

86.3.10 Add paper pulp and filter using a fine filter paper. Wash the filter thoroughly with ammonium sulfate-hydrogen sulfide wash solution. Discard the filtrate.

86.3.11 Transfer the filter paper and precipitate to the original flask, add 12 mL of H_2SO_4, and heat to char the paper. Add 20 mL of HNO_3, and evaporate to fumes to destroy organic matter. Add HNO_3 in 1 mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

86.3.12 Cool the solution, rinse the sides of the flask, and repeat the fuming to ensure the complete removal of HNO_3.

86.3.13 Cool, add 100 mL of water, and boil to dissolve the soluble salts. Add 15 mL of HCl, and digest for about 10 min.

86.3.14 Filter through a coarse filter paper into a 400 mL beaker. Wash the filter alternately with hot water and hot HCl (1 + 99). Discard the filter paper.

86.3.15 Add 10 mL of $FeCl_3$ solution to the filtrate. Add just enough NH_4OH (1 + 1) to precipitate the iron, tin, and chromium and to complex the copper (indicated by the formation of a blue color), and then add 1 mL to 2 mL in excess. Add paper pulp, and heat the solution to boiling to coagulate the precipitate. Filter the hot solution through a coarse filter paper, and wash alternately five times each with hot NH_4OH (1 + 99) and water into an 800 mL beaker. Reserve the filter and the filtrate. Dissolve the precipitate by washing the filter alternately with hot HCl (1 + 1) and hot water, and reserve the filter paper. Precipitate the iron, tin and chromium as before. Wash the reserved filter paper three times with hot NH_4OH (1 + 99) and then filter the hot solution into the 800 mL beaker reserved from the first filtration; wash alternately five times each with hot NH_4OH (1 + 99) and water.

86.3.16 Acidify the combined filtrates with HNO_3, and evaporate at low heat until salts begin to appear. Remove the beaker from the hot pleate and while the solution is still hot add 5 mL of HNO_3. When the reaction has subsided, add another 5 mL of HNO_3 and again wait until the reaction subsides. Continue adding 5-mL increments of HNO_3 in this manner until there is no further reaction with the chloride ions. Cover the beaker with a ribbed cover glass and warm gently until the vigorous evolution of gas ceases. Evaporate to fumes of SO_3. Cool, add 25 mL of water, and heat to dissolve the salts. Cool, transfer to a 250-mL beaker, add 3 mL of HNO_3, and dilute to 175 mL.

86.3.17 With the electrolyzing current off, position the anode and the accurately weighed cathode in the solution so that the gauze is completely immersed. Cover the beaker with a split cover glass.

86.3.18 Stir the solution with an automatic stirrer; start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1 A/dm^2. Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 A/dm^2 to 3 A/dm^2 (Note 22). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 22—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm^2, and 2 h to 3 h should be allowed for complete deposition.

86.3.19 Add about 0.5 g of sulfamic acid, rinse the underside of the cover glass and the inside walls of the beaker, and continue the electrolysis for 10 min to 15 min to ensure complete deposition of the copper.

86.3.20 Slowly withdraw the electrodes (or lower the beaker) with the current still flowing, and rinse them with a stream of water from a wash bottle. Return the voltage to zero, and turn off the switch.

86.3.21 Remove the cathode, rinse it thoroughly with water and then with acetone or ethanol. Dry it in an oven at 105 °C to 110 °C for 2 min to 3 min.

NOTE 23—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of HNO_3 and 5 mL of H_2SO_4 in 175 mL of water contained in a 300-mL tall-form beaker. Reverse the polarity of the electrodes, and electrolyze with a current density of 3 A/dm^2 until the copper has been removed from the original electrode. Reverse the polarity and redeposit the copper on the original electrode as directed in 86.3.17 and 86.3.18. Proceed as directed in 86.3.19 and 86.3.20.

86.3.22 Allow the electrode to cool to room temperature undesiccated, and weigh.

NOTE 24—To prepare the electrode for reuse, immerse it in HNO_3 (1 + 1) to dissolve the deposit of copper, rinse thoroughly with water and then with acetone or ethanol. Dry in an oven, cool to room temperature, and weigh.

87. Calculation

87.1 Calculate the percentage of copper as follows:

$$\text{Copper, } \% = [((A - B) - (C - D))/E] \times 100 \qquad (13)$$

where:

A = weight of electrode with deposit from the test solution, g,
B = weight of electrode used in A, g,
C = weight of electrode with deposit from the blank solution, g,
D = weight of electrode used in C, g, and
E = sample used, g.

88. Precision

88.1 Six laboratories cooperated in testing this method and obtained eight sets of data summarized in Table 7 for specimens 2, 3, and 4. Although samples covered by the method with copper compositions at approximately 0.03 % and 7.50 % were not available for testing, the precision data at the lower limit should be similar to those obtained for specimen 1 when using the method indicated, and at the upper limit similar to those obtained for specimen 4.

TABLE 7 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Low-alloy steel (NIST 152a, 0.023 Cu)	0.020	0.005	0.006
2. Cast iron (NIST 5k, 1.50 Cu)	1.49	0.02	0.03
3. Cast iron 2Ni	0.678	0.037	0.041
4. Cast iron 15Ni-2Cr-5Cu (NIST 115a, 5.52 Cu)	5.49	0.10	0.10

TIN BY THE SULFIDE-IODOMETRIC TITRATION METHOD

89. Scope

89.1 This method covers the determination of tin in compositions from 0.01 % to 0.35 %.

90. Summary of Method

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

91. Interferences

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

92. Apparatus

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

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

93. Reagents

93.1 *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).

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

93.3 *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).

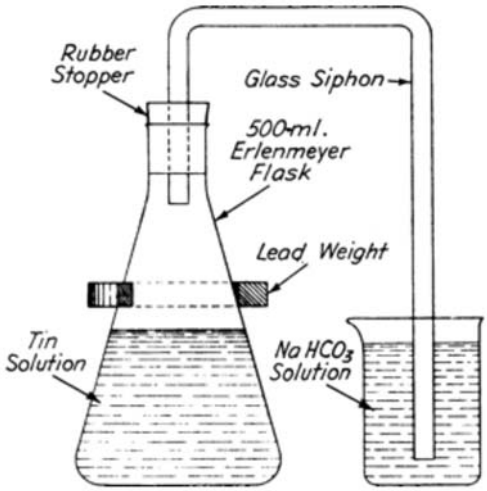

FIG. 1 Apparatus No. 7A for Reduction of Tin

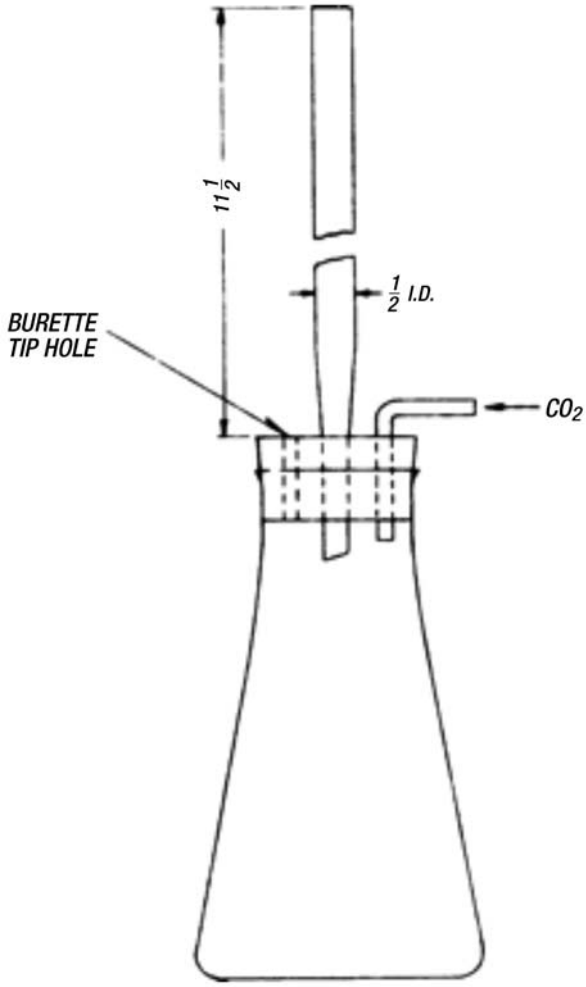

FIG. 2 Apparatus No. 7B for Reduction of Tin

93.4 *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:

93.4.1 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 94.19 to 94.21. Determine a blank using the same amounts of all reagents with tin omitted. Calculate the tin equivalent of the potassium iodate solution as follows:

$$\text{Tin equivalent} = \text{g Sn/mL} = A/(B - C) \quad (14)$$

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.

93.5 *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 93.4 but use 25 mL of the tin solution (1 mL = 0.001 g Sn).

93.6 *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.

93.7 *Test Lead,* granular.

93.8 *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.

94. Procedure

94.1 For the range from 0.01 % to 0.05 % tin, transfer a 10-g sample, (see 94.2.1 for white iron) 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 0.35 %.

94.2 If the sample type is other than white iron, add 115 mL of HCl (1 + 2) plus an addition 9 mL of HCl (1 + 2) and 1 mL of HNO_3 for each gram of sample. Heat until the sample is dissolved, and then boil for 2 min to 3 min. Treat samples of white iron as directed in 94.2.1 and 94.2.2.

94.2.1 Crush the material in an iron mortar and weigh only particles passing through a No. 100 (150-µm) sieve. Add 30 mL of HNO_3 and 10 mL of HBr. Heat cautiously to start dissolution of the sample. When the reaction becomes passive, add HF dropwise until dissolution is complete.

94.2.2 Evaporate the solution to a syrupy consistency and cool. Add 115 mL of HCl (1 + 2) and heat until salts are dissolved. Boil the solution 2 min to 3 min.

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

94.4 If the solution contains insoluble matter, add paper pulp, digest 15 min to 20 min, and then filter through medium filter paper into a 1-L Erlenmeyer flask. Suction may be used if necessary. Wash the filter 4 times or 5 times with water. Reserve the filtrate. Proceed as directed in 94.4.1 or 94.4.2 according to preference, bearing in mind that the latter procedure may be the easier to apply when copius amounts of insoluble matter are encountered.

94.4.1 Transfer the paper and precipitate to the original flask, add 20 mL of HNO_3 and 10 mL of $HClO_4$, heat moderately to oxidize organic matter, and finally heat to mild fumes of $HClO_4$. Cool the solution, add 1 mL to 2 mL of HF, and repeat the fuming.

94.4.2 Transfer the paper and precipitate to a platinum crucible. Dry the paper and heat at 600 ºC until the carbon is removed. Finally ignite for 30 min at 1100 ºC Cool, add 3 drops of HNO_3 and 1 mL to 2 mL of HF, and evaporate to dryness. Add 10 mL of HNO_3 (1 + 1) and digest at 90 ºC to 100 ºC for 5 min. Transfer the contents of the crucible to the original flask, add 10 mL of $HClO_4$, and heat to mild fumes of $HClO_4$.

94.5 Cool the solution from 94.4.1 or 94.4.2, add 100 mL of water and digest at or near boiling for about 45 min.

94.6 If tungsten is present, as indicated by the presence of a bright yellow precipitate of tungstic acid, add a slight excess of NH_4OH and 20 g of tartaric acid. When the tartaric acid has dissolved, again add a slight excess of NH_4OH and digest near the boiling point until dissolution is complete, or nearly so.

94.7 Add 5 mL of H_2SO_4 and heat at 85 ºC to 95 ºC for 30 min. If insoluble matter persists, repeat the steps as directed in 94.4 through 94.7. When dissolution is complete, combine the solution with the filtrate reserved in 94.4.

94.8 If the volume is less than 600 mL, dilute the solution approximately to that volume and treat with H_2S; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 h to 15 h.

94.9 Add paper pulp and filter using a fine filter paper. Wash the filter thoroughly with ammonium sulfate-hydrogen sulfide wash solution. Discard the filtrate.

94.10 Transfer the filter paper and precipitate to the original flask, add 12 mL of H_2SO_4, and heat to char the paper. Add 20 mL of HNO_3, and evaporate to fumes to destroy organic matter. Add HNO_3 in 1 mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

94.11 Cool the solution, rinse the sides of the flask, and repeat the fuming to ensure the complete removal of HNO_3.

94.12 Cool, add 100 mL of water, and boil to dissolve the soluble salts. Add 15 mL of HCl, and digest for about 10 min.

94.13 Filter through a coarse filter paper into a 400 mL beaker. Wash the filter alternately with hot water and hot HCl (1 + 99). Discard the filter paper.

94.14 Add 10 mL of $FeCl_3$ solution to the filtrate. Add just enough NH_4OH (1 + 1) to precipitate the iron, tin, and chromium and to complex the copper (indicated by the formation of a blue color), and then add 1 mL to 2 mL in excess. Add paper pulp, and heat the solution to boiling to coagulate the precipitate. Filter the hot solution through a coarse filter paper, and wash alternately five times each with hot NH_4OH (1 + 99) and water into an 800 mL beaker. Reserve

the filter and the filtrate. Dissolve the precipitate by washing the filter alternately with hot HCl (1 + 1) and hot water, and reserve the filter paper. Precipitate the iron, tin and chromium as before. Wash the reserved filter paper three times with hot NH_4OH (1 + 99) and then filter the hot solution into the 800 mL beaker reserved from the first filtration; wash alternately five times each with hot NH_4OH (1 + 99) and water.

94.15 When two 10-g samples are used, proceed as directed in 94.16 through 94.21. When a single 10-g sample is used, proceed as directed in 94.18 through 94.21.

94.16 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).

94.17 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 times to 10 times with hot NH_4OH (1 + 99). Discard the filtrate.

94.18 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).

94.19 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.

94.20 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 25—If Apparatus in 92.1 is used, ignore the reference to the flow of carbon dioxide in 94.19 and 94.20. 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.

94.21 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 26—If Apparatus in 92.1 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 94.21.

TABLE 8 Statistical Information—Tin

Test Specimen	Tin Found, %	Number of Laboratories	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E350	0.011	5	0.002	0.003
2. No. 3, E350	0.028	5	0.002	0.001
3. No. 5, E350	0.113	7	0.009	0.020

95. Calculation

95.1 Calculate the percent of tin as follows:

$$\text{Tin},\% = [((A - B) \times C)/D] \times 100 \quad (15)$$

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.

96. Precision

96.1 Five to seven laboratories cooperated in testing this method, three of them submitting one additional set of data, all of which are summarized in Table 8. Although samples covered by this method were not available for testing, the precision data obtained for specimens using the method indicated in Table 8 should apply.

TOTAL CARBON BY THE COMBUSTION GRAVIMETRIC METHOD

This method, which consisted of Sections 97 through 107 of this standard, was discontinued in 2012.

CARBON, GRAPHITIC, BY THE DIRECT COMBUSTION INFRARED ABSORPTION METHODS

108. Scope

108.1 This test method covers the determination of graphitic carbon in compositions from 1.0 % to 3.0 %.

NOTE 27—The upper limit of the scope has been set at 3.0 % because sufficient numbers of test materials containing higher graphitic carbon contents were unavailable for testing in accordance with Practice E173. Recognizing that commercial carbon determinators are capable of handling higher compositions, this test method references a calibration procedure up to 4.5 %. Users of this standard are cautioned that the use of this test method above 3.0 % is not supported by interlaboratory testing.

109. Summary of Test Method

109.1 After decomposition of the sample in HNO_3 in the presence of methanol and treatment with HF, the graphitic carbon is removed by filtering through a glass-fiber filter. The glass-fiber filter containing the graphite is placed in the high-frequency induction furnace in a stream of oxygen and the graphite burned to carbon dioxide, which is measured in an infrared absorption apparatus.

110. Interferences

110.1 Elements ordinarily present do not interfere if their compositions are under the maximum limits shown in 1.1. However, some cast iron alloys, when extensively heat treated, yield carbides that are not soluble by this test method and may give high values for graphitic carbon.

111. Apparatus

111.1 *Combustion Apparatus:*

111.1.1 *Infrared Absorption Method*—Induction furnace. See the Infrared Absorption Method A or C of the Total Carbon by the Combustion-Instrumental Method in Test Methods E1019.

111.2 *Filter,*[9] glass-fiber, 47-mm, pore size 0.3 µm.

111.3 *Filtering Apparatus*—For use with 47-mm glass-fiber filters and suitable for use with acids.

112. Reagents

112.1 *Methanol* (CH_3OH).

112.2 *Sodium Hydroxide Wash Solution* (120 g/L)—Cautiously dissolve 60 g of sodium hydroxide (NaOH) in about 200 mL of water. When dissolution is complete, cool, dilute to 500 mL with water, and store in a plastic bottle.

112.3 *Tungsten Accelerator.*

113. Procedure

113.1 *Sample Dissolution:*

113.1.1 Select the sample weight in accordance with the following:

Graphitic Carbon, %	Sample Weight, g
1.0 to 1.5	2
1.5 to 3.0	1

Weigh the sample to the nearest 0.5 mg and transfer to a 250-mL beaker. For cast iron use drillings and for ductile iron, use solid portions approximately 10 mm by 10 mm by 0.3 mm in size.

113.1.2 For the blank determination, weigh and transfer to a 250-mL beaker the same weight of accelerator iron as the weight of sample selected in 113.1.1.

NOTE 28—Duplicate blanks are recommended. It is also recommended that the operator analyze five replicate portions of a standard sample with alloy characteristics and a known graphitic carbon content close to the samples to be analyzed. The repeatability of these analyses should be less than 0.10 % and the average value should agree with the known graphitic carbon content within 0.10 %. If it does not, the test should be repeated until these criteria are met. Calculate repeatability as follows:

$$\text{Repeatability} = 1.41\sqrt{\sum(\bar{x} - x)^2} \quad (16)$$

where:

$\bar{x}$ = average of the five determinations and
x = value of a single determination.

113.1.3 Add 25 mL of methanol, 50 mL of water, and 5 mL of HNO_3. Cover the beaker at once and let stand 12 h to 16 h. Add 20 mL of HNO_3 and let stand until further action ceases. Place on a hot plate heated to 50 °C to 60 °C. When vigorous action ceases, add 4 drops to 5 drops of HF. Continue heating until dissolution is complete. If necessary, add water to maintain the original volume.

113.2 *Filtration:*

113.2.1 Place two glass-fiber filters in a vacuum filtration apparatus and moisten with water. Filter the solution with very gentle suction. Transfer the graphite to the filter and police the beaker thoroughly. Wash the sides of the funnel to deposit all the graphite on the fiber glass filter disk.

113.2.2 Wash the filter disk once with HCl (1 + 1), twice with hot water, three times with hot NaOH wash solution, twice with hot HCl (1 + 1) and five times with hot water, in the order given.

113.2.3 Turn off the suction and remove the top part of the filter assembly. Remove the top filter disk from the filter support, fold in half, and place in an induction furnace combustion crucible containing the same accelerators to be used in determining the blank for the sample. Remove the bottom filter disk from the filter support and use it to gently wipe any graphite off of the upper and lower parts of the filter apparatus. Fold the filter disk in half and place it in the same combustion crucible.

113.2.4 Dry the crucible containing the filters and accelerators for 2 h at 105 °C, and store in a desiccator.

113.3 *Combustion with Induction Furnace, Infrared Determination:*

113.3.1 *Preparation of Apparatus*—Proceed in accordance with the Preparation of Apparatus Section of the Total Carbon by the Combustion-Instrumental Measurement Method in Test Methods E1019.

113.3.2 Calibrate the instrument as described for Range II and Range III of the Calibration Section of the Total Carbon by the Combustion-Instrumental Measurement Method in Test Methods E1019.

113.3.3 *Blank*—Proceed as in 113.1.2, 113.1.3, 113.2.1 and 113.2.2. To the induction furnace combustion crucible add 1 g of iron and tin, copper-tin, or tungsten accelerator, or the required combination of these, to produce the necessary combustion temperature in the induction furnace being used and proceed as in 113.2.3 and 113.2.4. Place the crucible on the furnace pedestal and raise the pedestal into position. Start the analysis cycle. Refer to the manufacturer's recommended procedure regarding entry of sample weight and blank value. Record the blank value obtained.

113.3.4 *Sample Combustion*—Proceed as in 113.3.3 for the sample. Use the same accelerator selection used in determining the blank for the sample. Record the carbon value obtained.

114. Calculation

114.1 *Combustion with Induction Furnace, Infrared Determination:*

114.1.1 Calculate the percent of graphitic carbon as follows:

$$\text{Graphitic carbon, \%} = D - E \quad (17)$$

where:

D = % carbon found in sample determination, and

[9] Gelman Type A/E, 47-mm glass-fiber filter has been found suitable for this application.

E = average % carbon found in blank determination.

115. Precision and Bias

115.1 *Precision*—Five laboratories cooperated in testing this test method and obtained the precision data summarized in Table 9.

115.2 *Bias*—The accuracy of this test method can be inferred from the data in Table 9 by comparing the certified values for graphitic carbon with the average values obtained.

NOTE 29—Although this test method was tested to only 2.8 %, most commercial instruments are believed to be capable of analyzing samples containing graphitic carbon up to 4.5 %.

COPPER BY THE NEOCUPROINE SPECTROPHOTOMETRIC METHOD

116. Scope

116.1 This method covers the determination of copper in compositions from 0.03 % to 7.50 %.

117. Summary of Method

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

118. Concentration Range

118.1 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 30—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.

119. Stability of Color

119.1 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.

120. Interferences

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

121. Reagents

121.1 *Chloroform* ($CHCl_3$).

121.2 *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.

121.3 *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.

121.4 *2,9-Dimethyl-1,10-Phenanthroline (Neocuproine) Solution* (1 g/L)—Dissolve 0.1 g of neocuproine in 100 mL of absolute ethanol.

NOTE 31—In addition to absolute ethanol, 95 % ethanol or denatured No. 30 or 3A alcohol have been found suitable for preparing this solution.

121.5 *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.

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

122. Preparation of Calibration Curve

122.1 *Calibration Solutions*—Using pipets, transfer 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, 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 122.3.

122.2 *Reagent Blank Solution*—Transfer 50 mL of water to a 150-mL beaker. Proceed in accordance with 122.3.

122.3 *Color Development:*

122.3.1 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 32), adjust the pH to 5.0 ± 1.0 with NH_4OH (1 + 1). Add 10 mL of neocuproine solution.

TABLE 9 Statistical Information-Graphitic Carbon Direct Combustion and Infrared Absorption Methods

	Test Specimen	Statistics	IR (5 laboratories)	Gravimetric (2 laboratories)	IR and Gravimetric (7 laboratories)
1.	Ni-Cr Ductile Iron	R_1, E173	0.062	0.094	0.072
	NIST 341 (1.23 %;	R_2, E173	0.152	0.169	0.143
	range: 1.21 to 1.23 %)	Graphitic carbon found, %	1.352	1.348	1.351
2.	Cast Iron	R_1, E173	0.073	0.086	0.077
	NIST 51 (1.98 %;	R_2, E173	0.073[A]	0.086[A]	0.077[A]
	range: 1.96 to 2.00 %)	Graphitic carbon found, %	1.963	1.971	1.965
3.	Ni-Cr Cast Iron	R_1, E173	0.094	0.047	0.084
	NIST 82b (2.37 %;	R_2, E173	0.111	0.061	0.100
	range: 2.36 to 2.39 %)	Graphitic carbon found,%	2.318	2.337	2.324
4.	Cast Iron	R_1, E173	0.133	0.044	0.115
	NIST 122e (2.78 %;	R_2, E173	0.223	0.172	0.198
	range: 2.77 to 2.78 %)	Graphitic carbon found, %	2.705	2.722	2.710

[A] MSW > MSL ±C $R_1 = R_2$

NOTE 32—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.

122.3.2 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.

122.4 *Reference Solution*—$CHCl_3$.

122.5 *Spectrophotometry:*

122.5.1 *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 455 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

122.5.2 *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.

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

123. Procedure

123.1 *Test Solution:*

123.1.1 Select a sample in accordance with the following:

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.03 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	1.00	0.5	500	15
0.80 to 1.50	1.00	0.1	500	10
1.40 to 3.00	1.00	0.1	1000	10
2.80 to 5.00	0.60	0.1	1000	10
4.80 to 7.50	0.40	0.1	1000	5

Transfer it to a 250-mL Erlenmeyer flask.

123.1.2 If the sample is other than white iron, proceed as directed in 123.1.2.2; treat samples of white iron as directed in 123.1.2.1.

123.1.2.1 For white iron, crush the material in an iron mortar and weigh only particles passing through a No. 50 (300-µm) sieve. Transfer the weighed sample to a 250-mL Erlenmeyer flask. Add 15 mL of HNO_3 and 5 mL of HBr. Heat until dissolution is complete. Add 15 mL of $HClO_4$ and a sufficient amount of HF to volatilize the silica.

123.1.2.2 For samples other than white iron, 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.

123.1.3 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 33) to a volumetric flask that provides for the dilution in accordance with 123.1.1. Dilute to volume and mix.

NOTE 33—If silver is present in the alloy it must be removed by filtration at this point.

123.1.4 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 123.1.1 to a 150-mL beaker, and dilute to 50 mL. Proceed as directed in 123.4.

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

123.3 *Reference Solution*—$CHCl_3$.

123.4 *Color Development*—Proceed in accordance with 122.3.

123.5 *Spectrophotometry*—Take the spectrophotometric reading of the test solution in accordance with 122.5.

124. Calculation

124.1 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:

$$\text{Copper},\% = (A - B)/(C \times 10) \quad (18)$$

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.

TABLE 10 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 3, E350	0.021	0.004	0.010
2. Cast iron 1.07Ni-0.32Cr (NIST 82b, 0.038 Cu)	0.035	0.004	0.007
3. Cast iron high (0.79) phosphorus (NIST 7g, 0.128 Cu)	0.129	0.014	0.012
4. Cast iron (NIST 4j, 0.24 Cu)	0.239	0.017	0.016
5. Cast iron (NIST 5k, 1.50 Cu)	1.51	0.04	0.05
6. Cast iron 14Ni-5.5Cu-2Cr (NIST 115a, 5.52 Cu)	5.53	0.19	0.18

125. Precision

125.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 10. Although a sample covered by this method with copper composition at approximately 7.50% was not available for testing, the precision data for specimen 6 should apply.

LEAD BY THE ION-EXCHANGE—ATOMIC ABSORPTION METHOD

126. Scope

126.1 This method covers the determination of lead in compositions from 0.001 % to 0.15 %.

127. Summary of Method

127.1 A HCl 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 nm from a lead hollow-cathode tube is passed through the flame, and the absorbance is measured. The spectrometer is calibrated with solutions of known concentrations of lead.

128. Concentration Range

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

129. Interferences

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

130. Apparatus

130.1 *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 132.3.

130.2 *Ion-Exchange Column,* approximately 25 mm in diameter and 300 mm in length, 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. 3. 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.

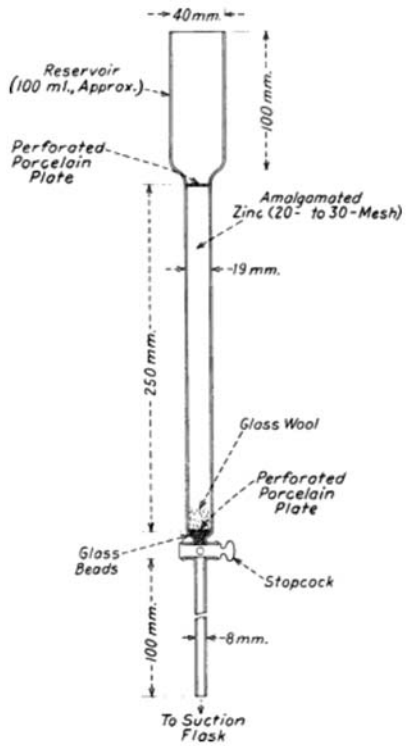

FIG. 3 Jones Reductor

131. Reagents

131.1 *Ion-Exchange Resin:*

131.1.1 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-nominal to 200-nominal mesh size.[10]

131.1.2 Transfer a supply of the resin (Note 34) 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 34—One pound of resin (45 % moisture) provides enough material for approximately 5 ion-exchange columns.

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

131.1.4 Prepare the column (Note 35) as follows: Place a 10-mm to 20-mm layer of glass wool or polyvinyl 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 polyvinyl 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 35—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.

131.2 *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.

132. Preparation of Calibration Curve

132.1 *Calibration Solutions*—Using pipets, transfer 2 mL, 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, 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 36—Prepare the test solution (133.1) and the reagent blank solution (133.2), and have them ready to aspirate immediately after aspirating the calibration solutions.

132.2 *Spectrometry:*

132.2.1 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.

132.2.2 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 132.1, 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 37—Recalibration is required whenever these parameters are changed.

132.2.3 Aspirate the lead solution used in 132.2.2 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:

$$s = (A - B) \times 0.40 \quad (19)$$

where:

A = highest of the six values found, and
B = lowest of the six values found.[11]

132.2.4 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 132.2.3 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 132.2.1 – 132.2.4.

132.2.5 Proceed immediately as directed in 133.3.

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

$$\text{Deviation from linearity} = (C - D)/E \quad (20)$$

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.

133. Procedure

133.1 *Test Solution:*

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

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

[11] 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).

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.

133.1.2 If the sample type is other than white iron, add 40 mL of HCl and 10 mL of HNO_3, or other ratios and concentrations of these acids as required for the decomposition of special grades of alloys. 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. Treat samples of white iron as directed in 133.1.2.1.

133.1.2.1 Crush the material in an iron mortar and use only particles passing through a No. 100 (150-m) sieve. Transfer the sample to a 600-mL beaker. Cover the beaker and add 40 mL of HNO_3 and 10 mL of HBr. Heat cautiously to dissolve the sample. Substitute a ribbed cover glass, evaporate the solution to a syrupy consistency, add 20 mL of HCl, and evaporate to dryness. Proceed as directed in 133.1.3.

133.1.3 Dilute to 50 mL and filter through a medium paper into a 250-mL Erlenmeyer flask. Wash the paper and residue alternately 3 times 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.

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

133.1.5 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 38). When the solution level is 10 mm to 20 mm above the top of the resin bed, rinse the 150-mL beaker 2 times 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 38—This is required in order to remove the residual iron present after the first pass through the column.

133.1.6 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.

133.1.7 Cover the 250-mL beaker reserved in 133.1.5 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 133.1.1 (Note 39). Cool, dilute to volume, and mix.

NOTE 39—Use a 10-mL volumetric flask for the reagent blank.

133.2 *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.

133.3 *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 132.2.3 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 40—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.

134. Calculation

134.1 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:

$$\text{Lead},\% = [((A \times B) - (C \times 10))/(D \times 10)] \qquad (21)$$

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.

TABLE 11 Statistical Information—Lead

Test Specimen	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	0.0028
6. No. 6, E353	0.106	0.023	0.031
7. No. 7, E350	0.217	0.010	0.049

135. Precision

135.1 Although samples covered by this method were not available for testing, the precision data obtained for other types of alloys, using the methods indicated in Table 11, should apply.

SULFUR BY THE CHROMATOGRAPHIC GRAVIMETRIC METHOD

This method, which consisted of Sections 136 through 143 of this standard, was discontinued in 1980.

CHROMIUM BY THE PEROXYDISULFATE-OXIDATION TITRIMETRIC METHOD

This method, which consisted of Sections 144 through 151 of this standard, was discontinued in 1980.

MANGANESE BY THE PEROXYDISULFATE-ARSENITE TITRIMETRIC METHOD

152. Scope

152.1 This method covers the determination of manganese in compositions from 0.10 % to 3.50 %

153. Summary of Method

153.1 Manganese ions in a H_2SO_4-H_3PO_4-HNO_3 medium, or in this medium with $HClO_4$ present, are oxidized to permanganic acid by ammonium peroxydisulfate in the presence of silver ions. The permanganic acid is titrated with standard sodium arsenite solution.

154. Interferences

154.1 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.

154.2 Graphitic carbon interferes in the titration; therefore it must be removed before oxidation of the manganese with ammonium peroxydisulfate.

155. Apparatus

155.1 *Platinum Cones.*

156. Reagents

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

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

156.3 *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.

156.4 *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.

156.5 *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.

156.6 *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.

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

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

156.9 *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 as directed in 157.1.3 – 157.1.6.

156.10 *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.

157. Procedure

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

157.1.1 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 41).

Manganese, %	Sample weight, g
0.1 to 2.0	1.00
1.9 to 3.5	0.50

NOTE 41—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.

157.1.2 Add 30 mL of water, 30 mL of mixed acids, and a few drops of HF, heat until the sample is decomposed, and boil to expel oxides of nitrogen. Add 50 mL of water and filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 42). Dilute to 250 mL and proceed as directed in 157.1.4 and 157.1.5.

NOTE 42—If there is reason to suspect that the sample contains acid-insoluble manganese compounds, transfer the paper and residue to a platinum crucible. Dry the paper and heat at 600 °C until the carbon has been removed. Finally ignite 30 min at 1100 °C, or until volatile oxides have been driven off. Cool, add 1 g to 3 g of sodium hydrogen sulfate (fused), and heat until fusion of the manganese compounds occurs. Leach the melt in a 250-mL beaker containing 40 mL of water. Remove the crucible and rinse it with water. Transfer the solution to the filtrate.

157.1.3 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 as directed in 157.1.4 – 157.1.6.

157.1.4 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 to boiling, and boil briskly for 60 s to 90 s. Cool to 5 °C to 10 °C in an ice bath.

157.1.5 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 composition of the sample as directed in 158 using the manganese equivalent found in 157.1.6.

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

$$\text{Manganese equivalent, g/mL} = A/B \quad (22)$$

where:

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

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

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

157.2.1 Proceed as directed in 157.1.1.

157.2.2 Add 30 mL of water, 30 mL of mixed acids, and a few drops of HF, heat until the sample is decomposed, and boil to expel oxides of nitrogen. Add 50 mL of water and filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 42). Dilute to 250 mL and proceed as directed in 157.1.4 and 157.1.5.

157.2.3 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 Solutions 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 as directed in 157.1.4 through 157.1.6.

157.3 *For Samples Containing More Than 15 mg of Chromium*—Proceed as directed in 157.3.1 if chromium is to be volatilized as chromyl chloride, or as directed in 157.3.2 if it is to be removed by precipitation with zinc oxide.

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

NOTE 43—The volatilization of chromium as chromyl chloride may be used for the separation of chromium when this can be accomplished without spattering and consequent loss of manganese during volatilization. (Molybdenum and tungsten in high compositions will precipitate during fuming, causing the physical loss just mentioned.)

157.3.1.1 Proceed as directed in 157.1.1.

157.3.1.2 Add 15 mL of HCl, 5 mL of HNO_3, and a few drops of HF. Heat until the sample has decomposed, then dilute to 75 mL. Cool and filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 42). 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 as directed in 157.1.4 and 157.1.5.

157.3.1.3 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 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 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 as directed in 157.1.4 through 157.1.6.

157.3.2 *Removal of Chromium by Precipitation with Zinc Oxide:*

NOTE 44—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 method.

157.3.2.1 Proceed as directed in 157.1.1.

TABLE 12 Statistical Information—Manganese

Test Specimen	Manganese Found, %[A]	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. White iron (NIST 3a, 0.048 Cr, 0.317 Mn)	0.311	0.008	0.048
2. Cast iron (NIST 4i, 0.104 Cr, 0.793 Mn)	0.799	0.021	0.061
3. Cast iron (BCS 236/2, 0.03 Cr, 1.14 Mn)	1.16	0.02	0.06
4. No. 4, E350	1.89	0.03	0.06

[A] Removal of chromium not required.

TABLE 13 Statistical Information—Manganese (Chromium Removal Procedure)

Test Specimen	Chromium Removal Procedure	Manganese Found, %, by Laboratory No.						Average Mn, %
		1	2	3	4	5	6	
1. Cast iron 13 Ni-4Cr-5Cu (BCS 173/1, 0.82 Mn)	volatilization	0.831	...	0.815	0.820	0.810	0.850	0.826
	volatilization	0.831	...	0.819	...	0.820	0.841	
	precipitation	...	0.819	0.813	0.810	0.820	...	0.817
	precipitation	...	0.820	0.820	...	0.820	...	

157.3.2.2 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 50 mL of HNO_3 (1 + 1). Heat gently until the sample and carbides have been decomposed (Note 45), boil to expel oxides of nitrogen, cool, and dilute to 100 mL.

NOTE 45—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 157.3.2.3.

157.3.2.3 Dilute to 100 mL, filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 42).

157.3.2.4 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 46). 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 46—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.

157.3.2.5 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 as directed in 157.3.2.3, and transfer the filtrate from the suction flask to the filtrate reserved in 157.3.2.4. Boil, dilute to 250 mL, and proceed as directed in 157.1.4 and 157.1.5.

157.3.2.6 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 as directed in 157.1.4 – 157.1.6.

158. Calculation

158.1 Calculate the percentage of manganese as follows:

$$\text{Manganese, \%} = [(A \times B)/C] \times 100 \quad (23)$$

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.

159. Precision

159.1 Eight laboratories cooperated in testing this method, with one laboratory reporting a second pair of values in each instance; the data are summarized in Table 12.

159.2 Six laboratories cooperated in testing this method using a test specimen for which removal of chromium was required; the data are summarized in Table 13. Acid insoluble manganese was present and was treated in accordance with Note 42.

PHOSPHORUS BY THE ALKALIMETRIC METHOD

160. Scope

160.1 This method covers the determination of phosphorus in compositions from 0.02 % to 0.90 %.

161. Summary of Method

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

162. Interferences

162.1 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.

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

162.3 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.

162.4 Graphitic carbon must be removed before precipitating the phosphorus.

163. Apparatus

163.1 *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, or equivalent, 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.

163.2 *Funnel, Glass, 60°,* fitted with a 25-mm diameter perforated porcelain filtering disk. Place a 5.5-cm fine qualitative, smooth-surface filter paper, over the perforated 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.

164. Reagents

164.1 *Ammonium Molybdate Solution (Acidic):*

164.1.1 *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.

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

164.1.3 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.

164.2 *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).

164.3 *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 164.7, 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:

$$\text{Phosphorus equivalent, g P/mL} = (A \times B)/C \qquad (24)$$

where:

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

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

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

164.6 *Potassium Permanganate Solution* (25 g/L)—Dissolve 26 g of potassium permanganate ($KMnO_4$) in water, dilute to 1 L, and mix.

164.7 *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 NIST 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:

$$\text{Phosphorus equivalent, g P/mL} = A \times (0.001347/B) \times 0.2042 \quad (25)$$

where:

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

165. Procedure

165.1 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
0.25 to 0.90	0.5

Transfer the sample to a 300-mL Erlenmeyer flask.

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

165.3 If the sample is other than a white iron, add 100 mL of HNO_3 (1 + 3) and, if the silicon composition is greater than 0.5 %, 3 drops to 5 drops of HF. Treat samples insoluble in HNO_3 (1 + 3) as directed in 165.4; treat samples of white iron as directed in 165.5. 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. Add H_2SO_3 dropwise until the precipitate dissolves, and boil 3 min to expel oxides of nitrogen. If graphitic carbon or other insoluble material is present, filter through an 11-cm coarse paper into a 300-mL Erlenmeyer flask. Wash the flask and paper several times with hot water, discard the precipitate. Adjust the volume to 100 mL, and cool to room temperature.

165.4 If the sample is not soluble in HNO_3 (1 + 3), dissolve it with HNO_3 and HCl; if the silicon composition is greater than 0.5 %, add 3 drops to 5 drops of HF. Heat, as required, to hasten dissolution. When the sample is decomposed, add 15 mL of $HClO_4$, heat to fumes, and evaporate nearly to dryness. Cool, add 75 mL of HNO_3 (1 + 3), and heat at 90 °C until the salts are dissolved. Add $KMnO_4$ solution dropwise, while heating the solution, until a permanent, brown precipitate forms, and boil 3 min. Add H_2SO_3 dropwise until the precipitate dissolves, and boil 3 min to expel oxides of nitrogen. If graphitic carbon or other insoluble matter is present, filter

through an 11-cm coarse paper into a 300-mL Erlenmeyer flask. Wash the flask and paper several times with hot water. Discard the precipitate, adjust the volume to 100 mL, and cool to room temperature.

165.5 If the sample is a white iron, crush it in an iron mortar and use only particles passing through a No. 50 (297-µm) sieve. Proceed as directed in 165.1 and 165.2, and then add 30 mL of HNO_3 and 10 mL of HBr. Heat cautiously to dissolve the sample. Add 3 mL to 5 mL of HF and 15 mL of $HClO_4$, heat to fumes, and evaporate nearly to dryness. Cool, add 75 mL of HNO_3 (1 + 3), and heat at 90 °C until the salts are dissolved. Add $KMnO_4$ solution dropwise, while heating the solution, until a permanent, brown precipitate forms, and boil 3 min. Add H_2SO_3 dropwise until the precipitate dissolves, and boil 3 min to expel the oxides of nitrogen. If insoluble matter is present, filter through a coarse paper into a 300-mL Erlenmeyer flask. Wash the flask and the paper several times with hot water. Discard the precipitate, adjust the volume to 100 mL, and cool to room temperature.

165.6 While swirling the flask, slowly add 20 mL of NH_4OH for a 0.5 or 1-g sample, or 17 mL of NH_4OH for a 2-g sample, so that no precipitate forms (Note 47). Adjust the temperature to 45 °C.

NOTE 47—The quantity 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.

165.7 Add 40 mL of ammonium molybdate solution, stopper the flask, and shake 10 min on a mechanical shaker. If the vanadium composition 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.

165.8 Filter the solution with the aid of suction using a Hirsch porcelain crucible (163.1) or a glass funnel fitted with a perforated porcelain filtering disk (163.2). Rinse the flask 3 times 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 times to 15 times with a total volume of approximately 100 mL of KNO_3 solution (Note 48). Discard the filtrate.

TABLE 14 Statistical Information—Phosphorus

Total Specimen	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. No. 5, E350	0.045	0.003	0.009
6. Cast iron (NIST 4j, 0.17 P)	0.166	0.007	0.012
7. No. 6, E350	0.274	0.017	0.017
8. Cast iron (NIST 7g, 0.794 P)	0.783	0.031	0.048

NOTE 48—Analysts not having experience with this method should familiarize themselves with the proper washing technique. Blanks obtained by the method as written should not be measurable provided the reagents are of the quality specified in Practices E50.

165.9 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, or a 50-mL buret for samples containing more than 0.5 % phosphorus, 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.

165.10 Remove and rinse the stopper. Dilute the solution to 150 mL with freshly boiled water which 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 HNO_3 standard solution until 1 drop causes the disappearance of the pink color. Record the buret reading.

166. Calculation

166.1 Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, \%} = \frac{(AB - CD) - (EB - FD)}{G} \times 100 \qquad (26)$$

where:

A = NaOH solution used for the sample (165.9), mL,
B = phosphorus eqivalent of the NaOH solution,
C = HNO_3 solution required by the sample (165.10), mL,
D = phosphorus equivalent of the HNO_3 solution,
E = NaOH solution used for the blank, mL,
F = HNO_3 solution required by the blank, mL, and
G = sample used, g.

167. Precision[12]

167.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 14. Although samples at the lower end of the scope were not tested, the precision data obtained for other types of alloys using the methods indicated in Table 14 should apply.

NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD

168. Scope

168.1 This method covers the determination of nickel in compositions from 0.1 % to 36.00 %.

169. Summary of Method

169.1 Nickel dimethylglyoximate is precipitated by adding an alcoholic solution of dimethylgloxime to a solution of the

[12] Supporting data are available from ASTM Headquarters. Request RR:E03-1002.

sample containing ammonium citrate. A second precipitation is performed to purify the precipitate prior to drying and weighing.

169.2 Alternatively, nickel and manganese are separated from other alloying elements by anion exchange in HCl to eliminate the need for the first precipitation with dimethylglyoxime. This separation must be used when cobalt is present in compositions greater than 0.5 % and may be used for all other samples. Nickel dimethylglyoximate is precipitated by adding dimethyglyoxime to the eluate; the precipitate is filtered, dried, and weighed.

170. Interferences

170.1 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. When the anion-exchange separation is used, manganese is present in the solution from which nickel is precipitated, and an excess of the precipitant is required.

171. Apparatus

171.1 *Anion-Exchange Column,* approximately 25 mm in diameter and 300 mm in length, 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. 3 may be adapted to this method. A reservoir for the eluants may be added at the top of the column.

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

171.3 *pH Meter.*

172. Reagents

172.1 *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.

172.2 *Anion Exchange Resin:*

172.2.1 Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a crosslinkage of 8 % and a 200-nominal to 400-nominal mesh size.[13] To remove those beads greater than 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 sufficient time (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, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), 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.

172.2.2 Prepare the column as follows: Place a 10-mm to 20-mm layer of glass wool or polyvinyl 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 polyvinyl chloride plastic fiber at the top of the resin bed to protect it from being carried into suspension when the solutions are added. While passing a minimum of 100 mL of HCl (3 + 1) through the column, with the hydrostatic head 100 mm above the top of the resin bed, adjust the flow rate, by means of the upper stopcock, to not more than 3.0 mL/min. Drain to 5 mm to 10 mm above the top of the resin bed and then close the lower stopcock.

172.3 *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.

173. Procedure

173.1 *Double Precipitation:*

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

Nickel, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.1 to 1.0	3.0	1.0
1.0 to 5.0	1.0	0.5
5.0 to 10.0	0.5	0.2
10.0 to 20.0	0.25	0.1
20.0 to 36.0	1.0	0.5

Transfer it to a 600-mL beaker.

173.1.2 If the sample is other than white iron, add 60 mL of HCl (1 + 1) and 10 mL of HNO_3. Heat to dissolve the sample and boil 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. Cool, and dilute to 100 mL with water. Treat samples of white iron as directed in 173.1.3.

173.1.3 If the sample is a white iron, crush it in an iron mortar and weigh only particles passing through a No. 100 (150-µm) sieve. Transfer the sample to a 250-mL beaker, and add 20 mL of HNO_3 and 20 mL of HBr. Cover the beaker and heat cautiously to dissolve the sample. Cool, rinse the cover glass, add 30 mL of $HClO_4$, and heat to strong fumes of $HClO_4$. Continue fuming for 5 min. Cool, and dilute to 100 mL with water.

173.1.4 Filter the solution obtained in 173.1.2 or 173.1.3 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. If the nickel composition is greater than 20 %, transfer the filtrate from the beaker to a 200-mL volumetric flask, dilute to volume, and mix. Using a pipet, transfer a 20-mL aliquot to a 600-mL beaker and add 10 mL of HCl.

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

173.1.5 Add 200 mL of water and 20 mL of ammonium citrate solution. 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.

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

173.1.7 Using a pH meter, adjust the pH to 7.4 ± 0.1 with NH_4OH. Remove the electrodes and rinse 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.

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

173.1.9 Add 30 mL of HNO_3 and 15 mL of $HClO_4$. Evaporate to strong fumes and continue fuming for 5 min. Cool and add 50 mL of water.

173.1.10 Filter through an 11-cm coarse paper into a 600-mL beaker. Wash the paper 5 times with HCl (5 + 95) and 3 times with water. Dilute the filtrate to 200 mL with water and proceed as directed in 173.3 – 173.7.

173.2 *Anion-Exchange Separation:*

173.2.1 Proceed as directed in 173.1.1.

173.2.2 If the sample is other than white iron, proceed as directed in 173.1.2.

173.2.3 If the sample is a white iron, proceed as directed in 173.1.2, but dilute with only 50 mL of water.

173.2.4 Filter the solution obtained in 173.2.2 or 173.2.3 through an 11-cm coarse paper, collecting the filtrate in a 250-mL beaker. Transfer any insoluble matter to the paper with hot HCl (5 + 95). Wash the paper alternately with hot water and hot HCl (5 + 95) until iron salts are removed. Finally, wash the paper 3 times with 5-mL portions of hot water. Discard the residue.

173.2.5 Carefully evaporate to dryness at moderate heat to avoid spattering. Cool, add 10 mL of HCl, and evaporate to dryness. Cool, add 20 mL of HCl (3 + 1) and heat, if necessary, to dissolve salts, but avoid loss of HCl by overheating or prolonged heating.

173.2.6 Precondition the ion-exchange column with 50 mL of HCl (3 + 1), and adjust the flow rate by means of the upper stopcock to not more than 3.0 mL/min. Allow the acid to drain to 5 mm to 10 mm from the top of the resin bed.

173.2.7 Place a clean 600-mL beaker under the ion-exchange column and open the bottom stopcock. Transfer the solution from 173.2.5 to the column. Allow the sample solution to drain to 5 mm to 10 mm from the top of the resin bed. Rinse the 250-mL beaker with a 5-mL portion of HCl (3 + 1) and transfer the rinsing to the column. When it has drained to 5 mm to 10 mm above the resin bed, add a second 5-mL rinse portion from the 250-mL beaker. Repeat this operation 3 more times, and allow the level to drop to 5 mm to 10 mm above the resin bed before adding the next. Add sufficient HCl (3 + 1) at the top of the column to collect a total of 200 mL in the 600-mL beaker. Close the lower stopcock and reserve the solution.

173.2.8 Precondition the column for the next sample as follows: Open the lower stopcock. Drain any remaining solution in the column to 5 mm to 10 mm from the top of the resin bed. Add HCl (1 + 19) in 50-mL increments until iron has been eluted and the eluate is visibly free of color (approximately 300 mL). Drain the solution to 5 mm to 10 mm from the top of the resin bed and close the lower stopcock. If the column is not to be used immediately, cover, and store. If another sample solution is to be put through the column, proceed as directed in 173.2.6.

173.2.9 Heat the solution reserved in 173.2.7 to boiling and evaporate to 60 mL to remove excess HCl. If the sample contains less than 20 % nickel, cool and dilute to 200 mL. If the sample contains more than 20 % nickel, cool, transfer the solution to a 200-mL volumetric flask, add 20 mL of HCl, dilute to volume, and mix. Using a pipet, transfer a 20 mL aliquot to a 600-mL beaker, and dilute to 200 mL with water.

173.3 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. Remove and rinse the electrodes with water, collecting the rinsings in the original beaker.

173.4 Add 2 mL of HCl and, while stirring the solution, add 10 mL of dimethylglyoxime solution plus an additional 0.4 mL for each milligram of nickel present. If the separation was made by anion-exchange, add an additional 0.4 mL for each milligram of manganese present.

173.5 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.

173.6 With the aid of suction, filter using a weighed (Note 49) fritted glass crucible. Wash the beaker and precipitate 6 times with cold water.

NOTE 49—Heat the crucible at 150 °C, and cool in a desiccator before weighing.

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

174. Calculation

174.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = \frac{(A - B) \times 0.2032}{C} \times 100 \qquad (27)$$

where:

A = weight of crucible and precipitate, g,
B = weight of crucible, g, and
C = sample represented in the final test solution, g.

TABLE 15 Statistical Information—Nickel

Test Specimen	Nickel Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Cast iron (NIST 7g, 0.121 Ni)	0.115	0.006	0.006
2. Ni-Cr cast iron 1 Ni – .3 Cr (NIST 82b, 1.22 Ni)	1.22	0.05	0.06
3. Ductile iron (NIST 341, 20.32 Ni)	20.31	0.20	0.20

175. Precision

175.1 1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 15. Although a sample covered by this method with a nickel composition at approximately 36 % was not available for testing, the precision data for specimen 3 should apply.

NICKEL BY THE ION EXCHANGE-ATOMIC ABSORPTION METHOD

176. Scope

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

177. Summary of Method

177.1 Nickel is separated from interfering elements by elution from an anion exchange column using a HCl 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.

178. Concentration Range

178.1 The recommended concentration range is from 0.001 mg to 0.010 mg of nickel per mL of solution.

179. Interferences

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

180. Apparatus

180.1 *Atomic Absorption Spectrophotometer,* 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 defined in 182.3.

180.2 *Anion-Exchange Column,* approximately 25 mm in diameter and 300 mm in length, 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. 3 may be adapted to this method. A reservoir for the eluants may be added at the top of the column. However, the eluants must be added as described in 183.1.4.

181. Reagents

181.1 *Anion Exchange Resin:*

181.1.1 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-nominal to 400-nominal mesh size. 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.

181.1.2 Prepare the column as follows: Place a 10-mm to 20-mm layer of glass wool or polyvinyl 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 polyvinyl 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-mm to 20-mm above the top of the resin bed, close the lower stopcock.

181.2 *Nickel, Standard Solution*(1 mL = 0.1 mg Ni)—Transfer 1.000 g of nickel (purity: 99.9 % minimum) to a 400-mL beaker. Add 50 mL of HNO_3 (1 + 1), cover and heat gently until dissolution is complete. Remove cover and evaporate to dryness slowly to prevent loss of 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 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. Dilute to volume with water, and mix.

NOTE 50—Prepare the dilute nickel standard solution immediately before preparation of the calibration solution described in 182.1 to maintain proper concentration.

182. Preparation of Calibration Curve

182.1 *Calibration Solutions*—Using pipets, transfer 0 mL, 1 mL, 3 mL, 5 mL, 7 mL, 10 mL, 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.

182.2 *Spectrometry:*

182.2.1 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.

182.2.2 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 as directed in 182.1 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 51—Recalibration is required whenever these parameters are changed.

182.2.3 Aspirate the nickel solution used in 182.2.2 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:

$$s = (A - B) \times 0.40 \quad (28)$$

where:

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

182.2.4 Beginning with the solution to which no nickel was added in 182.1, 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 182.2.3 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 the steps as directed in 182.2.1 – 182.2.4.

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

$$\text{Deviation from linearity} = (C - D)/E \quad (29)$$

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.

183. Procedure

183.1 *Test Solution:*

183.1.1 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 it to a 400-mL beaker.

183.1.2 If the sample is other than white iron, add 25 mL of 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 52—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.

183.1.3 If the sample is a white iron, crush it in an iron mortar and weigh only particles passing through a No. 100 (150-µm) sieve. Transfer the sample to a 400-mL beaker, and add 20 mL of HNO_3 and 20 mL of HBr. Cover the beaker and heat cautiously to dissolve the sample. Cool, rinse the cover glass, add 30 mL of $HClO_4$, and heat to strong fumes of $HClO_4$. Evaporate to dryness, carefully and with moderate heat. 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 52).

183.1.4 Place a clean 400-mL beaker under the ion-exchange column. Transfer the solution obtained in 183.1.2 or 183.1.3 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 times 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 3.0 mL/min and add HCl (3 + 1) to the column until a total of 200 mL has been collected. Reserve the solution.

183.1.5 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 53). 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 as directed in 181.1.2.

NOTE 53—Approximately 300 mL of HCl (1 + 9) are required.

183.1.6 To the eluate obtained in 183.1.4, 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 % (183.1.1) 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 183.1.1, and warm gently to dissolve salts. Cool to room temperature, and transfer to appropriate volumetric flask (183.1.1). Dilute to volume with water, and mix.

183.2 Prepare a reagent blank by treating the same amounts of all reagents as directed in 183.1.1 – 183.1.6, but omitting the sample. Use reagents from the same lots for blank and test solutions.

TABLE 16 Statistical Information—Nickel

Test Specimen	Nickel Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No 1, E350	0.0058	0.002	0.002
2. No 2, E350	0.055	0.002	0.007
3. Cast Iron (NIST 7g, 120 Ni)	0.122	0.009	0.015
4. No 4, E350	0.217	0.012	0.020
5. Cast Iron (NIST 82[a], 1.07 Ni)	1.07	0.052	0.069

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

NOTE 54—After each group of four or fewer test solutions and reagent blank solutions has been aspirated, apply the test with the standard solution as directed in 182.2.4 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 182.2.2, 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.

184. Calculation

184.1 Convert the absorbance of the test solution and the reagent blank to mg of nickel per mL of the final test solution by means of the calibration curve. Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = \frac{(A - B) \times C}{W \times 10} \quad (30)$$

where:

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

185. Precision[14]

185.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 16. Although samples covered by this method at the lower end of the scope were not tested, the data obtained for other types of alloys using the methods indicated in Table 16 apply.

TIN BY THE SOLVENT EXTRACTION—ATOMIC ABSORPTION METHOD

186. Scope

186.1 This method covers the determination of the tin in the range from 0.002 % to 0.10 %.

187. Summary of Method

187.1 Tin is extracted from a dilute HCl 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.

188. Concentration Range

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

189. Interferences

189.1 Copper, when present above 0.1 g, interferes by precipitating as cuprous iodide (CuI). This interference may be eliminated by incorporating a suitable copper separation scheme into the procedure prior to the solvent extraction step.

190. Apparatus

190.1 *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 premix nitrous oxide – acetylene burner. The performance of the instrument must be such that, the upper limit of the concentration range (40 µg/mL) produces an absorbance of 0.15 or higher, and a calibration curve whose deviation from linearity is within the limits specified in 192.4.

191. Reagents

191.1 *Ascorbic Acid.*

191.2 *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.

191.3 *Methyl Isobutyl Ketone (MIBK).*

191.4 *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.

191.5 *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.

191.6 *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.

192. Procedure

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

NOTE 55—Volumetric flasks with ground-glass stoppers must be used.

192.2 *Extraction:*

192.2.1 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.

[14] Supporting data are available from ASTM Headquarters. Request RR:E01-1009.

192.2.2 Using a pipet, add 10.0 mL of TOPO-MIBK solution, stopper the flask, invert, and shake vigorously several times for a period of 1 min. Allow the phases to separate. Add water to bring the entire organic layer up into the neck portion of the flask. Stopper, invert several times, and allow the phases to separate.

NOTE 56—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

192.3 *Spectrometry:*

192.3.1 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.

192.3.2 Following the instrument manufacturer's specific directions, ignite the burner using the air – acetylene mode of 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 57—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 according to the instrument manufacturer's approved procedures, clean the slot, and relight as in 192.3.2.

192.3.3 Aspirate the solution with the highest concentration (40 µg Sn/mL) from the series prepared in 192.1 a sufficient number of times to establish that the absorbance is not drifting.

NOTE 58—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 59—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.

192.3.4 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/mL) differs from the average values obtained in 192.3.3 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 192.3.1 – 192.3.4.

192.3.5 Proceed immediately as directed in 193.3.

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

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

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.

193. Procedure

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

193.2 *Test Solution:*

193.2.1 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
0.002 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 it to a 250-mL polytetrafluoroethylene beaker.

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

193.2.3 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 and dilute to approximately 50 mL with water. Filter through medium porosity, hard-surface filter paper. Wash the paper several times with water. Collect the filtrate and washings in a 250 mL beaker. Discard the filter paper. Add 20 mL of HCl (1 + 1) to the solution and again evaporate to 15 mL.

193.2.4 Rinse the sides of the beaker with about 5 mL of water and cool. If an aliquot is to be taken (refer to table in 193.2.1), 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.

193.2.5 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.

193.2.6 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 the TOPO-MIBK solution to the flask, stopper, invert, and shake vigorously several times for 1 min.

193.2.7 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.

193.3 *Spectrometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 58) and record the absorbance values. Take three readings on each solution (Note 59). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drifts as in 192.3.4 and 192.3.5.

TABLE 17 Statistical Information—Tin

Test Specimen	Tin Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E350	0.0034	0.0006	0.0007
2. Cast iron (NIST 5k), 0.009 Sn (not certified)	0.009	0.001	0.002
3. No. 3, E350	0.011	0.001	0.002
4. No. 6, E350	0.097	0.011	0.011

194. Calculation

194.1 Convert the average absorbance of the test and the reagent blank solutions to micrograms of tin per mL of the final solution, by means of the calibration curve. Calculate the percentage of tin as follows:

$$\text{Tin, \%} = [((D - E) \times F)/(G \times 1000)] \quad (32)$$

where:

D = tin, µg, per mL of the final test solution,
E = tin, µg, per mL of the final reagent blank solution,
F = aliquot factor (refer to table in 193.2.1), and
G = sample used, g.

195. Precision and Accuracy[15]

195.1 *Precision*—Eleven laboratories cooperated in the testing of this method and obtained the precision data listed as No. 2 in Table 17. This method differs only slightly from the method for tin, Method E350, in that a filtration step was added to remove acid insoluble material (graphite). The fact that the precision obtained for No. 2 by this method is the same as the precision obtained for No. 3, Method E350, suggests that the precision of the two methods is the same.

195.2 *Accuracy*—No information on the accuracy of this method is available.

MOLYBDENUM BY THE SPECTROPHOTOMETRIC METHOD

196. Scope

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

197. Summary of Method

197.1 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.

198. Concentration Range

198.1 The recommended concentration range is 0.0003 mg to 0.003 mg of molybdenum per mL of solution using a l-cm cell.

NOTE 60—This method has been written for cells having a l-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

199. Stability of Color

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

200. Interferences

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

201. Reagents

201.1 *Butyl Acetate:*

NOTE 61—Operations with this chemical should be carried out away from heat and open flame and are best done in a well ventilated hood. Avoid prolonged breathing of vapor.

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

201.3 *Iron*[16](Purity: 99.8 % minimum, molybdenum 0.001 % maximum.)

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

201.5 *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.

201.6 *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.

201.7 *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.

201.8 *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.

201.9 *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.

201.10 *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 tin, and store in an air-tight bottle.

NOTE 62—This solution is used for color development in 202.3, 203.3, 204.3, and 205.3. When an absorption cell is used sequentially for a number of spectrophotometric measurements, a white film of an insoluble tin compound may adhere to the inside of the cell and must be removed

[15] Supporting data are available from ASTM Headquarters. Request RR:E01-1022.

[16] Johnson-Mathey JMC 847 sponge iron has been found suitable for this purpose. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

before further measurements are made.

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

202.1 *Calibration Solutions:*

202.1.1 Transfer 0.3 g of iron to each of four 250-mL Erlenmeyer flasks. Using pipets, transfer 2 mL, 5 mL, 10 mL, 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.

202.1.2 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.

202.1.3 Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 202.3.

202.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 202.1.2, 202.1.3, and 202.3.

202.3 *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, 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, 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.

NOTE 63—This funnel should be cleaned thoroughly after each filtration to avoid development of a pink color that would contaminate the filtrate.

202.4 *Reference Solution*—Butyl acetate.

202.5 *Spectrophotometry:*

202.5.1 *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.

202.5.2 *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.

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

203. Preparation of Calibration Curve for Compositions from 0.05 % to 0.55 %

203.1 *Calibration Solutions:*

203.1.1 Transfer 0.3 g of iron to each of four 250-mL Erlenmeyer flasks. Using pipets, transfer 2 mL, 5 mL, 10 mL, 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.

203.1.2 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.

203.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 203.3.

203.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 203.1.2, 203.1.3, and 203.3.

203.3 *Color Development*— Using a pipet, transfer 50 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 50 mL of butyl acetate, measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, 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, 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. (See Note 63.)

203.4 *Reference Solution*—Butyl acetate.

203.5 *Spectrophotometry:*

203.5.1 *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.

203.5.2 *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.

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

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

204.1 *Calibration Solutions:*

204.1.1 Transfer 0.3 g of iron to each of five 250-mL Erlenmeyer flasks. Using pipets, transfer 5 mL, 10 mL, 15 mL, 20 mL, 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.

204.1.2 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.

204.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 204.3.

204.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 204.1.2, 204.1.3, and 204.3.

204.3 *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, 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. (See Note 63.)

204.4 *Reference Solution*—Butyl acetate.

204.5 *Spectrophotometry:*

204.5.1 *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.

204.5.2 *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.

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

205. Procedure

205.1 *Test Solution:*

205.1.1 Transfer a 0.3-g sample, weighed to the nearest milligram to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution, and heat until dissolution is complete. One to two drops of HF may be added for the decomposition of some alloy types containing high percentages of silicon.

205.1.2 Increase the temperature and heat to $HClO_4$ fumes. Continue fuming until chromium, if present, is oxidized, and the white 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.

205.1.3 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	Iron Solution B, mL	Butyl acetate, mL	Weight of sample in final butyl acetate solution, g
0.01 to 0.05	200	100	None	25	0.15
0.05 to 0.55	500	50	None	50	0.03
0.40 to 1.50	500	25	25	100	0.015

205.1.4 Proceed as directed in 205.3.

205.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 205.1.2, 205.1.3, and 205.3, using the same dilution and aliquots used for the test solution.

205.3 *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, 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. (See Note 63.)

205.4 *Reference Solution*—Butyl acetate.

205.5 *Spectrophotometry*—Take the spectrophotometric reading of the test solution and of the reagent blank solution as directed in 204.5.

206. Calculation

206.1 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 percentage of molybdenum as follows:

$$\text{Molybdenum, \%} = \frac{A}{B \times 10} \quad (33)$$

TABLE 18 Statistical Information—Molybdenum

Test Specimen	Molybdenum Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E352	0.037	0.002	0.006
2. Cast iron, Leco 501–741	0.195	0.018	0.03
3. Cast iron (NIST 107, 0.69 Mo)	0.699	0.03	0.04
4. No. 5, E350	1.03	0.04	0.07
5. No. 4, E353	1.34	0.03	0.09

where:

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

B = sample, g, represented in 25 mL, 50 mL, or 100 mL, as appropriate, of butyl acetate (see 205.1.3).

207. Precision and Bias[17]

207.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 18. This method is identical with the methods for molybdenum Methods E350, E352, and E353. The fact that the data from the two cast iron samples (Table 18, No. 2 and 3) had similar precision to the specimens used to test the other methods suggests that the precision for these methods is the same.

207.2 *Bias*—The accuracy can be inferred by comparing the certified values for molybdenum with the values found for molybdenum for those specimens listed in Table 18.

CHROMIUM BY THE ATOMIC ABSORPTION METHOD

208. Scope

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

209. Summary of Method

209.1 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.

210. Concentration Range

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

211. Interferences

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

212. Apparatus

212.1 *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 214.4. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this method.

213. Reagents

213.1 *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.

213.2 *Iron,*[18] Low Chromium—Cr 0.0001%.

213.3 *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.

214. Preparation of Calibration Curves

214.1 *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 of 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 7 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 concentration. Dilute to volume and mix.

214.2 *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 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 concentration. Dilute to volume and mix.

214.3 *Spectrometry:*

214.3.1 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.

214.3.2 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 as directed in 214.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to

[17] Supporting data are available from ASTM Headquarters. Request RR:E01-1023.

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

obtain maximum response. Whenever one or more of these parameters are changed, recalibration is required.

214.3.3 Aspirate the chromium solutions used in 214.3.2 to assure that the absorbance reading is repeatable. Record 6 readings, and calculate the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (34)$$

where:

A = the highest of 6 values found, and
B = the lowest of the 6 values found.

214.3.4 Using water as a reference, and beginning with the solution to which no addition of chromium was made in 214.1 and 214.2, 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 6 values calculated in 214.3.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the 6 values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, correct it, and repeat the steps in 214.3.1 – 214.3.4.

214.3.5 Proceed immediately as directed in Section 215.

214.4 *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:

$$\text{Deviation from linearity} = (C - D)/E \quad (35)$$

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 instrument or hollow cathode lamp, and repeat the calibration. The absorbance value for *C* must be 0.200 or higher.

214.5 *Calibration for Compositions from 0.10 % to 1.00 %*—Proceed as directed in 214.4.

215. Procedure

215.1 *Test Solution:*

215.1.1 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
0.005–0.10	1	0.10	100	0	0	100
0.10–1.00	1	0.10	100	10	9	100

Transfer it to a 250-mL borosilicate beaker.

215.1.2 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.

215.1.3 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 hr. 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.

215.1.4 Transfer this solution to the filtrate from 215.1.2 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 as directed in 215.3. For samples with expected chromium compositions 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.

215.2 Prepare for each concentration range a reagent blank by treating the same amount of all reagents as directed in 215.1.1 – 215.1.4 including the low chromium iron. Use reagents from the same lots for blank and test solutions.

215.3 *Spectrometry*—Using water as a reference solution, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of 4 or fewer test solutions and reagent blank solutions has been aspirated, apply the test using the standard solution as directed in 214.3.4, depending on the concentration range. If the value differs from the average of the 6 values by more than twice the standard deviation, *s*, found in 214.3.3, or more than 0.01 multiplied by the average of 6 values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration and aspiration of test solutions.

216. Calculation

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

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (36)$$

TABLE 19 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. No. 1, E350	0.0063	0.0014	0.003
2. NIST 3C 0.047 Cr	0.045	0.003	0.004
3. NIST 107b 0.56 Cr	0.559	0.026	0.052
4. No. 5, E350	0.961	0.036	0.093

where:

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

217. Precision and Bias[19]

217.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 19.

217.2 *Bias*—The accuracy can be inferred from the data in Table 19 by comparing the certified values for chromium with the average value obtained by using this method.

CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

218. Scope

218.1 This method covers the determination of chromium in compositions from 0.05 % to 30.0 %.

219. Summary of Method

219.1 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 titrated with excess ferrous ammonium sulfate to reduce chromium and the excess 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.

220. Interferences

220.1 The elements ordinarily present do not interfere if their compositions are less than the maximum limits shown in 1.1. This method may not dissolve all of the chromium carbides in Class II, Type B and C alloy iron castings.

220.2 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:

$$(2.6A + 0.05B + 0.01C)D \quad (37)$$

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.

221. Apparatus

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

222. Reagents

222.1 *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.

222.2 *Ferrous Ammonium Sulfate, Standard Solution* (0.05 *N* and 0.01 *N*)—Dissolve 20 g and 40 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 as directed in 223.1, 223.2, or 223.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

222.3 *Potassium Dichromate, Standard Solution* (0.05 *N* and 0.10 *N*)—Dissolve 2.4518 g and 4.9036 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.

222.4 *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.

222.5 *Potassium Permanganate, Standard Solution* (0.05 *N* and 0.10 *N*):

222.5.1 *Preparation*—Dissolve 1.6 g and 3.2 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.

222.5.2 *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 mL 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.

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

[19] Supporting data are available from ASTM Headquarters. Request RR:E03-1030.

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

222.7.1 *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 ($Na2SO_4$), stir, and filter through a fine paper to remove the $BaSO_4$. Store in a dark-colored bottle.

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

222.8 *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 ($FeSO_4 \cdot 7H_2O$).

223. Standardization of Ferrous Ammonium Sulfate Solution

223.1 *Against Potassium Permanganate Solution:*

223.1.1 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 0.05 *N* or 0.10 *N* $Fe(NH_4)_2(SO_4)_2$ (222.2) with either 0.05 *N* or 0.10 *N* $KMnO_4$ solution (222.5) 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 (222.5) 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.

223.1.2 Calculate the normality of the $Fe(NH_4)_2(SO_4)_2$ solutions as follows:

$$\text{Normality} = AB/C \quad (38)$$

where:

A = normality of $KMnO_4$ solution (222.5),
B = $KMnO_4$ solution, mL, and
C = $Fe(NH_4)_2(SO_4)_2$ solution, mL.

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

223.2.1 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 0.05 *N* or 0.10 *N* $Fe(NH_4)_2(SO_4)_2$ (222.2) 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 either 0.05 *N* or 0.10 *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 either 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution to the blue end point. Record the buret reading. Subtract this volume of $K_2Cr_2O_7$ solution from the volume recorded for the first titration. Record the difference as the indicator blank.

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

$$\text{Normality} = (0.05 \text{ or } 0.10\,(A - B))/C \quad (39)$$

where:

A = 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution, mL, used in the first titration,
B = equivalent to the indicator blank, mL, and
C = $Fe(NH_4)_2(SO_4)_2$ solution, mL, used in the first titration.

223.3 *Against Potassium Dichromate Using Potentiometric End Point:*

223.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution into a 600-mL beaker. Reserve the remaining 0.05 *N* or 0.10 *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* or 0.10 *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)	ΔVoltage (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.

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

$$\text{Normality} = 0.05 \text{ or } 0.10\,A/B \quad (40)$$

where:

A = 0.05 N or 0.10 N $K_2Cr_2O_7$ solution, mL, and
B = $Fe(NH_4)_2(SO_4)_2$ solution, mL.

224. Procedure

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Normality of Titrants
0.05 to 0.50	3.50	2.0	0.05
0.40 to 1.00	2.00	1.0	0.05
0.80 to 1.60	1.25	0.5	0.05
1.50 to 3.50	0.50	0.3	0.05
3.30 to 8.00	0.25	0.1	0.05
8.00 to 14.00[A]	0.50	0.1	0.10
14.00 to 20.00[A]	0.40	0.1	0.10
20.00 to 30.00[A]	0.20	0.1	0.10

[A] Use 50 mL burets for this composition range instead of the 25 mL burets specified in the procedure.

Transfer it to a 600-mL beaker.

224.2 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 iron. Boil 2 min to expel oxides of nitrogen.

224.3 If the alloy is insoluble in the acids specified in 224.2, add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, or bromine and HCl in a ratio of 1 to 3 (plus a few drops of HF), which are sufficient to dissolve the sample. When decomposition is complete, add 80 mL of H_2SO_4 (1 + 5) and 5 mL of H_3PO_4, and evaporate to light fumes. Rinse the cover and walls of the beaker, again evaporate to fumes, and fume strongly for 1 min. Cool, add 100 mL of water, and heat at 85 °C to 100 °C until the salts are dissolved.

224.4 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 times to 12 times with warm water, and reserve the filtrate.

224.5 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, and transfer the solution to the reserved filtrate (224.4) and dilute to 200 mL.

224.6 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 (222.4), 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 224.7.

224.7 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 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 as directed in 224.8. If vanadium is absent and the criteria of 220.2 are met, proceed as directed in 224.9. If vanadium is absent and the criteria of 220.2 are not met, or if the potentiometric titration is preferred and vanadium is absent, proceed as directed in 224.10.

224.8 *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.

224.9 *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.

224.10 *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 with the stirrer running until the yellow color disappears. Then 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

TABLE 20 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1. Cast Iron (NIST 3b, 0.052 Cr)	0.044	0.008	0.024
2. Cast Iron (NIST 115a, 1.98 Cr)	1.96	0.10	0.16
3. No. 5, E353	21.62	0.18	0.58

TABLE 21 Statistical Information—Chromium

Test Specimen	Chromium Found, %								
	Laboratory Number								
	1	2	3	4	5	6	7	8	9
1. HC 250 + V		25.48	23.15	24.51	25.34	25.41			25.50
2. ACIPCO High Cr Cast Iron		25.44	23.76	24.54	25.32	25.42			25.06

solution in 0.1-mL increments recording the voltage after equilibrium for each increment. Inspect the data for the maximum voltage change between increments of standard dichromate solution (see 223.3). Determine the voltage change for the increments before and after the maximum change and interpolate the end point to the nearest 0.01 mL as described in 223.3.

225. Calculation

225.1 If $KMnO_4$ was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (41)$$

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.

225.2 If $K_2Cr_2O_7$ was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (42)$$

where:

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

226. Precision and Bias[20]

226.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data shown in Tables 20 and 21. Although a sample at the high end of the scope was not evaluated by Practice E173, the precision data for other types of alloys using the methods indicated in Table 20 should apply.

226.2 *Bias*—No information on the accuracy of this method is known. The accuracy of this method may be judged, however, by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing (see Table 20).

VANADIUM BY THE ATOMIC ABSORPTION METHOD

227. Scope

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

[20] Supporting data are available from ASTM Headquarters. Request RR:E03-1036.

228. Summary of Method

228.1 The sample is dissolved in HCl, HNO_3, and $HClO_4$. 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 318.4 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.

229. Concentration Range

229.1 The recommended concentration range is 0.002 mg to 0.016 mg vanadium/mL of solution.

230. Interferences

230.1 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.

231. Apparatus

231.1 *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 as described in Guide E1024.

232. Reagents

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

232.2 *Vanadium, Standard Solution* (1 mL = 0.2 mg V)—Dissolve 0.200 g of vanadium (purity, 99.9 % min) in 20 mL of 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. It is prepared as follows: Dry 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).

233. Preparation of Calibration Curve

233.1 *Calibration Solutions*—To each of five, 250-mL borosilicate beakers, add 10 mL of $HClO_4$. Using a microburet, transfer 0.0 mL, 1.0 mL, 2.0 mL, 4.5 mL, 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, wash well with warm HCl (2 + 100). Cool, add 10 mL of $AlCl_3$ solution (232.1), dilute to volume, and mix.

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

233.2 *Spectrometry:*

233.2.1 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.

233.2.2 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 as directed in 233.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more these parameters are changed, recalibration is necessary.

233.2.3 Aspirate the vanadium solution used in 233.2.2 to assure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (43)$$

where:

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

233.2.4 Using water as a reference, and beginning with the solution to which no addition of vanadium was made in 233.1, 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 233.2.3 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 233.2.1 through 233.2.4.

233.2.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Test for linearity as given in Guide E1024.

234. Procedure

234.1 *Test Solution:*

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

234.1.2 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 (232.1), dilute to volume, and mix.

234.1.3 Prepare a reagent blank by using a 250-mL borosilicate beaker and proceeding as directed in 234.1.2. Use reagents from the same lots as those used for the sample solution.

TABLE 22 Statistical Information—Vanadium

Test Specimen	Vanadium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
Pig iron (0.008 V)	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. 1, E350	0.107	0.008	0.014
No. 2, E352	0.161	0.007	0.011

234.2 *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 sample and reagent blank solutions has been aspirated, apply the test using the standard solution as directed in 233.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 233.2.3, 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.v

235. Calculation

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

$$\text{Vanadium, \%} = ((A - B) \times 10)/C \quad (44)$$

where:

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

236. Precision and Bias[21]

236.1 *Precision*—Twenty-three laboratories participated in testing this 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.

236.2 *Bias*—No information on the accuracy of this method is known. The accuracy of this 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

237. Scope

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

[21] Supporting data are available from ASTM Headquarters. Request RR:E01-1040.

238. Summary of Method

238.1 The sample is dissolved in mineral acids and evaporated to $HClO_4$ 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.

239. Concentration Range

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

240. Interferences

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

240.2 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
429.667	Zr, Cr, Ni, Mo
446.021	Nb, Zr, V
456.236	Ti (only if 100 times greater than Ce)

241. Apparatus

241.1 An atomic emission instrument equipped with a direct current argon 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 according to 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 in accordance with their capabilities.

242. Reagents

242.1 *Cerium Standard Solution* (1 mL = 1.0 mg Ce)—Dry the cerium ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ (purity: 99.9 % minimum) (Note 69) at 82 °C to 85 °C for 4 h to 6 h and store in a dessicator over anhydrous magnesium perchlorate dessicant. 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.

242.2 *Iron,* cerium and lanthanum free.

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

242.3 *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 1.1782 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.

242.4 *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.

242.5 *Cerium Solution for Wavelength Optimization*—Transfer approximately 10 mL of cerium standard solution (1 mL = 1.0 mg Ce) as prepared in 242.1 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.

242.6 *Lanthanum Solution for Wavelength Optimization*—Transfer approximately 10 mL of lanthanum standard solution (1 mL = 1.0 mg La) as prepared in 242.3 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.

243. Procedure

243.1 *Calibration Solutions:*

243.1.1 *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 (242.2), 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 242.4. 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 polytetrafluoroethylene cover and heat using low heat until dissolution is complete. Add 15 mL of $HClO_4$, cover, and heat to $HClO_4$ 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 polytetrafluoroethylene 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.

243.1.2 *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 (242.2) and 5.0 mL of Ce standard solution (1 mL = 1.0 mg Ce) as prepared in 242.1 and 3.0 mL of La standard solution (1 mL = 1.0 mg La) as prepared in 242.3. 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 polytetrafluoroethylene cover and heat using low heat until dissolution is complete. Add 15 mL of

$HClO_4$, cover, and heat to $HClO_4$ 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.

243.1.3 *Matrix Blank Solution—Both Concentration Ranges*—To a 250-mL beaker (Note 71), add 1.0 g of iron (242.2). 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 polytetrafluoroethylene cover and heat using low heat until dissolution is complete. Add 15 mL of $HClO_4$, cover, and heat to $HClO_4$ 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.

243.2 *Test Solution*—Transfer a 1.0 g sample, weighed to the nearest 1.0 mg, to a 250-mL polytetrafluoroethylene 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 polytetrafluoroethylene cover and heat using low heat until dissolution is complete. Add 15 mL of $HClO_4$, cover, and heat to $HClO_4$ 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. If necessary, filter the solution through high porosity filter paper into a 100-mL volumetric flask. Cool, dilute to volume with water, and mix.

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

243.3.1 *Cerium*—Using the wavelength optimization solution described in 242.5, select the cerium 456.24 nm wavelength. Further optimize the instrument with the high calibration solution according to manufacturer's instructions.

243.3.2 *Lanthanum*—Using the wavelength optimization solution described in 242.6, select the lanthanum 408.67 nm wavelength. Further optimize the instrument with the high calibration solution according to manufacturer's instructions.

243.4 *Measurement:*

243.4.1 *Calibration Solutions*—Enter the value for the appropriate calibration solution (mg/L) 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.

NOTE 72—**Caution:***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 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.

243.4.2 *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 73—To ensure close calibration tolerances, a series of test solutions can be measured by recalibrating before each test sample.

TABLE 23 Statistical Information—Cerium

Test Specimen	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

Test Specimen	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

244. Calculation

244.1 Convert the instrument readings (in mg/L) to % analyte in the sample as follows:

$$\text{Cerium, \%} = \frac{A \times B}{C \times 10} \quad (45)$$

where:

A = cerium mg/L, in test solution,
B = volume of final test solution (243.2), L, and
C = weight of sample, g.

$$\text{Lanthanum, \%} = \frac{D \times B}{C \times 10} \quad (46)$$

where:

D = lanthanum in test solution, mg/L.

245. Precision and Bias[22]

245.1 *Precision*—Eight laboratories cooperated in testing this method and obtained the data summarized in Tables 23 and 24.

245.2 *Bias*—No information on the accuracy of this method is known. The accuracy of this 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

246. Scope

246.1 This method covers the determination of titanium in compositions from 0.006 % to 0.35 %.

247. Summmary of Method

247.1 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.

248. Concentration Range

248.1 The recommended concentration range is 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.

249. Stability of Color

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

250. Interferences

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

251. Apparatus

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

252. Reagents

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

252.2 *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 HCl. Prepare as needed.

252.3 *Potassium Hydrogen Sulfate, Fused* (a mixture of $K_2S_2O_7$ and $KHSO_4$).

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

252.5 *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 74). 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 74—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.

253. Preparation of Calibration Curve

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

253.2 *Calibration Solutions*—Using pipets, transfer 0.5 mL, 1 mL, 2 mL, 4 mL, 6 mL, 8 mL, 10 mL, 12 mL, and 14 mL of titanium solution (1 mL = 0.010 mg Ti) to 50-mL volumetric flasks. Proceed as directed in 253.5.

NOTE 75—Take spectrophotometric readings of the calibration solutions containing 0.5 mL, 1 mL, 2 mL, 4 mL, and 6 mL of titanium solution using a 2-cm light path. Use a 1-cm light path for the remaining solutions.

253.3 *Reference Solution*—Water.

253.4 *Reagent Blank*—Transfer 10 mL of water to a 50-mL volumetric flask and proceed as directed in 253.5.

253.5 *Color Development*:

253.5.1 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.

253.6 *Spectrophotometry:*

253.6.1 *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.

253.6.2 *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.

253.7 *Calibration Curve*—Subtract the reagent blank reading from each of the calibration solution readings. Plot the blank-corrected spectrophotometric readings of the calibration

[22] Supporting data are available from ASTM Headquarters. Request RR:E03-1042.

solutions against milligrams of titanium per 50 mL of solution. Prepare separate curves for 1-cm and 2-cm light path cells.

254. Procedure

254.1 *Test Solution*

254.1.1 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
0.006 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 0.35	0.40	0.5	100	10.00	1

Transfer it to a 250-mL beaker.

254.1.2 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 76—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.

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.

254.1.3 Filter through an 11-cm medium-porosity filter paper containing paper pulp into a 100-mL volumetric flask as directed in 254.1.1 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.

254.1.4 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 (254.1.3). Dilute to volume, and mix.

254.1.5 Using a pipet, transfer a 10-mL portion to a 50-mL volumetric flask and treat as directed in 253.5.1 using 1 mL of HCl (1 + 1).

254.2 *Sample Blank Solution*—Using a pipet, transfer a second 10-mL portion of the test solution to a 50-mL volumetric flask and treat as directed in 254.1.1 and 253.5.1, omitting the addition of DAPM.

TABLE 25 Statistical Information—Titanium

Test Specimen	Titanium Found, %	Repeatability, % (R_1, E173)	Reproducibility,% (R_2, E173)
1. Low Alloy (NIST 19 g, 0.027 Ti)	0.028	0.0013	0.0043
2. Low Alloy (NIST 170a, 0.281 Ti)	0.282	0.0097	0.0228
3. Cast Iron (NIST 122d, 0.007 Ti)	0.006	0.0019	0.0037
4. Blast Furnace Iron (NIST 1144a, 0.32 Ti)	0.33	0.0118	0.0168

254.3 *Reagent Blank Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with the sample omitted (254.1.1 – 254.1.5).

254.4 *Reference Solutions*—Water and the sample blank solution, as described in 254.2.

254.5 *Spectrophotometry*—Take the spectrophotometric reading of the reagent blank solution versus water and of the test solution versus the sample blank solution, as directed in 253.6.

255. Calculation

255.1 Convert the spectrophotometric reading of the test solution to milligrams of titanium by means of the appropriate calibration curve. Calculate the percentage of titanium as follows:

$$\text{Titanium, \%} = (A - B)/(C \times 100) \times 100 \quad (47)$$

where:

A = titanium, mg, found in the final color development solution,
B = titanium found, mg, in the reagent blank, and
C = original sample weight (g) as determined in 254.1.1.

256. Precision and Bias

256.1 *Precision*—Eight laboratories cooperated in testing this method and obtained the data summarized in Table 25.

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

MOLYBDENUM BY THE ION EXCHANGE—8-HYDROXYQUINOLINE GRAVIMETRIC METHOD

257. Scope

257.1 This method covers the determination of molybdenum in compositions from 1.5 % to 5.0 %.

258. Summary of Method

258.1 Molybdenum is separated from interfering elements on an anion-exchange resin column using a sequence of HF + HCl eluent solutions. The isolated molybdenum is precipitated with 8-hydroxyquinoline and weighed as the anhydrous complex.

259. Interferences

259.1 All interfering elements which are normally present are removed by the anion exchange separation.

260. Apparatus

260.1 *Ion Exchange Column, Polystyrene*, approximately 400 mm in length and 25 mm in inside diameter, the bottom tapered to a 2-mm bore outlet, fitted with a hosecock or stopcock to control the liquid flow. All parts of the apparatus must be constructed of HF-resistant plastic, such as polytetrafluoroethylene, polyethylene, or polyvinyl chloride (Note 77).

NOTE 77—The ion exchange column system must be carefully assembled and checked to avoid possible leakage of solutions containing HF.

261. Reagents

261.1 *Ammonium Chloride Solution* (240 g/L)—Dissolve 240 g of ammonium chloride (NH_4Cl) in 800 mL of water. Warm to room temperature, dilute to 1 L and mix.

261.2 *Ammonium Fluoride* (NH_4F).

261.3 *Ammonium Oxalate* ($NH_4OCOCOONH_4H_2O$).

261.4 *EDTA Solution* (10 g/L)—Dissolve 10 g of EDTA-disodium salt in water. Dilute to 1 L and mix.

261.5 *Eluent Solutions* (**Warning**—See Note 78.)

NOTE 78—**Warning:** HF causes serious burns which may not be immediately painful; read the paragraph about HF in the Hazards section of Practices E50.

261.5.1 *Hydrofluoric Acid/Hydrochloric Acid/Water* (4 + 1 + 95)—To 800 mL of water in a 1-L polyethylene graduated cylinder, add 40 mL of HF and 10 mL of HCl; dilute to 1 L and mix. Store in an HF-resistant plastic bottle.

261.5.2 *Hydrofluoric Acid/Hydrochloric Acid/Water* (1 + 5 + 4)—To 300 mL of water in a 1-L polyethylene graduated cylinder, add 100 mL of HF and 500 mL of HCl; dilute to 1 L and mix. Store in an HF-resistant plastic bottle.

261.5.3 *Hydrofluoric Acid/Hydrochloric Acid/Water* (20 + 25 + 55)—To 500 mL of water in a 1-L polyethylene graduated cylinder, add 200 mL HF and 250 mL HCl; dilute to 1 L and mix. Store in an HF-resistant plastic bottle.

261.5.4 *Hydrofluoric Acid/Ammonium Chloride/Water* (4 + 60 + 36)—To 600 mL of ammonium chloride solution (240 g/L) in a 1-L polyethylene graduated cylinder, add 40 mL HF; dilute to 1 L and mix. Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH_4Cl on a weight/volume basis).

261.5.5 *Ammonium Fluoride/Ammonium Chloride Solution*—To 600 mL of ammonium chloride solution (240 g/L) in a 1-L polyethylene graduated cylinder, add 41 g of NH_4F. Add water to the 900 mL mark and stir to dissolve. Dilute to 1 L and mix. With narrow-range pH paper, verify that the pH is between 5.6 and 5.8. If it is above this range, adjust the solution with dropwise additions of HF; it it is below this range, adjust the solution with dropwise additions of NH_4OH. Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH_4Cl and 4.1 % in NH_4F on a weight/volume basis.)

261.6 *8-Hydroxyquinoline Solution* (30 g/L)—Dissolve 30 g of 8-hydroxyquinoline in 120 mL of glacial acetic acid (CH_3COOH). Cautiously add water, with stirring to a total solution volume of 600 mL. Warm to 40 °C. Add NH_4OH (1 + 1) dropwise with stirring until a slight permanent precipitate is formed. Carefully add glacial CH_3COOH with stirring until the precipitate first dissolves. Dilute to 1 L.

261.7 *Ion-Exchange Resin:*

261.7.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and of 200-nominal to 400-nominal U.S. mesh size.[23] To remove those beads greater than about 180 µm in diameter, as well as the very small diameter 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 into 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.

261.7.2 Prepare the column as follows: Place a 10-mm to 20-mm layer of polyvinyl 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 150 mm to 175 mm. Place a 20-mm layer of polyvinyl chloride plastic fiber on the top of the resin surface 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. When the solution level is 5 mm to 10 mm above the top of the resin bed add 100 mL of HCl (1 + 9) to the column. Repeat this cycle twice more and finally wash the resin bed with 200 mL HCl (1 + 3) turning off the stopcock when the solution level is 10 mm to 20 mm above the top of the resin bed.

261.8 *Sodium Hydroxide Solution*(100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in about 100 mL of water. When dissolution is complete, cool, and dilute to 1 L. Store in a plastic bottle.

261.9 *Sodium Hydroxide Solution*(10 g/L)—Dissolve 10 g of NaOH in about 100 mL of water. Cool and dilute to 1 L. Store in a plastic bottle.

262. Procedure

262.1 Transfer 1 g of sample weighed to the nearest 0.1 mg to a 200-mL polytetrafluoroethylene beaker marked at the 100 mL level on the outside. Add 10 mL of HF and cover with a polytetrafluoroethylene watchglass. Warm the solution with low heat and cautiously add HNO_3 in 1-mL increments allowing the reaction to subside between additions. High chromium samples may also require cautious dropwise additions of HCl. When dissolution is complete, cool the beaker, remove the cover with platinum-tipped tongs and cautiously rinse it into the solution with water.

262.2 Over a steambath of other low temperature arrangement evaporate the solution to dryness. Cool, wash down the sides of the beaker with HCl (1 + 1) and again evaporate to dryness over low heat. Cool, add 5 mL of HF and 25 mL water. Warm over low heat until all salts are dissolved (Note 79). Cool to room temperature and dilute to 100 mL with water.

[23] AG 1-X8 (catalog number 140-1451), 200 mesh to 400 mesh, chloride form, which is available from Bio-Rad Laboratories, Hercules, CA 94547, has been found satisfactory (www.bio-rad.com).

NOTE 79—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

262.3 Drain the solution in the ion exchange column by passing 100 mL of HF/HCl/water (4 + 1 + 95) through it at a ratio of approximately 2 mL/min. Allow the solution to drain to the top of the resin bed. Collect the effluent in a plastic beaker and discard it.

262.4 Place an 800 mL plastic beaker under the column. Place a small plastic funnel holding a high-porosity hard-surface filter paper in the top of the column. Ensure that an air seal does not form between the funnel and the column. Cautiously filter the sample solution onto the column. Adjust the effluent flow to about 2 mL/min. Rinse the beaker with HF/HCl/water (4 + 1 + 95) transferring the washings to the paper. Cautiously police the beaker with a polytetrafluoroethylene policeman, if necessary, and rinse onto the paper with HF/HCl/water (4 + 1 + 95). Wash the paper well with HF/HCl/water (4 + 1 + 95). Cautiously, remove and discard paper (Note 80).

NOTE 80—If insoluble molybdenum compounds are suspected or known to be present, halt the flow from the column when the washing of the paper is complete. Cautiously transfer the paper to a platinum crucible and ignite at 500 °C (no higher) in a muffle furnace. Cool in a desiccator, add 1 g anhydrous sodium carbonate powder (Na_2CO_3) and fuse over a burner. Cool, add 20 mL water and heat to dissolve the melt. Carefully acidify with dropwise additions of HCl (1 + 4) until effervescence ceases plus 10 drops excess. Evaporate to dryness, cool, add 20 mL HF/HCl/water (4 + 1 + 95), heat to dissolve, cool, and transfer this solution to the column. Resume the 2 mL/min flow from the column.

262.5 Continue to add HF/HCl/water (4 + 1 + 95) until 650 mL have been collected in the 800 mL plastic beaker (Note 81). Drain solution to the top of the resin bed. Cautiously discard this solution.

NOTE 81—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper and manganese.

262.6 Place an 800-mL plastic beaker under the column and elute 500 mL of HF/HCl/water (1 + 5 + 4) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 82).

NOTE 82—This solution contains all the tungsten, titanium, zirconium, and hafnium.

262.7 Place an 800-mL polytetrafluoroethylene beaker under the column and elute the molybdenum with 500 mL of HF/HCl/water (20 + 25 + 55) at a rate of 2 mL min. Drain solution to the top of the resin bed. Proceed with this eluent solution as descrived in 262.11.

262.8 Place an 800-mL plastic beaker under the column and elute 300 mL of HF/NH_4Cl/water (4 + 60 + 36) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 83).

NOTE 83—This solution contains all the niobium.

262.9 Place an 800-mL plastic beaker under the column and elute 350 mL of NH_4F/NH_4Cl solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 84).

NOTE 84—This solution contains all the tantalum.

262.10 Place an 800-mL plastic beaker under the column and elute 100 mL of water, then 100 mL of HCl (1 + 3), stopping the flow when the liquid level is 10 mm to 20 mm above the resin bed. Cautiously discard the solution. The column is now ready to be stored for future use or to be preconditioned for another sample (262.3).

262.11 To the eluent containing the molybdenum (from 262.7) cautiously add 15 mL of H_2SO_4 (1 + 1) and evaporate to light fumes on a steam bath or other carefully controlled heat source (see Note 85).

NOTE 85—**Warning:** Ensure that the applied temperature does not exceed the softening point of polytetrafluoroethylene. Cool and cautiously rinse into 1 400-mL borosilicate glass beaker. Heat to low volume (about 10 mL), cool, add 2 mL of HNO_3, and evaporate to strong fumes of SO_3.

262.12 Cool to room temperature, dilute to about 30 mL with water, add 5 mL of HNO_3 and 5 mL of HCl. Cover and heat for 10 min.

262.13 Dilute to 100 mL. Heat to boiling and while hot, cautiously add NaOH solution (100 g/L) until litmus paper moistened with the solution just turns blue, then add 10 mL excess. Boil for 1 min. If a precipitate is present, filter through high porosity, surface hardened filter paper and wash paper thoroughly with warm NaOH solution (10 g/L). Discard paper. If no precipitate is present proceed directly to 262.14.

262.14 Adjust the volume of the solution or filtrate obtained in 262.13 to about 200 mL. Add 10 mL of EDTA solution (10 g/L) and 3 g of ammonium oxalate. Warm gently to obtain a clear solution and cool to room temperature.. Adjust the pH to 4.0 using a pH meter and dropwise additions of HCl (1 + 1) and NaOH solution (10 g/L).

262.15 Heat the solution to boiling, remove from heat and slowly add 20 mL of 8-hydroxyquinoline solution (30 g/L) while stirring. Heat at just below the boiling point for 10 min, stirring occasionally.

262.16 Filter through a tared medium-pososity fritted glass filtering crucible using gentle suction. Wash the contents of the beaker into the filtering crucible with hot water and wash the precipitate with additional hot water for a total of about 100 mL.

262.17 Dry the precipitate in a drying oven set at 125 °C for at least 4 h. Cool the filtering crucible for at least 2 h in a desiccator and weigh.

263. Calculation

263.1 Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, } \% = [(A - B) \times 23.05]/C \quad (48)$$

where:

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

264. Precision and Bias

264.1 *Precision*— Seven laboratories cooperated in testing this method and obtained the data summarized in Table 26. While the testing range exceeds the upper limit of the Scope, the data for Test Material 3 were included to illustrate the ruggedness of the method's precision at levels near the upper limit of the Scope.

TABLE 26 Statistical Information—Molybdenum Ion Exchange—8-Hydroxyquinoline Gravimetric Method

Test	Molybdenum Found, %	Repeatability, (R_1,E173[A])	Reproducibility, (R_2, E173[A])
1. White cast iron (NIST 1146, 1.51 Mo)	1.48	0.070	0.086
2. No. 1, E354	3.92	0.219	0.250
3. No. 3, E352	8.85	0.180	0.188

[A]The test was conducted in accordance with the 1980 version of Practice E173.

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

265. Keywords

265.1 atomic absorption; carbon content; cast iron; cerium; chromium; cobalt; combustion analysis; copper; graphitic carbon; gravimetric; infrared absorption; ion exchange; lanthanum; lead; magnesium; manganese; molybdenum; nickel; phosphorus; silicon; spectrophotometric; sulfur; tin; titanium; titrimetric; vanadium

APPENDIX

(Nonmandatory Information)

X1. TEST OF SUITABILITY OF IRON AND STRONTIUM CHLORIDE

X1.1 Iron

X1.1.1 Transfer $(5 \times F)g$ of iron (76.1) weighed to the nearest 10 mg, to a 400-mL beaker; dissolve it, evaporate the solution to dryness and bake as directed in 76.1. Add 15 mL of HCl and heat gently until salts are dissolved. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Transfer 20.0 mL to each of three 25-mL volumetric flasks, dilute one of them to volume, and mix. To the other two add 2.0 mL and 4.0 mL, respectively, of magnesium solution B (76.3), dilute to volume, and mix.

X1.1.2 Prepare a reagent blank by evaporating to dryness the volumes of HCl (1 + 1) and HNO_3 used in X1.1.1 to dissolve the iron. Add 15 mL of HCl and heat gently to dissolve any salts. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Transfer 20.0 mL to each of three 25-mL volumetric flasks, dilute one of them to volume, and mix. To the other two add 2.0 mL and 4.0 mL, respectively, of magnesium solution B (76.3), dilute to volume, and mix.

X1.1.3 With the hollow cathode tube in position, energized and stabilized, locate the wavelength setting in the vicinity of 285.2 nm that gives the maximum response of the detector system.

X1.1.4 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the solution to which 4 mL of magnesium standard solution was added in X1.1.1 a sufficient number of times to establish that the reading is not drifting. Record the absorbance. Aspirate the other two solutions and the three solutions prepared as directed in X1.1.2.

X1.1.5 Plot two curves on rectangular coordinate paper, one based on the absorbance values recorded for the three solutions from X1.1.1 and the other based on the three values found for the solutions from X1.1.2 against milligrams of magnesium added, namely 0, $0.004 \times F$, and $0.008 \times F$ (75.1.4). Extrapolate each curve to zero absorbance and record the corresponding values for milligrams of magnesium in 25 mL of the final solution.

X1.1.6 Calculate the percentage of magnesium in the iron as follows:

$$\text{Magnesium, \%} = (A - B)/(10 \times F) \qquad \text{(X1.1)}$$

where:

A = magnesium, mg, in 25 mL of the final solution of iron,

B = magnesium, mg, in 25 mL of the final blank solution, and

F = sensitivity factor (75.1.4).

X1.2 Strontium Chloride

X1.2.1 Transfer 10.0 mL of the solution prepared as directed in 76.4 to each of three 25-mL volumetric flasks, dilute one of them to volume, and mix. To the other two add 2.0 mL and 4.0 mL, respectively, of magnesium solution B (76.3), dilute to volume, and mix.

X1.2.2 With the hollow cathode tube in position, energized and stabilized, locate the wavelength setting in the vicinity of 285.2 nm that gives the maximum response of the detector system.

X1.2.3 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the solution to which 4 mL of magnesium standard solution was added in X1.2.1 a sufficient number of times to establish that the reading is not drifting. Record the absorbance. Aspirate the other two solutions and record the absorbance values.

X1.2.4 Plot a curve on rectangular coordinate paper based on the absorbance values of the three solutions (X1.2.3) against

milligrams of magnesium added, namely 0, $0.004 \times F$, and $0.008 \times F$ (75.1.4). Extrapolate the curve to zero absorbance and record the corresponding value for milligrams of magnesium in 25 mL of the final solution.

X1.2.5 Calculate the percentage of magnesium in the strontium chloride as follows:

$$\text{Magnesium, \%} = A/(10 \times F) \quad \text{(X1.2)}$$

where:

A = magnesium, mg, in 25 mL of the final strontium chloride solution, and
F = sensitivity factor (75.1.4).