



Standard Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys¹

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

1. Scope

1.1 These test methods² cover the chemical analysis of stainless, heat-resisting, maraging, and other similar chromium-nickel-iron alloys having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	0.002 to 5.50
Boron	0.001 to 0.20
Carbon	0.01 to 1.50
Chromium	0.01 to 35.00
Cobalt	0.01 to 15.00
Columbium (Niobium)	0.01 to 4.00
Copper	0.01 to 5.00
Lead	0.001 to 0.50
Manganese	0.01 to 20.00
Molybdenum	0.01 to 7.00
Nickel	0.01 to 48.00
Nitrogen	0.001 to 0.50
Phosphorus	0.002 to 0.35
Selenium	0.01 to 0.50
Silicon	0.01 to 4.00
Sulfur	0.002 to 0.50
Tantalum	0.01 to 0.80
Tin	0.001 to 0.05
Titanium	0.01 to 4.50
Tungsten	0.01 to 4.50
Vanadium	0.005 to 1.00
Zirconium	0.001 to 0.20

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

	Sections
Aluminum, Total, by the 8-Quinololin Gravimetric Method (0.20 to 7.00 %)	119
Aluminum, Total, by the 8-Quinololin Photometric Method (0.003 to 0.20 %)	71
Carbon, Total, by the Combustion—Thermal Conductivity Method	^{2a}

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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² These test methods represent revisions of methods covered by ASTM Methods E 30 and E 38 which appear in this publication.

^{2a} Discontinued April 25, 1986. Its replacement appears as part of ASTM Method E 1019, found in *Annual Book of ASTM Standards*, Vol 03.05.

^{2b} Discontinued May 30, 1980.

^{2c} Discontinued April 29, 1988.

	Sections
Carbon, Total, by the Combustion Gravimetric Method (0.05 to 1.50 %)	98
Chromium by the Atomic Absorption Method (0.006 to 1.00 %)	202
Chromium by the Peroxydisulfate Oxidation—Titration Method (0.10 to 35.00 %)	212
Chromium by the Peroxydisulfate-Oxidation Titrimetric Method	^{2b}
Cobalt by the Ion-Exchange—Potentiometric Titration Method (2 to 15. %)	53
Cobalt by the Nitroso-R-Salt Photometric Method (0.01 to 5.0 %)	61
Copper by the Neocuproine Photometric Method (0.01 to 5.00 %)	109
Copper by the Sulfide Precipitation-Electrodeposition Gravimetric Method (0.01 to 5.00 %)	82
Lead by the Ion-Exchange—Atomic Absorption Method (0.001 to 0.50 %)	127
Manganese by the Periodate Photometric Method (0.01 to 5.00 %)	8
Molybdenum by the Ion Exchange—8-Hydroxyquinoline Gravimetric Method	242
Molybdenum by the Photometric Method (0.01 to 1.50 %)	190
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 to 48.0 %)	172
Phosphorus by the Alkalimetric Method (0.02 to 0.35 %)	164
Phosphorus by the Molybdenum Blue Photometric Method (0.002 to 0.35 %)	18
Silicon by the Gravimetric Method (0.05 to 4.00 %)	46
Sulfur by the Gravimetric Method	^{2c}
Sulfur by the Combustion-Iodate Titration Method (0.005 to 0.5 %)	37
Sulfur by the Chromatographic Gravimetric Method	^{2b}
Tin by the Solvent Extraction—Atomic Absorption Method (0.002 to 0.10 %)	180
Tin by the Sulfide-Iodometric Titration Method (0.01 to 0.05 %)	90
Titanium, Total, by the Diantiprylmethane Spectrophotometric Method (0.01 to 0.35 %)	231
Vanadium by the Atomic Absorption Method (0.006 to 0.15 %)	221

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

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

1.5 The values stated in SI units are to be regarded as standard. In some cases, exceptions allowed in Practice E 380 are also used.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific hazards statements are given in Section 5 and in special "Warning" paragraphs throughout these test methods.

2. Referenced Documents

2.1 ASTM Standards:

- D 1193 Specification for Reagent Water³
 - E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴
 - E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron⁵
 - E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁶
 - E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁶
 - E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁷
 - E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron⁶
 - E 351 Test Methods for Chemical Analysis of Cast Iron—All Types⁶
 - E 352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels⁶
 - E 354 Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic and Other Similar Iron, Nickel, and Cobalt Alloys⁶
 - E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)⁸
 - E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁶
 - E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys⁶
 - E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry⁶
 - E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis⁶
 - E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition⁹
- ### 2.2 Other Document:
- ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests¹⁰

3. Significance and Use

- 3.1 These test methods for the chemical analysis of metals

and alloys are primarily intended as referee methods to test such materials for compliance with compositional specifications, particularly those under the jurisdiction of ASTM Committee A1 on Steel, Stainless Steel, and Related Alloys. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide E 882.

4. Apparatus, Reagents, and Instrumental Practices

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

4.2 Reagents:

4.2.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the "Reagent Grade" Specifications of the American Chemical Society.¹¹ Other chemicals may be used, provided it is first ascertained that they are of sufficiently high purity to permit their use without adversely affecting the expected performance of the determination, as indicated in the section on "Precision and Bias."

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

4.3 *Photometric Practice*—Photometric prescribed in these test methods shall conform to Practice E 60.

5. Hazards

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

6. Sampling

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

7. Interlaboratory Studies and Rounding Calculated Values

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

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

MANGANESE BY THE META PERIODATE PHOTOMETRIC METHOD

8. Scope

8.1 This method covers the determination of manganese in concentrations from 0.01 to 5.00 %.

9. Summary of Method

9.1 Manganous ions are oxidized to permanganate ions by

¹¹ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of Reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia," United States Pharmacopeial Convention, Rockville, MD 20852.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 14.02.

⁵ Discontinued 1995; see 1994 Annual Book of ASTM Standards, Vol 03.05.

⁶ Annual Book of ASTM Standards, Vol 03.05.

⁷ Discontinued 1998; see 1997 Annual Book of ASTM Standards, Vol 03.05.

⁸ Discontinued 1997; see IEEE/ASTM SI 10—Standard, Vol 14.04.

⁹ Annual Book of ASTM Standards, Vol 03.06.

¹⁰ Available from American National Standards Institute, 11 West 42nd Street, 13th Floor, New York, NY 10036.

treatment with periodate. Tungsten when present at concentrations greater than 0.5 % is kept in solution with phosphoric acid. Solutions of the samples are fumed with perchloric acid so that the effect of periodate is limited to the oxidation of manganese. Photometric measurement is made at approximately 545 nm.

10. Concentration Range

10.1 The recommended concentration range is 0.15 to 0.8 mg of manganese per 50 mL of solution, using a 1-cm cell (see 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.

11. Stability of Color

11.1 The color is stable for at least 24 h.

12. Interferences

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

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

12.3 Tungsten, when present in amounts of more than 0.5 % interferes by producing a turbidity in the final solution. A special procedure is provided for use with samples containing more than 0.5 % tungsten which eliminates the problem by preventing the precipitation of the tungsten.

13. Reagents

13.1 *Manganese, Standard Solution* (1 mL = 0.032 mg Mn)—Transfer the equivalent of 0.4000 g of assayed, high-purity manganese (purity: 99.99 % minimum), to a 500-mL volumetric flask and dissolve in 20 mL of HNO₃ by heating. Cool, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 500-mL volumetric flask, dilute to volume, and mix.

13.2 *Nitric-Phosphoric Acid Mixture*—Cautiously, while stirring, add 100 mL of HNO₃ and 400 mL of H₃PO₄ to 400 mL of water. Cool, dilute to 1 L, and mix. Prepare fresh as needed.

13.3 *Potassium Metaperiodate Solution* (7.5 g/L)—Dissolve 7.5 g of potassium metaperiodate (KIO₄) in 200 mL of hot HNO₃ (1 + 1), add 400 mL of H₃PO₄, cool, dilute to 1 L, and mix.

13.4 *Water, Pretreated with Metaperiodate*—Add 20 mL of KIO₄ solution to 1 L of water, mix, heat at not less than 90°C for 20 to 30 min, and cool. Use this water to dilute solutions to volume that have been treated with KIO₄ solution to oxidize manganese, and thus avoid reduction of permanganate ions by any reducing agents in the untreated water. **Caution**—Avoid the use of this water for other purposes.

14. Preparation of Calibration Curve

14.1 *Calibration Solutions*—Using pipets, transfer 5, 10, 15, 20, and 25 mL of manganese standard solution (1 mL = 0.032 mg Mn) to 50-mL borosilicate glass volumetric flasks, and if necessary, dilute to approximately 25 mL. Proceed as directed in 14.3.

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

14.3 *Color Development*—Add 10 mL of KIO₄ solution, and heat the solutions at not less than 90°C for 20 to 30 min (Note 2). Cool, dilute to volume with pretreated water, and mix.

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

14.4 *Photometry*:

14.4.1 *Multiple-Cell Photometer*—Measure the cell correction using the Reference Solution (14.2) in absorption cells with a 1-cm light path and using a light band centered at approximately 545 nm. Using the test cell, take the photometric readings of the calibration solutions versus the Reference Solution (14.2).

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

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

15. Procedure

15.1 *Test Solution* — Select and weigh a sample in accordance with the following:

Manganese, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.01 to 0.5	0.80	0.5	100	20
0.45 to 1.0	0.35	0.3	100	20
0.85 to 2.0	0.80	0.5	500	20
1.95 to 5.0	0.80	0.5	500	10

Transfer it to a 300-mL Erlenmeyer flask.

15.1.1 To dissolve samples that do not require HF, add 8 to 10 mL of HCl (1 + 1), and heat. Add HNO₃ as needed to hasten dissolution, and then add 3 to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of HClO₄; evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, and digest if necessary to dissolve the salts. Cool and

transfer the solution to either a 100- or 500-ml volumetric flask as indicated in 6.1. Proceed to 15.2.2.

15.2 For samples whose dissolution is hastened by HF, add 8 to 10 mL of HCl (1 + 1), and heat. Add HNO₃ and a few drops of HF as needed to hasten dissolution, and then add 3 to 4 mL of HNO₃. When dissolution is complete, cool, then add 10 mL of HClO₄, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to either a 100- or 500-mL volumetric flask as indicated in 15.1. Proceed to 15.2.2.

15.2.1 *For Samples Containing More Than 0.5 % Tungsten:*

15.2.1.1 To dissolve samples that do not require HF, add 8 to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 to 6 mL of H₂SO₄, and 3 to 4 mL of HNO₃. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO₃. Cool, add 50 mL of water, and digest, if necessary, to dissolve the salts. Transfer the solution to either a 100- or 500-mL volumetric flask as directed in 15.1. Proceed to 15.2.2.

15.2.1.2 For samples whose dissolution is hastened by HF: Add 8 to 10 ml of H₃PO₄, 10 mL of HClO₄, 5 to 6 mL of H₂SO₄, 3 to 4 mL of HNO₃, and a few drops of HF. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes or SO₃. Cool, add 50 mL of water, digest, if necessary, to dissolve the salts, cool, and transfer the solution to a 100- or 500-mL volumetric flask as directed in 15.1. Proceed to 15.2.2.

15.2.2 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 to 20 mL of the filtrate, before taking aliquots.

15.2.3 Using a pipet, transfer 10 to 20-mL aliquots as specified in 15.1 two 50-mL borosilicate glass volumetric flasks. Treat one portion as directed in 15.4. Treat the other portion as directed in 15.5.1.

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

15.4 *Color Development*—Proceed as directed in 14.3.

15.5 *Reference Solutions:*

15.5.1 *Background Color Solution*—To one of the sample aliquots in a 50-mL volumetric flask, add 10 mL of nitric-phosphoric acid mixture, and heat the solution at not less than 90°C for 20 to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

15.5.2 *Reagent Blank Reference Solution*—Transfer the reagent blank solution (15.3) to the same size volumetric flask as used for the test solutions and transfer the same size aliquots as used for the test solutions to two 50-mL volumetric flasks. Treat one portion as directed in 15.4 and use as reference solution for test samples. Treat the other as directed in 15.5.1 and use as reference solution for Background Color Solutions.

15.6 *Photometry*—Establish the cell corrections with the Reagent Blank Reference solution to be used as a reference

solution for Background Color solutions. Take the photometric readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference Solutions as directed in 14.4.

16. Calculation

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

17. Precision and Bias

17.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 1.

17.2 *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 PHOTOMETRIC METHOD

18. Scope

18.1 This method covers the determination of phosphorus in concentrations from 0.002 to 0.35 %.

19. Summary of Method

19.1 See Section 19 of Test Methods E 350.

20. Concentration Range

20.1 See Section 20 of Test Methods E 350.

21. Stability of Color

21.1 See Section 21 of Test Methods E 350.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Photometric Method

Test Material	Manganese Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
1. Maraging steel 18Ni-8Co-5Mo	0.020	0.005	0.007
2. Maraging steel (NIST 1156, 0.21 Mn)	0.209	0.009	0.017
3. Stainless steel 24Cr-13Ni (NIST 447, 0.23 Mn)	0.208	0.008	0.016
4. Stainless steel 18Cr-9Ni (NIST 101e, 1.77 Mn)	1.79	0.04	0.06
5. Stainless steel 18.5Cr-9.5Ni (NIST 443, 3.38 Mn)	3.37	0.05	0.11
6. Stainless steel 20.5Cr-10Ni (NIST 444, 4.62 Mn)	4.60	0.04	0.13

^A This test was performed in accordance with the 1980 version of Practice E 173.

22. Interferences

22.1 See Section 22 of Test Methods E 352.

23. Apparatus

23.1 See Section 23 of Test Methods E 350.

24. Reagents

24.1 Proceed as directed in 24.1 through 24.7 of Test Methods E 350.

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

25.1 Proceed as directed in 25.1 through 25.6 of Test Methods E 350.

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

26.1 Proceed as directed in 26.1 through 26.6 of Test Methods E 350.

27. Procedure

27.1 *For Samples Containing Less Than 0.5 % Tungsten:*

27.1.1 *Test Solution:*

27.1.1.1 For concentrations not greater than 0.30 percent phosphorus, use a 1.0-g sample; for the concentration range from 0.30 to 0.35 % phosphorus, use a 0.85-g sample. Weigh the sample to the nearest 0.5 mg, and transfer it to a 250-mL Erlenmeyer flask.

27.1.1.2 Proceed as directed in 27.1.2 and 27.1.3 of Test Methods E 350.

27.1.2 Proceed as directed in 27.2 through 27.5 of Test Methods E 350.

27.2 *For Samples Containing More Than 0.5 % Tungsten:*

27.2.1 *Test Solution:*

27.2.1.1 For concentrations not greater than 0.30 % phosphorus, transfer 0.100-g samples, weighed to the nearest 0.1 mg, to two 100-mL Erlenmeyer flasks; for the concentration range from 0.30 to 0.35 % phosphorus, transfer 0.085-g samples, weighed to the nearest 0.1 mg, to two 100-mL Erlenmeyer flasks.

27.2.1.2 Proceed as directed in 26.2.1.2 and 26.2.1.3 of Test Methods E 352.

27.2.2 Proceed as directed in 26.2.2 through 26.2.5 of Test Methods E 352.

28. Calculation

28.1 Proceed as directed in Section 28, Test Methods E 350.

29. Precision

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

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

SULFUR BY THE GRAVIMETRIC METHOD

(This method, which consisted of Sections 30 through 36 of this standard, was discontinued in 1988.)

TABLE 2 Statistical Information—Phosphorus

Test Material	Phosphorus Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. Stainless steel 18Cr-9Ni (NBS 101e, 0.025 P)	0.025	0.001	0.004
2. Stainless steel 19Cr-14Ni-3Mo (NBS 160a, 0.027 P)	0.026	0.002	0.004
3. Stainless steel 17Cr-9Ni-0.25Se (NBS 339, 0.129 P)	0.128	0.007	0.012

^A This test was performed in accordance with the 1980 version of Practice E 173.

37. Scope

37.1 This method covers the determination of sulfur in concentrations from 0.005 to 0.5 %.

38. Summary of Method

38.1 See Section 38 of Test Methods E 350.

39. Interferences

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

40. Apparatus

40.1 See Section 40 of Test Methods E 350.

41. Reagents

41.1 Proceed as directed in 41.1 through 41.6 of Test Methods E 350.

42. Calibration

42.1 Proceed as directed in 42.1 through 42.6 of Test Methods E 350.

43. Procedure

43.1 Proceed as directed in 43.1 and 43.2 of Test Methods E 350.

44. Calculation

44.1 Proceed as directed in Section 44 of Test Methods E 350.

45. Precision

45.1 Twenty-two laboratories cooperated in testing this method; six used resistance furnaces and reported eight sets of values (Note 3); sixteen used induction furnaces (Note 4). They obtained the data summarized in Table 3 for material 7. Although samples covered by this method with sulfur concentration near the lower limit of the scope were not available for testing, the precision data obtained using the methods indicated in Table 3 should apply. None was available to permit a test near the upper limit of the scope.

NOTE 3—The recovery of sulfur as SO₂ ranged from 72 to 97 % with an average value of 83 % based on calibration standards designated *b*, *c*, and *d* in Table 3.

NOTE 4—The recovery of sulfur as SO₂ ranged from 80 to 96 % with an average value of 88 % based on calibration standards designated *b*, *c*,

TABLE 3 Statistical Information—Sulfur

Test Material	Sulfur Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
Induction Furnace			
1. No. 1, E352	0.006 ^B	0.0016	0.0032
2. No. 2, E352	0.008 ^B	0.0013	0.0044
3. No. 3, E350	0.014 ^B	0.0025	0.0029
4. No. 4, E350	0.016 ^B	0.0018	0.0024
5. No. 6, E350	0.032 ^C	0.0032	0.0049
6. No. 7, E350	0.141 ^D	0.0066	0.0126
7. Stainless steel 13Cr-0.3Mo (NBS 133a, 0.329S + NBS 10 g, 0.109S: 0.286S)	0.286 ^E	0.0135	0.0201
Resistance Furnace			
1. No. 1, E352	0.006 ^B	0.0014	0.0024
2. No. 2, E352	0.009 ^B	0.0007	0.0020
3. No. 3, E350	0.014 ^B	0.0014	0.0025
4. No. 4, E350	0.015 ^B	0.0017	0.0029
5. No. 6, E350	0.032 ^C	0.0028	0.0041
6. No. 7, E350	0.140 ^D	0.0074	0.0111
7. Stainless steel 13Cr-0.3Mo (NBS 133a, 0.329S + NBS 10g, 0.109 S: 0.286S)	0.288 ^E	0.0123	0.0206

^A This test was performed in accordance with the 1980 version of Practice E 173.

^B Calibration standards: See Footnote^A, Table 5, Methods E 350.

^C Calibration standards: See Footnote^B, Table 5, Methods E 350.

^D Calibration standards: See Footnote^C, Table 5, Methods E 350.

^E Calibration standards: see Footnote^D, Table 5, Methods E 350

and *d* in Table 3.

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

46.1 This method covers the determination of silicon in concentrations from 0.05 to 4.00 %.

47. Summary of Method

47.1 See Section 47 of Test Methods E 350.

48. Interferences

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

49. Reagents

49.1 Proceed as directed in 49.1 through 49.4 of Test Methods E 350.

50. Procedure

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

Silicon, %	Sample Weight, g	Tolerance in Sample Weight, mg		Dehydrating Acid, mL	
		H ₂ SO ₄	HClO ₄	H ₂ SO ₄ (1 + 4)	HClO ₄
0.05 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

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

50.2 Proceed as directed in 50.2 of Test Methods E 350 if tungsten is greater than 0.5 %.

50.3 Proceed as directed in 50.2 or 50.3 of Test Methods E 350 if tungsten is less than 0.5 %.

50.4 Proceed as directed in 50.4 through 50.6 of Test Methods E 350.

50.5 Proceed as directed in 50.7 of Test Methods E 350, but if the sample contains more than 0.5 % tungsten, ignite at 750 C instead of 1100 to 1150 C after volatilization of SiO₂.

51. Calculation

51.1 Proceed as directed in Section 51 of Test Methods E 350.

52. Precision

52.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 4. Samples with silicon concentrations near the extreme limits of the scope were not available for testing.

COBALT BY THE ION-EXCHANGE— POTENTIOMETRIC TITRATION METHOD

53. Scope

53.1 This method covers the determination of cobalt in concentrations from 2 to 15 %.

54. Summary of Method

54.1 See Section 54 of Test Methods E 351.

55. Interferences

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

56. Apparatus

56.1 See Section 56 of Test Methods E 351.

57. Reagents

57.1 Proceed as directed in 57.1 through 57.4 of Test Methods E 351.

58. Procedure

TABLE 4 Statistical Information—Silicon

Test Material	Silicon Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
HClO ₄ Dehydration			
1. Stainless steel 18Cr-9Ni (NBS 101e, 0.43 Si)	0.428	0.014	0.021
2. Stainless steel 19Cr-14Ni-3Mo (NBS 160a, 0.605 Si)	0.602	0.018	0.031
3. Stainless steel 18Cr-10Ni-0.4Ti (NBS 121c, 0.64 Si)	0.642	0.019	0.031
H ₂ SO ₄ Dehydration			
1. Stainless steel 18Cr-9Ni (NBS 101e, 0.43 Si)	0.428	0.021	0.033
2. Stainless steel 19Cr-14Ni-3Mo (NBS 160a, 0.605 Si)	0.603	0.017	0.014
3. Stainless steel 18Cr-10Ni-0.4Ti (NBS 121c, 0.64 Si)	0.642	0.026	0.033

^A This test was performed in accordance with the 1980 version of Practice E 173.

58.1 Proceed as directed in 57.1 through 57.6 of Test Methods E 352.

59. Calculation

59.1 Proceed as directed in Section 59 of Test Methods E 351.

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 methods indicated in Table 5 should apply.

**COBALT BY THE NITROSO-R-SALT
PHOTOMETRIC METHOD**

61. Scope

61.1 This method covers the determination of cobalt in concentrations from 0.01 to 5.0 %.

62. Summary of Method

62.1 See Section 54 of Test Methods E 350.

63. Concentration Range

63.1 See Section 55 of Test Methods E 350.

64. Stability of Color

64.1 See Section 56 of Test Methods E 350.

65. Interferences

65.1 See Section 57 of Test Methods E 350.

66. Reagents

66.1 Proceed as directed in 58.1 through 58.4 of Test Methods E 350.

67. Preparation of Calibration Curve

67.1 Proceed as directed in 59.1 through 59.5 of Test Methods E 350.

68. Procedure

68.1 *Test Solution:*

68.1.1 Proceed as directed in 67.1.1 through 67.1.3 of Test Methods E 352.

68.2 Proceed as directed in 60.2 through 60.4 of Test Methods E 350.

69. Calculation

TABLE 5 Statistical Information—Cobalt

Test Material	Cobalt Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. No. 1, E352	1.86	0.05	0.12
2. No. 2, E352	4.82	0.08	0.11
3. No. 3, E352	8.46	0.03	0.07
4. No. 4, E354	11.27	0.06	0.16
5. No. 5, E354	13.88	0.09	0.18

^AThis test was performed in accordance with the 1980 version of Practice E 173.

TABLE 6 Statistical Information—Cobalt

Test Material	Cobalt Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. No. 1, E350	0.011	0.005	0.007
2. Stainless steel, 17Cr-9Ni (NBS 339, 0.096 Co)	0.094	0.006	0.013
3. Stainless steel, 18Cr-9Ni-0.25Se (NBS 101e, 0.18 Co)	0.173	0.011	0.026
4. No. 4, E354	0.468	0.020	0.028
5. Stainless steel, 15Cr-15Ni-3Mo	1.01	0.04	0.06
6. No. 2, E352	1.87	0.09	0.13
7. No. 3, E352	4.94	0.08	0.17

^AThis test was performed in accordance with the 1980 version of Practice E 173.

69.1 Proceed as directed in Section 61 of Test Methods E 350.

70. Precision¹²

70.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 6 for materials 2, 3, and 5. Although samples covered by this method with cobalt concentrations near the extreme limits of the scope were not available for testing, the precision data obtained for other types of alloys, using the methods indicated in Table 6 should apply.

**TOTAL ALUMINUM BY THE
8-QUINOLINOL PHOTOMETRIC METHOD**

71. Scope

71.1 This method covers the determination of total aluminum in concentrations from 0.003 to 0.20 %.

72. Summary of Method

72.1 See Section 77 of Test Methods E 350.

73. Concentration Range

73.1 See Section 78 of Test Methods E 350.

74. Stability of Color

74.1 See Section 79 of Test Methods E 350.

75. Interferences

75.1 None of the elements usually present interfere if their concentrations are under the maximum limits shown in 1.1.

76. Apparatus

76.1 See Section 81 of Test Methods E 350.

77. Reagents

77.1. Proceed as directed in 82.1 through 82.9 of Test Methods E 350.

78. Preparation of Calibration Curve

78.1 Proceed as directed in 83.1 through 83.6 of Test Methods E 350.

¹² Supporting data are available from ASTM Headquarters. Request RR:E03-1027.

79. Procedure

79.1 Proceed as directed in 84.1 through 84.5 of Test Methods E 350.

80. Calculation

80.1 Proceed as directed in Section 85 of Test Methods E 350.

81. Precision

81.1 A minimum of eight laboratories cooperated in testing this method and obtained the data summarized in Table 7.

COPPER BY THE SULFIDE PRECIPITATION-ELECTRODEPOSITION GRAVIMETRIC METHOD

82. Scope

82.1 This method covers the determination of copper in concentrations from 0.01 to 5.00 %.

83. Summary of Method

83.1 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 5). Chloride ions are removed from the filtrate, and copper, as the metal, is deposited on a platinum cathode.

NOTE 5—This method describes the preliminary separations for the determination of tin by the sulfide-iodatimetric titration method.

84. Interferences

84.1 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 8).

85. Apparatus

85.1 Apparatus No. 9.

86. Reagents

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

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

86.3 *Sulfamic Acid* (H(NH₂)SO₃).

87. Procedure

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

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.01 to 1.0	10	10
0.0 to 2.5	5	5
2.5 to 5.0	2	2

Transfer it to a 1-L Erlenmeyer flask.

87.2 Add 115 mL of HCl (1+2) plus an additional 9 mL of HCl (1+2) and 1 mL of HNO₃ for each gram of sample. Heat until dissolution is complete, and then boil the solution for 2 to 3 min. If the solution is clear, proceed as directed in 87.3 and 87.8–87.21.

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

87.4 If the solution contains insoluble matter, add paper pulp, digest 15 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 or 5 times with water. Reserve the filtrate. Proceed as directed in 87.4.1 or 87.4.2 according to preference, bearing in mind that the latter procedure may be the easier to apply when copious amounts of insoluble matter are encountered.

87.4.1 Transfer the paper and precipitate to the original flask, add 20 mL of HNO₃ and 10 mL of HClO₄, heat moderately to oxidize organic matter, and finally heat to mild fumes of HClO₄. Cool the solution, add 1 to 2 mL of HF, and repeat the fuming.

87.4.2 Transfer the paper and precipitate to a platinum 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 HNO₃ and 1 to 2 mL of HF, and evaporate to dryness. Add 10 mL of HNO₃ (1+1) and digest at 90 to 100°C for 5 min. Transfer the contents of the crucible to the original flask, add 10 mL of HClO₄, and heat to mild fumes of HClO₄.

87.5 Cool the solution from 87.4.1 or 87.4.2, add 100 mL of water and digest at or near boiling for about 45 min.

87.6 If tungsten is present, as indicated by the presence of a bright yellow precipitate of tungstic acid, add a slight excess of NH₄OH and 20 g of tartaric acid. When the tartaric acid has dissolved, again add a slight excess of NH₄OH and digest near the boiling point until dissolution is complete, or nearly so.

87.7 Add 5 mL of H₂SO₄ and heat at 85 to 95°C for 30 min. If insoluble matter persists, repeat the steps as directed in 87.4–87.7. When dissolution is complete, combine the solution with the filtrate reserved in 87.4.

87.8 If the volume is less than 600 mL, dilute the solution approximately to that volume and treat with H₂S; 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

TABLE 7 Statistical Information—Aluminum

Test Material	Aluminum Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
1. Type 304 stainless steel 18Cr-8Ni	0.004	0.001	0.003
2. Type 304 stainless steel 18Cr-8Ni	0.045	0.006	0.010
3. Type 304 stainless steel 18Cr-8Ni	0.083	0.004	0.009
4. Type A286 stainless steel 15Cr-26Ni	0.19	0.01	0.04

^A This test was performed in accordance with the 1980 version of Practice E 173.

clear, but not longer than 12 to 15 h.

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

87.10 Transfer the filter paper and precipitate to the original flask, add 12 mL of H₂SO₄, and heat to char the paper. Add 20 mL of HNO₃, and evaporate to fumes to destroy organic matter. Add HNO₃ in 1-mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

87.11 Cool the solution, rinse the sides of the flask, and repeat the fuming to ensure the complete removal of HNO₃.

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

87.13 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.

87.14 Add 10 mL of FeCl₃ solution to the filtrate. Add just enough NH₄OH (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 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 NH₄OH (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 NH₄OH (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 NH₄ (1+99) and water.

NOTE 6—If tin is to be determined by using the same sample, reserve the precipitate and proceed as directed in 100.5 through 100.8.

87.15 Acidify the combined filtrates with HNO₃, 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 HNO₃. When the reaction has subsided, add another 5 mL of HNO₃ and again wait until the reaction subsides. Continue adding 5-mL increments of HNO₃ 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 SO₃. Cool, add 25 mL of water, and heat to dissolve the salts. Cool, transfer to a 250-mL beaker, add 3 mL of HNO₃, and dilute to 175 mL.

87.16 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.

87.17 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/dm². Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 to 3 A/dm² (Note 7). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 7—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm², and 2 to 3 h should be

allowed for complete deposition.

87.18 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 to 15 min to ensure complete deposition of the copper.

87.19 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.

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

NOTE 8—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of HNO₃ and 5 mL of H₂SO₄ 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/dm² until the copper has been removed from the original electrode. Reverse the polarity and redeposit the copper on the original electrode as directed in 76.17 and 76.18. Proceed as directed in 87.18 and 87.19.

87.21 Allow the electrode to cool to room temperature undessicated, and weigh.

NOTE 9—To prepare the electrode for reuse, immerse it in HNO₃ (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.

88. Calculation

88.1 Calculate the percentage of copper as follows:

$$\text{Copper, \%} = [(A - B) - (C - D)]/E \times 100 \quad (2)$$

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.

89. Precision

89.1 Six laboratories cooperated in testing this method and obtained eight sets of data summarized in Table 8 for material 3. Although samples covered by this method with copper concentrations at the lower and upper limits of the scope were

TABLE 8 Statistical Information—Copper

Test Material	Copper Found, %	Repeatability (R ₁ , Practice E 173 ^A)	Reproducibility (R ₂ , Practice E 173 ^A)
1. Low-alloy steel (NBS 152a, 0.0023 Cu)	0.020	0.005	0.006
2. No. 2, E352	0.079	0.003	0.006
3. Stainless steel 18Cr-9Ni (NBS 101e, 0.359 Cu)	0.364	0.009	0.010
4. No. 4, E351	5.49	0.10	0.10

^A This test was performed in accordance with the 1980 version of Practice E 173.

not available for testing, the precision data obtained using the methods indicated should apply.

TIN BY THE SULFIDE-IODOMETRIC TITRATION METHOD

90. Scope

90.1 This method covers the determination of tin in concentrations from 0.01 to 0.05 %.

91. Summary of Method

91.1 See Section 96 of Test Methods E 350.

92. Interferences

92.1 See Section 97 of Test Methods E 350.

93. Apparatus

93.1 See Section 98 of Test Methods E 350.

94. Reagents

94.1 Proceed as directed in 99.1 through 99.8 of Test Methods E 350.

95. Procedure

95.1 Transfer a 10-g sample, weighed to the nearest 10 mg, to each of two 1-L Erlenmeyer flasks.

95.2 Proceed as directed in 100.2 through 100.8 of Test Methods E 350.

96. Calculation

96.1 Proceed as directed in 101.1 of Test Methods E 350.

97. Precision

97.1 Five laboratories cooperated in testing this method and obtained eight sets of data summarized in Table 9. Samples covered by this method with tin concentrations at approximately 0.01 and 0.05 % were not available for testing.

TOTAL CARBON BY THE COMBUSTION GRAVIMETRIC METHOD

98. Scope

98.1 This method covers the determination of carbon in concentrations from 0.05 to 1.50 %.

99. Summary of Test Method

99.1 The sample is burned in a stream of oxygen, and the

carbon dioxide in the evolved gases is collected in a suitable absorbent and weighed.

99.2 Oxygen flow rates and sweep times as well as control of plate current for induction heating depend upon the equipment used, and the type of sample analyzed. The control of these parameters should be established by analysis of control samples similar in carbon content and alloy characteristics to the sample to be analyzed.

100. Interferences

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

101. Apparatus

101.1 *Apparatus No. 1.*

NOTE 10—The induction furnace must be equipped with suitable controls to regulate the power input to the induction coil.

NOTE 11—The preferred position for a graduated flowmeter is at the exit end of the furnace. The graduated flowmeter may be positioned at the inlet, but in either case a sulfuric acid bubbler tube must be positioned at the exit end of the equipment.

101.2 *Balance, Analytical*—Either a single-pan or double-pan balance may be used. The balance shall weigh to the nearest 0.1 mg and have a standard deviation for a single weighing of 0.05 mg or less.

NOTE 12—For precision-testing this balance see 7.4 of Methods E 319, or its equivalent.

102. Reagents

102.1 *Acetone*—The residue after evaporation must be <0.0005 %.

102.2 *Iron (Low-Carbon) Accelerator*—Iron chips (Note 13).

102.3 *Oxygen*—Purified as described in 8.1.3 of Practices E 50.

102.4 *Tin (Low-Carbon) Accelerator*, granular (Note 13).

102.5 *Tin-coated Copper Accelerator*, granular. Copper and tin metals in the ratio of approximately 30:1 may also be used.

NOTE 13—Prior to use, all accelerators should be washed three times with acetone by decantation until free of organic contaminants and then dried.

103. Preparation of Apparatus—Induction Furnace

103.1 The train of the induction furnace shall include an oxygen purifier, catalyst heater (Note 14), particle filter, and carbon dioxide purifier. The oxygen must flow from the top of the combustion tube through a small orifice so as to impinge directly on the surface of the sample.

NOTE 14—The catalyst heater contains copper oxide heater to about 300°C to ensure complete conversion of CO to CO₂.

103.2 *Conditioning of Apparatus:*

103.2.1 Transfer 1 g of a sample containing approximately 0.5 % carbon and 1 g of the accelerators (see Section 102) to a cupelet, crucible, or boat.

TABLE 9 Statistical Information—Tin

Test Material	Tin Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. Stainless steel 18Cr-9Ni (NBS 101e, 0.020 Sn)	0.022	0.003	0.005

^A This test was performed in accordance with the 1980 version of Practice E 173.

103.2.2 Open the furnace, position the cupelet, crucible, or boat with the sample in the combustion tube, close the furnace, and adjust the oxygen flow rate to 1200 to 1500 mL/min. Sweep the system with oxygen for 30 s.

103.2.3 Open the stopcock(s) of the absorption bulb and connect it to the carbon train.

NOTE 15—The Fleming, Turner, and Nesbitt bulbs have all proved satisfactory. Bulbs shall not be handled with bare fingers at any time. Weighing time, that is, the interval from the completion of the burn and sweep to the completion of the weighing, must be closely controlled and kept rigidly constant. If a two-pan balance is used, a bulb may be used as a tare and may be carried alongside the sample bulb at all times in the procedure.

103.2.4 Turn on the power switch of the furnace, record the time (if an automatic timer is used, adjust it for a 5-min burning period), and burn the sample for 5 min while controlling the plate current to provide a temperature of at least 1325°C. During the burning it may be necessary to reduce the plate current to maintain the temperature and prevent sample loss.

NOTE 16—During the sample burn, oxygen is consumed at a rapid rate. If necessary, manually increase the oxygen flow rate to maintain a positive pressure within the combustion tube.

103.2.5 Sweep the system with oxygen (maintaining the original flow rate) after the combustion is complete.

NOTE 17—Oxygen flow rates and sweep times vary to some extent with equipment used, and the type of sample to be analyzed. Sweep times of 2 to 5 min have been found to be adequate in most cases. A control sample with carbon content and alloy characteristics similar to the sample to be analyzed should be used to control these parameters.

103.2.6 Detach the absorption bulb, close the stopcock(s), and set the bulb by the balance to cool. Remove the sample from the furnace.

104. Preparation of Apparatus—Resistance Furnace

104.1 The resistance furnace shall contain as part of the train an oxygen purifier, catalyst heater (see the Oxygen Purifiers portion of the Apparatus Section of Practices E 50), particle filter, and carbon dioxide purifier. Turn on the current and adjust the furnace temperature to at least 1325°C.

104.2 Conditioning of Apparatus:

104.2.1 Fill the boat with Alundum bedding material (Note 18). Make a furrow in the Alundum large enough to contain the sample and the accelerator. Place in the furrow 1 g of a sample containing approximately 0.5% carbon so that the particles are in intimate contact. In the same manner add 1 g of one of the accelerators (see Section 102).

NOTE 18—The Alundum bedding material should be previously heated in oxygen at 1325°C for 15 min, cooled, and stored under cover.

104.2.2 Open the stopcock(s) of the absorption bulb (Note 15) and connect it to the carbon train.

104.2.3 Cover the boat with a suitable cover and introduce it into the combustion tube. Close the tube and preheat the sample for 1 to 2 min. Turn on the oxygen, adjust the oxygen flow rate to 300 to 500 mL per min, and maintain this rate for 6 to 13 min (Note 16).

NOTE 19—Oxygen flow rates and sweep times vary to some extent with equipment used and the type of sample to be analyzed. A control sample

with carbon content and alloy characteristics similar to the sample to be analyzed should be used to control these parameters.

104.2.4 Detach the absorption bulb, close the stopcocks(s), and set the bulb by the balance to cool. Remove the sample from the combustion tube, and shut off the oxygen.

105. Blank Procedure

105.1 Induction Furnace:

105.1.1 Open the stopcock(s) of the absorption bulb momentarily to the atmosphere to equilibrate bulb conditions, and weigh the bulb which has been conditioned as directed in 103.2.

105.1.2 Add an amount of low-carbon iron equal to the sample weight to be used and 1 g of tin or tin-copper accelerator to a cupelet, crucible, or boat. Proceed as directed in 103.2.2–103.2.6.

105.1.3 Open the stopcock(s) momentarily and weigh the absorption bulb.

105.1.4 Repeat the determination of the blank until it is constant within 0.2 mg and the average does not exceed 0.3 mg. If the blank does not become constant within this limit, determine the source of the difficulty and repeat the blank determination before proceeding.

105.2 Resistance Furnace:

105.2.1 Open the stopcock(s) of the absorption bulb momentarily to the atmosphere to equilibrate bulb conditions, and weigh the bulb which has been conditioned as directed in 104.2.

105.2.2 Add an amount of low-carbon iron equal to the sample weight to be used and 1 g of tin or tin-copper accelerator to the combustion boat containing Alundum bedding material (Note 18). Proceed as directed in 104.2.2–104.2.4.

105.2.3 Proceed as directed in 105.1.3 and 105.1.4.

105.2.4 Proceed as directed in Section 106.

106. Procedure

106.1 Select a control sample the carbon content and alloy characteristics of which are similar to those of the sample being analyzed, and proceed as directed in 106.2–106.5.

NOTE 20—The value obtained should not differ from the established value by more than 0.004 % carbon at levels from 0.05 to 0.2 %, nor more than 2 % of the amount present in the higher ranges of carbon.

NOTE 21—Low results may be due to (1) incomplete burning of the sample, which may be detected by examining the slag; (2) a leak in the system, which may be checked by means of a manometer; (3) improper filling of the absorption bulb, resulting in “channeling”; or (4) exhaustion of the CO₂ absorbent. High results may be due to inadequate purification of the oxygen or failure to remove oxides of sulfur.

106.2 Open the stopcock(s) momentarily and weigh the absorption bulb.

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

Carbon, %	Sample Weight, g
0.05 to 0.4	2.729
0.2 to 1.0	1.365
0.7 to 1.5	1.000
1.3 to 5.0	0.500

Transfer it to a crucible, cupelet, or boat containing Alundum (Note 18).

106.4 Add an amount of low-carbon iron equal to the sample weight and 1 g of tin or tin-copper accelerator and proceed as directed in 103.2.2–103.2.6 and 104.2.2–104.2.4.

106.5 Open the stopcock(s) momentarily and weigh the absorption bulb.

107. Calculation

107.1 Calculate the percent of carbon as follows:

$$\text{Carbon, \%} = [(A - B) \times 0.2729] / C \times 100 \quad (3)$$

where:

- A = carbon dioxide found, g,
- B = carbon dioxide found in the blank, g, and
- C = sample used, g.

108. Precision

108.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 10.

Repeatability (R_1) and reproducibility (R_2) are defined in Practice E 173 and were respectively calculated from within laboratory standard deviation σ_w and the total standard deviation S . Since these last terms are related by:

$$S^2 = \sigma_w^2 + \sigma_d^2 \quad (4)$$

where σ_d is the among laboratories standard deviation, both S and σ_w can be evaluated by an analysis of variance if replicate determinations (duplicates in this case) are carried out on each specimen by a number of laboratories. With single determinations on each specimen, only the total standard deviation S can be evaluated.

108.1.1 The repeatability is related to and can be estimated from σ_w as follows: Let X_1 and X_2 be the difference between two values obtained within a laboratory. The standard deviation σ_d of this difference is

$$\sigma_d^2 = \sigma_{w1}^2 + \sigma_w^2 = (1.41 \sigma_w)^2 \quad (5)$$

Since

$$\sigma_w = \sigma_{w1} = \sigma_{w2} \quad (6)$$

the repeatability, which in accordance with Practice E 173 is actually the 95 % confidence limit for σ_d , is then

$$R_1 = 2\sigma_d = (2)(1.41)\sigma_w = 2.82 \sigma_w \quad (7)$$

108.1.2 The reproducibility is related in the same way to the total standard deviation, namely

TABLE 10 Statistical Information—Carbon

Test Material	Carbon Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. Stainless steel (NBS 101e, 0.054 C)	0.052	0.006	0.006
2. Stainless steel (NBS 160a, 0.062 C)	0.061 ^B	—	0.007
3. Ni-Cr steel (NBS 32e, 0.409 C)	0.40	0.02	0.02
4. Ni-Cr alloy (NBS 341, 1.81 C)	1.79	0.04	0.06

^A This test was performed in accordance with the 1980 version of Practice E 173.

^B Based on single determinations by each laboratory; all other values on duplicate determinations by each laboratory.

$$R_2 = 2.82 S \quad (8)$$

COPPER BY THE NEOCUPROINE PHOTOMETRIC METHOD

109. Scope

109.1 This method covers the determination of copper in concentrations from 0.01 to 5.00 %.

110. Summary of Method

110.1 See Section 115 of Test Methods E 350.

111. Concentration Range

111.1 See Section 116 of Test Methods E 350.

112. Stability of Color

112.1 See Section 117 of Test Methods E 350.

113. Interferences

113.1 See Section 118 of Test Methods E 350.

114. Reagents

114.1 Proceed as directed in 119.1 through 119.6 of Test Methods E 350.

115. Preparation of Calibration Curve

115.1 Proceed as directed in 120.1 through 120.6 of Test Methods E 350.

116. Procedure

116.1 *Test Solution:*

116.1.1 Proceed as directed in 123.1.1 of Test Methods E 351.

116.1.2 Proceed as directed in 96.1.2 of Test Methods E 352.

116.1.3 Proceed as directed in 121.1.3 and 121.1.4 of Test Methods E 350.

116.2 Proceed as directed in 121.2 through 121.5 of Test Methods E 350.

117. Calculation

117.1 Proceed as directed in Section 122 of Test Methods E 350.

118. Precision

118.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 11. Although samples covered by this method with copper concentrations near the lower and upper limits of the scope were not available for testing, the precision data obtained for the other specimens by the methods indicated should apply.

TOTAL ALUMINUM BY THE 8-QUINOLINOL GRAVIMETRIC METHOD

119. Scope

TABLE 11 Statistical Information—Copper

Test Material	Copper Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. No. 1, E354	0.006	0.001	0.004
2. No. 2, E354	0.014	0.002	0.006
3. No. 3, E354	0.033	0.005	0.004
4. No. 5, E352	0.078	0.005	0.010
5. No. 6, E352	0.118	0.007	0.016
6. Stainless steel 19Cr-14Ni-3Mo (NBS 160a, 0.174 Cu)	0.176	0.019	0.021
7. Stainless steel 17Cr-9Ni-0.25Se (NBS 339, 0.199 Cu)	0.200	0.012	0.018
8. Stainless steel 26Ni-15Cr (NBS 348, 0.22 Cu)	0.221	0.013	0.022
9. Stainless steel 18Cr-9Ni (NBS 101e, 0.359 Cu)	0.361	0.015	0.036
10. No. 5, E351	1.51	0.04	0.036
11. No. 6, E351	5.53	0.19	0.18

^A This test was performed in accordance with the 1980 version of Practice E 173.

119.1 This method covers the determination of total aluminum in concentrations from 0.20 to 7.00 %.

120. Summary of Method

120.1 See Section 125 of Test Methods E 350.

121. Interferences

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

122. Apparatus

122.1 See Section 127 of Test Methods E 350.

123. Reagents

123.1 Proceed as directed in 128.1 through 128.7 of Test Methods E 350.

124. Procedure

124.1 Proceed as directed in 129.1 through 129.10 of Test Methods E 350.

124.2 If the aluminum concentration is less than 1.50 %, proceed as directed in 129.11 through 129.13 of Test Methods E 350. If the aluminum concentration is greater than 1.50 %, transfer the solution to a 250-mL volumetric flask, dilute to volume, and mix. Select the proper aliquot in accordance with the following:

Aluminum, %	Aliquot, mL	Weight of Sample in Aliquot, g
1.50 to 3.50	100	0.400
3.50 to 7.00	50	0.200

Using a pipet, transfer it to a 600-mL beaker. Proceed as directed in 129.11 through 129.13 of Test Methods E 350.

125. Calculation

125.1 Calculate the percentage of total aluminum as follows:

$$\text{Total aluminum, \%} = [(A - B) \times 0.0587]/C \times 100 \quad (9)$$

where:

- A = aluminum quinolate found, g,
- B = correction for blank, in g, and
- C = sample in final aliquot, g.

126. Precision¹⁰

126.1 Nine laboratories cooperated in testing this method, with one laboratory reporting a second pair of values; the data are summarized in Table 12. Although samples covered by this method with aluminum concentrations at the upper limit and in the middle range of the scope were not available for testing, the data obtained using the methods indicated in Table 12 should apply.

LEAD BY THE ION-EXCHANGE—ATOMIC ABSORPTION METHOD

127. Scope

127.1 This method covers the determination of lead in concentrations from 0.001 to 0.50 %.

128. Summary of Method

128.1 See Section 133 of Test Methods E 350.

129. Concentration Range

129.1 See Section 134 of Test Methods E 350.

130. Interferences

130.1 See Section 135 of Test Methods E 350.

131. Apparatus

131.1 See Section 136 of Test Methods E 350.

132. Reagents

132.1 Proceed as directed in 137.1 and 137.2 of Test Methods E 350.

133. Preparation of Calibration Curve

133.1 Proceed as directed in 138.1 through 138.3 of Test Methods E 350.

134. Procedure

134.1 Proceed as directed in 106.1 through 106.3 of Test Methods E 352.

TABLE 12 Statistical Information—Aluminum

Test Material	Aluminum Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. Stainless steel 26Ni-15Cr (NBS 348, 0.23 Al)	0.232	0.036	0.041
2. Stainless steel 15Cr-7Ni-2Mo-1Al (NBS 344, 1.16 Al)	1.16	0.06	0.10
3. No. 3, E354	1.21	0.02	0.08
4. No. 4, E350	1.44	0.07	0.16
5. No. 5, E354	2.88	0.06	0.12
6. No. 6, E354	5.84	0.16	0.26

^A This test was performed in accordance with the 1980 version of Practice E 173.

135. Calculation

135.1 Proceed as directed in 140.1 of Test Methods E 350.

136. Precision⁴

136.1 A minimum of eight laboratories cooperated in testing this method and obtained the data summarized in Table 13.

SULFUR BY THE CHROMATOGRAPHIC GRAVIMETRIC METHOD

(This method, which consisted of Sections 137 through 144 of this standard, was discontinued in 1980.)

CHROMIUM BY THE PEROXYDISULFATE-OXIDATION TITRIMETRIC METHOD

(This method, which consisted of Sections 145 through 152 of this standard, was discontinued in 1980.)

TOTAL CARBON BY THE COMBUSTION-THERMAL CONDUCTIVITY METHOD

(This method, which consisted of Sections 153 through 163 of this standard, was discontinued in 1986. Its replacement appears in Test Methods E 1019.)

PHOSPHORUS BY THE ALKALIMETRIC METHOD

164. Scope

164.1 This method covers the determination of phosphorus in concentrations from 0.02 to 0.35 % in samples containing not more than 0.5 % tungsten and not more than a total of 1 % columbium and tantalum.

165. Summary of Method

165.1 Phosphorus is separated as ammonium phosphomolybdate. The precipitate is dissolved in standard NaOH solution, and the excess NaOH is titrated with standard HNO₃.

166. Interferences

166.1 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 to 20°C.

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

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

167. Apparatus

167.1 *Funnel, Hirsch Porcelain*, 56-mm plate diameter and 94-mm top diameter. Place a 5.5-cm fine qualitative, smooth-surface filter paper over the perforated filter plate. Place an 11-cm fine qualitative, rough-surface filter paper on the funnel, moisten it with KNO₃ 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.

167.2 *Funnel, Glass, 60°*, fitted with a 25-mm diameter perforated porcelain filtering disk. Place a 5.5-cm fine paper over the perforated plate. Place an 11-cm fine paper on the funnel, moisten it with KNO₃ 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.

168. Reagents

168.1 *Ammonium Molybdate Solution (Acidic)*—Reagent No. 102. Filter just prior to use.

168.2 *Ferrous Sulfate Solution (100 g/L)*—Dissolve 100 g of ferrous sulfate heptahydrate (FeSO₄·7H₂O) in 1 L of H₂SO₄ (5 + 95).

168.3 *Nitric Acid, Standard Solution (1 mL = approximately 0.00013 g P)*—Transfer 6.3 mL of HNO₃ 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 168.7, to a 125-mL Erlenmeyer flask. Add 3 drops of phenolphthalein indicator solution and titrate with the HNO₃ until 1 drop causes the pink color to disappear. Calculate the phosphorus equivalent as follows:

$$\text{Phosphorus equivalent, g P/mL} = ((A \times B)/C) \quad (10)$$

where:

A = NaOH solution, mL,

B = phosphorus equivalent and of the NaOH solution, and

C = HNO₃ solution, mL.

168.4 *Phenolphthalein Indicator Solution*—Reagent No. 117.

168.5 *Potassium Nitrate Solution (10 g/L)*—Dissolve 10 g of potassium nitrate (KNO₃) in water, dilute to 1 L, and mix.

168.6 *Potassium Permanganate Solution (25 g/L)*—Dissolve 25 g of potassium permanganate (KMnO₄) in water, dilute to 1 L, and mix.

168.7 *Sodium Hydroxide, Standard Solution (1 mL = approximately 0.00013 g P)*—Transfer 4.0 g of sodium

TABLE 13 Statistical Information—Lead

Test Material	Lead Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
1. Type 304 stainless steel 18Cr-8Ni	0.0004	0.0002	0.0003
2. Type 304 stainless steel 18Cr-8Ni	0.0010	0.0001	0.0005
3. Type 304 stainless steel 18Cr-8Ni	0.0029	0.0004	0.0004
4. Type 304 stainless steel 18Cr-8Ni	0.0063	0.0009	0.0010
5. Type 304 stainless steel 18Cr-8Ni	0.0126	0.0012	0.0028
6. Test specimen No. 1 + No. 7 mixed in ratio of 1 + 1 (0.102 Pb)	0.106	0.023	0.031
7. No. 7, E350	0.217	0.010	0.049

^A This test was performed in accordance with the 1980 version of Practice E 173.

hydroxide (NaOH) to a 1-L volumetric flask, and dissolve in freshly boiled water that has been cooled to room temperature. Dilute to volume with the boiled water and mix. Standardize the solution as follows: Transfer to a 300-mL Erlenmeyer flask 0.5000 g of the National Bureau of Standards standard sample of potassium acid phthalate (KHC₈H₄O₄) 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 one drop produces a pink color. Calculate the phosphorus equivalent as follows:

$$\text{Phosphorus equivalent, g P/mL} = \frac{(A \times 0.001347)}{(B \times 0.2042)} \quad (11)$$

where:

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

169. Procedure

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

Phosphorus, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.01 to 0.10	2.0	5
0.10 to 0.25	1.0	5
0.25 to 0.35	0.5	2

Transfer the sample to a 400-mL beaker.

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

169.3 Add 35 mL of HNO₃ and 40 mL of HCl and, if the silicon concentration is greater than 0.5 %, add 3 to 5 drops of HF. Cover the beaker and heat, as required, to hasten dissolution. Add 15 mL of HClO₄. Remove and rinse the cover. Place a ribbed cover glass on the beaker and evaporate to fumes. Continue heating for 5 min until the chromium is oxidized. Cool slightly, and add 40 mL of water and paper pulp. Filter through an 11-cm fine paper into a 300-mL Erlenmeyer flask. Wash the beaker and paper containing the residue with 75 mL of HNO₃ (1 + 3). Heat the solution, and add KMnO₄ dropwise until a permanent brown precipitate forms, and boil 3 min. Add H₂SO₃ dropwise until the precipitate dissolves, and boil 3 min to expel the oxides of nitrogen.

169.4 Evaporate the solution to 100 mL, and cool to room temperature. While swirling the flask, slowly add 20 mL of NH₄OH, so that no precipitate forms (Note 27). Adjust the temperature to 45°C.

NOTE 22—The quantity of NH₄OH specified should result in a pH of 0.1 to 0.6 after the addition of the NH₄OH 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 NH₄OH will precipitate iron as ferric hydroxide. Failure to carefully control the acidity will retard the precipitation of the ammonium phosphomolybdate.

169.5 Add 40 mL of ammonium molybdate solution, stopper the flask, and shake 10 min on a mechanical shaker. If the vanadium concentration is less than 0.1 %, allow the precipitate to settle at least 20 min at room temperature; for samples

containing higher concentrations of vanadium, cool the solution to 10 to 20°C, add 5 mL of ferrous sulfate solution and 2 to 3 drops of H₂SO₃, and allow the precipitate to settle at least 20 min at 10 to 20°C.

TABLE 14 Statistical Information—Phosphorus

Test Material	Phosphorus Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
1. Stainless steel 13 Cr (NBS 73c, 0.018 P)	0.017	0.001	0.006
2. High-alloy steel 22Cr-4Ni-9Mn (NBS 346, 0.018 P)	0.017	0.004	0.007
3. Stainless steel 13Cr (NBS 133a, 0.026 P)	0.024	0.003	0.011
4. Stainless steel (NBS 101e, 0.025 P)	0.024	0.003	0.009
5. Stainless steel (NBS 339, 0.129 P)	0.125	0.008	0.018
6. Stainless steel (303-Se)	0.151	0.015	0.015

^A This test was performed in accordance with the 1980 version of Practice E 173.

169.6 Filter the solution with the aid of suction using a Hirsch porcelain crucible (167.1) or a glass funnel fitted with a perforated porcelain filtering disk (167.2). Rinse the flask 3 to 5 times with a total volume of approximately 40 mL of KNO₃ solution, transferring all the precipitate to the filter. Wash the filter paper 12 to 15 times with a total volume of approximately 100 mL of KNO₃ solution (Note 23). Discard the filtrate.

NOTE 23—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 E 50.

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

169.8 Remove and rinse the stopper. Dilute the solution to 150 mL with freshly boiled water that has been cooled to room temperature, and add 3 drops of phenolphthalein indicator solution. Using a 25-mL buret, titrate the excess NaOH with the standard HNO₃ until 1 drop causes the disappearance of the pink color. Record the buret reading.

170. Calculation

170.1 Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, \%} = \frac{(AB - CD) - (EB - FD)}{G} \times 100 \quad (12)$$

where:

- A = NaOH solution, mL, used for the sample (169.7),
- B = phosphorus equivalent of the NaOH solution,
- C = HNO₃, mL, solution required by the sample (169.8),
- D = phosphorus equivalent of the HNO₃ solution,
- E = NaOH solution, mL, used for the blank,

F = HNO_3 solution, mL, required by the blank, and
 G = sample used, g.

171. Precision¹³

171.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 14. Samples at the higher end of the scope were not available for testing.

NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD

172. Scope

172.1 This method covers the determination of nickel in concentrations from 0.1 to 48.0 %.

173. Summary of Method

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

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

174. Interferences

174.1 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.

175. Apparatus

175.1 *Anion-Exchange Column*, Approximately 25 mm in diameter and 300 mm long, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. Apparatus No. 8 may be adopted to this method. A reservoir for the eluants may be added at the top of the column.

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

175.3 *pH Meter*—Apparatus No. 3A.

176. Reagents

176.1 *Ammonium Citrate Solution* (200 g/L)—Dissolve 200 g of diammonium hydrogen citrate $[(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7]$ in 600 mL of water. Filter and dilute to 1 L.

176.2 Anion Exchange Resin:

176.2.1 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 to 400 nominal mesh size.¹⁴ 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 to 6 min, decant 150 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.

176.2.2 Prepare the column as follows: Place a 10 to 20-mm layer of glass wool or poly(vinyl chloride) plastic fiber in the bottom of the column and add a sufficient amount of the prepared resin to fill the column to a height of approximately 140 mm. Place a 20 mm layer of glass wool or poly(vinyl chloride) plastic fiber at 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 to not more than 3.0 mL/min. Drain 10 to 20 mm above the top of the resin bed and then close the lower stopcock.

176.3 *Dimethylglyoxime Solution in Alcohol* (10 g/L)—Reagent No. 104.

177. Procedure

177.1 Double Precipitation:

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

Nickel, %	Sample Weight, g	Tolerance 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 48.0	1.0	0.5

Transfer it to a 600-mL beaker.

177.1.2 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.

177.1.3 Filter the solution 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

¹³ Supporting data are available from ASTM Headquarters. Request RR:E03-1002.

¹⁴ Dowex 1, manufactured by the Dow Chemical Co., Midland, MI, has been found satisfactory.

are removed. Finally, wash the paper three times with 5-mL portions of hot water. Discard the residue. If the nickel concentration 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.

177.1.4 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.

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

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

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

177.1.8 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.

177.1.9 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 177.3–177.7.

177.2 Anion-Exchange Separation:

177.2.1 Proceed as directed in 177.1.1.

177.2.2 Proceed as directed in 177.1.2, but dilute with only 50 mL of water.

177.2.3 Filter the solution obtained in 177.2.2 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.

177.2.4 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.

177.2.5 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 10 to 20 mm from the top of the resin bed.

177.2.6 Place a clean 600-mL beaker under the ion-exchange column and open the bottom stopcock. Transfer the solution from 177.2.4 to the column. Allow the sample to drain to 5 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 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 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.

177.2.7 Precondition the column for the next sample as follows: Open the lower stopcock. Drain any remaining solution in the column to 5 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 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 177.2.5.

177.2.8 Heat the solution reserved in 177.2.6 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, and transfer 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.

177.3 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.

177.4 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.

177.5 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 to 70°C for 30 min and allow to stand for at least 4 h at 20 to 25°C.

177.6 With the aid of suction, filter using a weighed (Note 24) fritted glass crucible. Wash the beaker and precipitate 6 times with cold water.

NOTE 24—Heat the crucible at 150°C and cool in a desiccator before weighing.

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

178. Calculation

178.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = (A - B) \times 0.2032/C \times 100 \quad (13)$$

where:

A = weight of crucible and precipitate, g,

B = weight of crucible, g, and

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

179. Precision⁴

179.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 15. Although samples covered by this method near the lower and upper ends of the scope were not tested, the data obtained for other types of alloys using the methods indicated in Table 15 should apply.

TIN BY THE SOLVENT EXTRACTION—ATOMIC ABSORPTION METHOD

TABLE 15 Statistical Information—Nickel

Test Material	Nickel Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. No. 1, E352	0.135	0.012	0.015
2. High chromium steel 13 Cr (NBS 73c, 0.246 Ni)	0.241	0.019	0.018
3. Stainless steel 18 Cr-9 Ni-25 Se (NBS 101e, 9.48 Ni)	9.44	0.14	0.25
4. Stainless steel 19 Cr-14 Ni-3 Mo (NBS 160 a, 14.13 Ni)	14.16	0.25	0.31
5. No. 4, E354	20.26	0.23	0.17
6. No. 5, E354	77.13	0.56	0.55

^A This test was performed in accordance with the 1980 version of Practice E 173.

180. Scope

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

181. Summary of Method

181.1 Tin is extracted from a dilute hydrochloric acid solution of the sample, containing ascorbic acid and potassium iodide, into a solution of trioctylphosphine oxide (TOPO) in methyl isobutyl ketone (MIBK). The MIBK extract is aspirated into the nitrous oxide-acetylene flame. Spectral energy at 2863 Å from a tin hollow-cathode lamp or tin electrodeless discharge lamp is passed through the flame and the absorbance is measured.

182. Concentration Range

182.1 The recommended concentration range is from 4 to 20 µg of tin per millilitre in the final 10 mL of TOPO-MIBK extract.

183. Interferences

183.1 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.

184. Apparatus

184.1 *Atomic Absorption Spectrophotometer*, capable of resolving the 2863 Å 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 186.4.

185. Reagents

185.1 *Ascorbic Acid*.

185.2 *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.

185.3 *Methyl Isobutyl Ketone (MIBK)*.

185.4 *Tin, Standard Solution A* (1 mL = 1.0 mg Sn)—Dissolve 1.000 g of tin (purity 99.9 % min) in 100 mL of HCl.

Cool, transfer to a 1-L volumetric flask, dilute to volume with HCl (1 + 2), and mix.

185.5 *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.

185.6 *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.

186. Preparation of Calibration Curve

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

NOTE 25—Volumetric flasks with ground glass stoppers must be used.

186.2 *Extraction*:

186.2.1 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.

186.2.2 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 26—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

186.3 *Photometry*:

186.3.1 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 2863 Å.

186.3.2 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 to 30 s. Aspirate MIBK for 30 s, then readjust the detector response to zero, if necessary.

NOTE 27—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 186.3.1.

186.3.3 Aspirate the solution with the highest concentration (40 µg Sn/mL) from the series prepared in 186.1 a sufficient number of times to establish that the absorbance is not drifting.

NOTE 28—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 29—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.

186.3.4 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 186.3.3 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 186.3.1–186.3.4.

186.3.5 Proceed immediately as directed in 187.3.

186.4 *Calibration Curve*—Plot the average net absorbance values against micrograms of tin per millilitre on rectangular coordinate paper. Calculate the deviation from linearity of the curve as follows:

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

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.

187. Procedure

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

187.2 *Test Solution*:

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

Tin, %	Sample Weight, g
0.002 to 0.005	3.00
0.004 to 0.010	2.00
0.009 to 0.050	1.00
0.045 to 0.100	0.50

Transfer it to a 400-mL poly(tetrafluoroethylene) beaker.

187.2.2 Add 100 mL of HCl (1 + 1), 10 drops of 30 % H₂O₂, and 5 drops of HF. Cover the beaker with a poly(tetrafluoroethylene) cover and heat at a low temperature (approximately 90°C) until dissolution is complete.

NOTE 30—For some steels, it will be necessary to periodically add an additional 10 drops of 30 % H₂O₂ to hasten the dissolution of the sample. If silicon is above 0.5 %, use 10 to 12 drops of HF.

187.2.3 Remove the cover with platinum-tipped tongs and cautiously rinse into the beaker with water. Cautiously evaporate the solution at a low temperature (approximately 90°C) to 15 mL. Rinse the sides of the beaker with water, add 20 mL of HCl (1 + 1), and again evaporate to 15 mL. Rinse the sides of the beaker with about 5 mL of water and cool.

187.2.4 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.

187.2.5 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

TABLE 16 Statistical Information—Tin

Test Material	Tin Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
1. No. 1, E350	0.0034	0.0006	0.0007
2. Stainless steel, Type 416 (13Cr) 0.005 Sn (not certified)	0.0042	0.0006	0.0011
3. No. 2, E350	0.0079	0.0009	0.0014
4. Stainless steel, Type 316 (18Cr-13Ni-2Mo) 0.006 Sn (not certified)	0.0066	0.0009	0.0014
5. Stainless steel, Type 304 (13Cr-10Ni) 0.017 Sn (not certified)	0.017	0.002	0.004
6. No. 6, E350	0.097	0.011	0.011

^A This test was performed in accordance with the 1980 version of Practice E 173.

the flask, stopper, invert, and shake vigorously several times for 1 min.

187.2.6 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.

187.3 *Photometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 28) and record the absorbance values. Take three readings on each solution (Note 29). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drift as in 186.3.4 and 186.3.5.

188. Calculation

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

$$\text{Tin, \%} = [(D - E)/(F \times 1000)] \quad (15)$$

where:

- D = tin, µg, per mL of the final test solution,
- E = tin, µg, per mL of the final reagent blank solution, and
- F = sample used, g.

189. Precision and Bias¹⁵

189.1 *Precision*—Eleven laboratories cooperated in testing this method on No. 2, 4, and 5 in Table 16. This method differs only slightly from the method for tin Test Method E 350, in that the amounts of reagents used to dissolve the samples were increased. The fact that the precision of No. 2, 4, and 5 in Table 16 correspond closely with that obtained for the samples of similar tin content of Test Method E 350 suggests that the precision of the two methods is the same.

189.2 *Bias*—No information on the accuracy of this method is available. The accuracy of a method may be judged, however, by comparing accepted reference values with the arithmetic average obtained by interlaboratory testing. The values listed for these samples, while not certified, were obtained by other methods and are believed to be substantially correct.

¹⁵ Supporting data are available from ASTM Headquarters. Request RR:E03-1022.

MOLYBDENUM BY THE PHOTOMETRIC METHOD

190. Scope

190.1 This method covers the determination of molybdenum in concentrations from 0.01 to 1.50 %.

191. Summary of Method

191.1 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. Photometric measurement is made at approximately 475 nm.

192. Concentration Range

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

NOTE 31—This 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.

193. Stability of Color

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

194. Interferences

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

195. Reagents

195.1 Butyl Acetate:

NOTE 32—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.

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

195.3 *Iron*¹⁶—Purity: 99.8 % minimum, molybdenum 0.001 % max.

195.4 *Iron Solution A* (1 mL = 70 mg Fe)—Dissolve 25 g of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$) in 75 mL of hot water. Cool and add 10 mL of H_2SO_4 . Cool, and dilute to 100 mL.

195.5 *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.

195.6 *Molybdenum, Standard Solution A* (1 mL = 0.2 mg Mo)—Reagent No. 8A, or 8B, Practice E 50.

195.7 *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.

195.8 *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.

195.9 *Sodium Thiocyanate Solution* (100 g/L)—Reagent No. 137, Practice E 50.

195.10 *Stannous Chloride Solution* (350 g/L)—Transfer 350 g of stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and 200 g of tartaric acid to a 1-L beaker, add 400 mL of HCl (1 + 1), and heat at 60 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 33—This solution is used for color development in 196.3, 197.3, 198.3, and 199.3. When an absorption cell is used sequentially for a number of photometric measurements, a white film of an insoluble tin compound may adhere to the inside of the cell and must be removed before further measurements are made.

196. Preparation of Calibration Curve for Concentrations from 0.01 to 0.05 %

196.1 Calibration Solutions:

196.1.1 Transfer 0.3 g of iron to each of four 250-mL Erlenmeyer flasks. Using pipets, transfer 2, 5, 10, and 15 mL of molybdenum solution C (1 mL = 0.01 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

196.1.2 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.

196.1.3 Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 196.3.

196.2 *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 196.1.2, 196.1.3, and 196.3.

196.3 *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 34—This funnel should be cleaned thoroughly after each filtration to avoid development of a pink color that would contaminate the filtrate.

196.4 *Reference Solution*—Butyl acetate.

196.5 Photometry:

196.5.1 *Multiple-Cell Photometer*—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 photometric readings of the calibration solutions.

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

¹⁶ Johnson-Matthey JMC 847 sponge iron has been found suitable for this purpose.

light band centered at approximately 475 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions and the reagent blank.

196.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of molybdenum per 25 mL of butyl acetate.

197. Preparation of Calibration Curve for Concentrations from 0.05 to 0.55 %

197.1 Calibration Solutions:

197.1.1 Transfer 0.3 g of iron to each of four 250-mL Erlenmeyer flasks. Using pipets, transfer 2, 5, 10, and 15 mL of molybdenum solution B (1 mL = 0.1 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

197.1.2 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.

197.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 197.3.

197.2 *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 197.1.2, 197.1.3, and 197.3.

197.3 *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 34.)

197.4 *Reference Solution*—Butyl acetate.

197.5 Photometry:

197.5.1 *Multiple-Cell Photometer*—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 photometric readings of the calibration solutions.

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

197.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of molybdenum per 50 mL of butyl acetate.

198. Preparation of Calibration Curve for Concentrations from 0.40 to 1.50 %

198.1 Calibration Solutions:

198.1.1 Transfer 0.3 g of iron to each of five 250-mL

Erlenmeyer flasks. Using pipets, transfer 5, 10, 15, 20, and 25 mL of molybdenum solution A (1 mL = 0.2 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

198.1.2 Increase the temperature and evaporate to HClO_4 fumes. Cool, add 30 mL of water and 70 mL of H_2SO_4 (1 + 1). Heat to boiling and cool in a water bath.

198.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 198.3.

198.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 300 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 198.1.2, 198.1.3, and 198.3.

198.3 *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, 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 34.)

198.4 *Reference Solution*—Butyl acetate.

198.5 Photometry:

198.5.1 *Multiple-Cell Photometer*—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 photometric readings of the calibration solutions.

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

198.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of molybdenum per 100 mL of butyl acetate.

199. Procedure

199.1 Test Solution:

199.1.1 Transfer a 0.3-g sample, weighed to the nearest milligram to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving acid. Add HCl, or HCO_3 , or combinations of the two with or without several drops of HF, and heat until dissolution is complete.

199.1.2 Increase the temperature and heat to HClO_4 fumes. Continue fuming until chromium, if present, is oxidized and the white HClO_4 fumes are present only in the neck of the flask. Add, with care, 1.0 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 H₂SO₄ (1 + 1), heat to boiling, and cool in a water bath. If the solution is not clear, filter the solution through an 11-cm fine filter paper, collecting the filtrate in a volumetric flask that provides for dilution in accordance with the guide given in 199.1.3. Wash the paper with five 5-mL portions of H₂SO₄ (1 + 99), collecting these in the same volumetric flask. Proceed as directed in 199.3. If the solution is clear, proceed to 199.1.3.

199.1.3 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

Proceed as directed in 199.3.

199.2 *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 199.1.2, 199.1.3, and 199.3, using the same dilution and aliquots used for the test solution.

199.3 *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 SnCl₂ 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 H₂SO₄ (1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl₂ solution. Replace the stopper and shake vigorously 2 min. Allow the phases to separate, 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 34.)

199.4 *Reference Solution*—Butyl acetate.

199.5 *Photometry*—Take the photometric reading of the test solution and of the reagent blank solution as directed in 199.5.

200. Calculation

TABLE 17 Statistical Information—Molybdenum

Test Material	Molybdenum Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
1. No. 1, E350	0.012	0.001	0.005
2. Stainless steel 13Cr (NBS 73c 0.091 Mo)	0.089	0.010	0.010
3. No. 3, E350	0.163	0.012	0.03
4. Stainless steel 18Cr-10Ni (NBS 101e 0.426 Mo)	0.432	0.010	0.017
5. No. 4, E350	0.51	0.02	0.06
6. Stainless steel 18Cr-15Ni 2Ti (NBS 348 1.30 Mo)	1.34	0.032	0.092

^A This test was performed in accordance with the 1980 version of Practice E 173.

200.1 Convert the net photometric 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:

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

where:

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

B = sample, g, represented in 25, 50, or 100 mL, as appropriate, of butyl acetate and the aliquot used (see aliquot guide 199.1.3).

201. Precision and Bias¹⁷

201.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 17. This method is identical with molybdenum in accordance with Test Methods E 350, E 351, and E 352. The fact that the precision for different materials is comparable suggests that the precision of these methods are the same.

201.2 *Bias*—The accuracy of a method can be judged by comparing the certified value of a standard with the arithmetic average of the test data.

CHROMIUM BY THE ATOMIC ABSORPTION METHOD

202. Scope

202.1 This method covers the determination of chromium in concentrations from 0.006 to 1.00 %.

203. Summary of Method

203.1 The sample is dissolved in mineral acids and the residue fused, dissolved, and combined with the soluble portion. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrophotometer. Spectral energy at approximately 3579Å from a chromium hollow-cathode lamp is passed through the flame, and the absorbance is measured. The spectrophotometer is calibrated with solutions of known chromium concentrations.

204. Concentration Range

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

205. Interferences

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

206. Apparatus

206.1 *Atomic Absorption Spectrophotometer*, capable of

¹⁷ Supporting data are available from ASTM Headquarters. Request RR:E03-1023.

resolving the 3579Å 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 208.4. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this method.

207. Reagents

207.1 *Chromium, Standard Solution* (1 mL = 0.1 mg Cr)—Transfer 2.8290 g of potassium dichromate (K₂Cr₂O₇) (NBS 136 or equivalent) to an 800-mL borosilicate beaker, add 500 mL of water, and mix. When dissolution is complete, add 5 mL of H₂SO₄ and, while stirring, add 10 mL of H₂O₂ (30 %). Heat at near boiling for 5 min to remove excess H₂O₂. 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.

207.2 *Iron*,¹⁸ Low Chromium—Cr <0.0001 %.

207.3 *Potassium Carbonate Solution* (50 g/L)—Dissolve 50 g of potassium carbonate (K₂CO₃) in water, and dilute to 1 L. Store the solution in a polyethylene bottle.

208. Preparation of Calibration Curves

208.1 *Calibration Solutions for Concentrations 0.005 to 0.10 %*—To each of seven 250-mL borosilicate beakers, transfer 1.0 g of low chromium iron weighed to the nearest 1 mg. Add to each beaker 20 mL of HCl and 10 mL of HNO₃ 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 K₂CO₃ solution to each of 7 flasks. Using pipets, transfer 1, 3, 5, 7, 10, and 15 mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium concentration. Dilute to volume and mix.

208.2 *Calibration Solution for Concentrations 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 HNO₃. 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 K₂CO₃ solution. Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Transfer 10-mL aliquots to each of seven 100-mL volumetric flasks and add 9 mL of HCl to each flask. Using pipets, transfer 1, 3, 5, 7, 10, and 15 mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium concentration. Dilute to volume and mix.

208.3 *Photometry*:

208.3.1 With the chromium hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 3579Å line. The wavelength setting in the vicinity of 4289Å may be used provided that the instrument meets the performance requirements.

208.3.2 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 208.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is required.

208.3.3 Aspirate the chromium solutions used in 208.3.2 to assure that the absorbance reading is repeatable. Record 6 readings, and calculate the standard deviation, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \tag{17}$$

where:

A = the highest of 6 values found, and

B = the lowest of the 6 values found.¹⁹

208.3.4 Using water as a reference solution, and beginning with the solution to which no addition of chromium was made in 208.1 and 208.2, 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 208.3.3 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 208.3.1–208.3.4.

208.3.5 Proceed immediately as directed in Section 209.

208.4 *Calibration for Concentrations from 0.005 to 0.10 %*—Plot the net absorbance values against milligrams of chromium per millilitre on rectangular coordinate paper. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \tag{18}$$

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.

208.5 *Calibration for Concentrations from 0.010 to 1.00 %*—Proceed as directed in 208.4.

209. Procedure

209.1 *Test Solution*:

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution After Dis-solution, 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.

209.1.2 Add 20 mL HCl, 10 mL HNO₃, and 5 drops of HF. Heat to dissolve. Remove from the hot plate and dilute to

¹⁸ Johnson-Matthey sponge iron or Spex iron has been found suitable for this purpose.

¹⁹ The value 0.40, which is used to estimate the standard deviation from the range of six values, was published by Dixon, W. J. and Massey, F. J., *Introduction to Statistical Analysis*, McGraw-Hill, New York, NY, 1957, p. 404, Table 8b (1).

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.

209.1.3 Transfer the paper and contents to a platinum crucible. Dry on a hot plate, and transfer to a muffle furnace that is less than 400°C. Gradually heat to 600°C and hold at this temperature for 1 h. Cool, add 0.5 g of K₂CO₃, and carefully fuse over a free flame until a clear melt is obtained (see Note 35). 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 35—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.

209.1.4 Transfer this solution to the filtrate from 209.1.2 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 concentrations less than 0.10 %, proceed as directed in 209.3. For samples with expected chromium concentration 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.

209.2 Prepare for each concentration range a reagent blank by treating the same amount of all reagents as directed in 209.1.1–209.1.4, including the low chromium iron. Use reagents from the same lots for blank and test solutions.

209.3 *Photometry*—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 208.3.4, 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 208.3.3, 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.

210. Calculation

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

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (19)$$

TABLE 18 Statistical Information—Chromium

Test Material	Chromium Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
1. No. 1, E350	0.0063	0.0014	0.003
2. No. 3, E351	0.559	0.026	0.052
3. No. 5, E350	0.961	0.036	0.093

^A This test was performed in accordance with the 1980 version of Practice E 173.

where:

A = chromium, mg, per mL of final test solution,

B = chromium, mg, per mL of final reagent blank solution, and

C = final volume of test solution, and

W = weight of sample, in g, in final volume of test solution.

211. Precision and Bias²⁰

211.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 18.

211.2 *Bias*—The accuracy can be inferred from the data in Table 18 by comparing the certified values for chromium with the average value obtained by using this method.

CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

212. Scope

212.1 This method covers the determination of chromium in concentrations from 0.10 to 35.00 %.

213. Summary of Method

213.1 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 36—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 percent 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.

214. Interferences

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

214.2 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 K₂Cr₂O₇ 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:

$$(2.6A + 0.05B + 0.01C) D \quad (20)$$

²⁰ Supporting data are available from ASTM Headquarters. Request RR: E03-1030.

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.

215. Apparatus

215.1 *Apparatus for Potentiometric Titrations*—Apparatus No. 3B (Practices E 50) with a saturated calomel reference and platinum indicator electrode.

216. Reagents

216.1 *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.

216.2 *Ferrous Ammonium Sulfate, Standard Solution* (0.05 N and 0.10 N)—Reagent No. 5 (Practices E 50) but use 20 and 40 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, respectively, instead of the specified weight. Standardize the solution as directed in 217.1, 217.2, or 217.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

216.3 *Potassium Dichromate, Standard Solution* (0.05 N and 0.10 N)—Reagent No. 10 (Practices E 50) but use 2.4518 and 4.9036 g of recrystallized $K_2Cr_2O_7$ (NBS 136c) or equivalent primary standard grade, instead of the specified weight.

216.4 *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.

216.5 *Potassium Permanganate, Standard Solution* (0.05 N and 0.10 N)—Reagent No. 13 (Practices E 50) but use 1.6 and 3.2 g of $KMnO_4$, respectively, instead of the specified weight. Standardize as directed in 34.2 of Practices E 50 but use 0.1500 g of sodium oxalate (NBS 40h) or equivalent primary standard grade.

216.6 *Silver Nitrate Solution* (8 g/L)—Reagent No. 133 (Practices E 50).

216.7 *Sodium Diphenylamine Sulfonate Indicator Solution* (2.0 g/L)—Reagent No. 121 (Practices E 50).

216.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 M)—Reagent No. 122 (Practices E 50).

217. Standardization of Ferrous Ammonium Sulfate Solution

217.1 *Against Potassium Permanganate Solution:*

217.1.1 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 or 0.10 N $Fe(NH_4)_2(SO_4)_2$ with either 0.05 or 0.10 N $KMnO_4$ solution (216.5) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 1 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 (216.5) 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.

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

$$\text{Normality} = AB/C \quad (21)$$

where:

- A = normality of $KMnO_4$ solution (216.5),
- B = $KMnO_4$ solution, mL, and
- C = $Fe(NH_4)_2(SO_4)_2$ solution, mL.

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

217.2.1 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 or 0.10 N $Fe(NH_4)_2(SO_4)_2$ (216.2) 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 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 or 0.10 N $K_2Cr_2O_7$ solution to the blue end point. Subtract this volume of $K_2Cr_2O_7$ solution from the volume recorded for the first titration and record the difference as the indicator blank.

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

$$\text{Normality} = (0.05 \text{ or } 0.10 (A - B))/C \quad (22)$$

where:

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

217.3 *Against Potassium Dichromate Using Potentiometric End Point:*

217.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 or 0.10 N $K_2Cr_2O_7$ solution into a 600-mL beaker. Reserve the remaining 0.05 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 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 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 ₂ Cr ₂ O ₇ Back Titrant (mL)	Voltage (mV)	Δ Voltage (mV)	Difference Before and After Maximum
20.80	555		
20.90	570	50	50
21.00	620	100	20
21.10	720	80	
21.20	800		
21.30	835		
21.40	854		

Maximum voltage change occurred between 21.00 and 21.10 mL of K₂Cr₂O₇ 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 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.

217.3.2 Calculate the normality of the Fe(NH₄)₂(SO₄)₂ solution as follows:

$$\text{Normality} = 0.05 \text{ or } 0.10 \text{ A/B} \quad (23)$$

where:

A = 0.05 or 0.10 N K₂Cr₂O₇ solution, mL, and

B = Fe(NH₄)₂(SO₄)₂ solution, mL.

218. Procedure

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Normality of Titrants
0.10to0.50	3.50	2.0	0.05
0.40to1.00	2.00	1.0	0.05
0.80to1.60	1.25	0.5	0.05
1.50to3.50	0.50	0.3	0.05
3.30to8.00	0.25	0.1	0.05
8.00to14.00 ^A	0.50	0.1	0.10
13.00to20.00 ^A	0.40	0.1	0.10
18.00to30.00 ^A	0.25	0.1	0.10
28.00to33.00 ^A	0.20	0.1	0.10

^A Use 50-mL burets for this concentration range instead of the 25-mL burets specified in the procedure.

Transfer it to a 600-mL beaker.

218.2 Add 80 mL of H₂SO₄ (1 + 5) and 5 mL of H₃PO₄. Cover the beaker with a ribbed cover glass and heat at 85 to 100°C until the sample is decomposed. Add sufficient HNO₃ in small increments to oxidize iron. Boil 2 min to expel oxides of nitrogen. Proceed as directed in 218.4.

218.3 If the alloy does not dissolve in the acids specified in 218.2, add amounts of HCl or HNO₃, 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 dissolution is complete, add 80 mL of H₂SO₄ (1 + 5), 5 mL of H₃PO₄, and evaporate to light fumes. Rinse the cover

walls of the beaker. Again evaporate to fumes and fume for 1 min. Cool, add 100 mL of water, and heat at 85 to 100°C until salts are dissolved.

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

218.5 Transfer the paper and residue to a platinum crucible, char the paper, and ignite at 850 to 900°C for 15 min. Cool, add sufficient H₂SO₄ (1 + 1) to moisten the residue, and then 3 to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until H₂SO₄ is removed. Fuse the residue with a minimum amount of either fused sodium hydrogen sulfate (sodium pyrosulfate—Na₂S₂O₇) or potassium pyrosulfate (K₂S₂O₇). Cool the crucible, place in a 250-mL beaker, and dissolve the melt in 20 mL of H₂SO₄ (1 + 10). Remove the crucible, rinse with water, transfer the solution to the reserved filtrate (218.4), and dilute to 200 mL.

218.6 Add 5 mL of AgNO₃ solution and 20 mL of (NH₄)₂S₂O₈ solution. If a beaker is used, cover it with a ribbed cover glass. Boil the solution 8 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 KMnO₄ solution (216.4), 5 mL more of AgNO₃ solution, 20 mL more of (NH₄)₂S₂O₈ solution, and boil for an additional 8 to 10 min. Add hot water to maintain the volume at 200 mL during this operation and the operations that follow in 218.7.

218.7 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 a precipitate of MnO₂ 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 218.8. If vanadium is absent and the criteria of 214.2 are met, proceed as directed in 218.9. If vanadium is absent and the criteria of 214.2 are not met, or if potentiometric titration is preferred and vanadium is absent, proceed as directed in 218.10.

218.8 *Titration With Potassium Permanganate*—While swirling the flask, add 1 to 2 drops of 1,10 phenanthroline indicator solution and then add sufficient Fe(NH₄)₂(SO₄)₂ solution to effect a change in color from clear green to pink. Add 1 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 KMnO₄ standard solution. Add KMnO₄ 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.

218.9 *Titration with Potassium Dichromate to the Diphenylamine Sulfonate End Point*—While swirling the flask, add Fe(NH₄)₂(SO₄)₂ solution from a 25-mL buret until the disappearance of the yellow color. Then add 1 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.

218.10 *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 while stirring until the yellow color disappears. Then add 1 to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Using another 25-mL buret add 0.05 N $K_2Cr_2O_7$ standard solution in 0.1-mL increments recording the voltage after equilibrium for each increment. Inspect the data for the maximum voltage change between increments of standard dichromate solution (see 217.3). 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 217.3.

219. Calculation

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

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (24)$$

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.

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

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (25)$$

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.

220. Precision and Bias²¹

220.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 19. Although samples at the lower and midrange of the scope were not tested, the precision data for other types of alloys using the methods indicated in Table 19 should apply.

220.2 *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 19).

VANADIUM BY THE ATOMIC ABSORPTION METHOD

221. Scope

221.1 This method covers the determination of vanadium in concentrations from 0.006 to 0.15 %.

222. Summary of Method

222.1 The sample is dissolved in hydrochloric, nitric, and perchloric acids. An aluminum solution is added as a spectrochemical buffer. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrophotometer. 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.

223. Concentration Range

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

224. Interferences

224.1 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 interfere when present in concentrations greater than 0.5 and 1.0 %, respectively.

225. Apparatus

225.1 *Atomic Absorption Spectrophotometer*, 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 E 1024.

226. Reagents

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

226.2 *Vanadium, Standard Solution* (1 mL = 0.2 mg V)—Dissolve 0.200 g of vanadium (purity: 99.9 % minimum) in 20

TABLE 19 Statistical Information—Chromium

Test Material	Chromium Found, %	Repeatability (R_1 , E 173 ^A)	Reproducibility (R_2 , E 173 ^A)
1. No. 2, E 350	0.481	0.015	0.053
2. No. 2, E 351	1.96	0.10	0.16
3. No. 3, E 352	3.68	0.16	0.48
4. Stainless Steel, 13Cr (NBS 133a, 12.89Cr)	12.87	0.26	0.28
5. High Alloy Valve Steel (NBS 346, 21.61Cr)	21.62	0.18	0.58
6. A286 (NBS 348, 14.54Cr)	14.55	0.15	0.31

^A This test was performed in accordance with the 1980 version of Practice E 173.

²¹ Supporting data are available from ASTM Headquarters. Request RR:E03-1036.

mL of aqua regia (three volumes of HCl to one volume of HNO₃). Evaporate to near dryness and add 10 mL of HCl. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

NOTE 37—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 (NH₄VO₃) minimum purity: 99.9 %, in an air oven at 105 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).

227. Preparation of Calibration Curve

227.1 *Calibration Solutions*—To each of five, 250-mL borosilicate beakers, add 10 mL of HClO₄. Using a microburet, transfer 0.0, 1.0, 2.0, 4.5, and 8.0 mL of vanadium standard solution to each beaker, respectively. Cover with a watch glass, heat, and evaporate to fumes. Continue heating until solutions are near dryness (Note 38). 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 AlCl₃ solution (226.1), dilute to volume, and mix.

NOTE 38—The remaining amount of HClO₄ must be at a minimum.

227.2 Photometry:

227.2.1 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.

227.2.2 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 227.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is necessary.

227.2.3 Aspirate the vanadium solution used in 227.2.2 to assure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviations, *s*, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (26)$$

where:

A = the highest absorbance of the six values found, and
B = the lowest absorbance of the six values found.¹⁵

227.2.4 Using water as a reference, and beginning with the solution to which no addition of vanadium was made in 227.1, 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 227.2.3 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 227.2.1–227.2.4.

227.2.5 *Calibration Curve*—Plot the average net absorbance values against milligrams of vanadium per millilitre on rect-

angular coordinate paper. Test for linearity as given in Guide E 1024.

228. Procedure

228.1 Test Solution:

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

228.1.2 Add 20 mL of HCl, 4 mL of HNO₃, and cover with a cover glass. Heat until dissolution is complete. Add 10 mL of HClO₄ and evaporate to fumes. Continue heating until solutions are near dryness (Note 48). 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 AlCl₃ solution (226.1), dilute to volume, and mix.

228.1.3 Prepare a reagent blank by using a 250-mL borosilicate beaker and proceeding as directed in 228.1.2. Use reagents from the same lots as those used for the sample solution.

228.2 *Photometry*—Using water as a reference, aspirate and record the absorbance of the calibration, sample, and reagent blank solutions. After each group of four or fewer samples and reagent blank solutions have been aspirated, apply the test using the standard solution as directed in 227.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 227.2.3, 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.

TABLE 20 Statistical Information—Vanadium

Test Material	Vanadium Found, %	Repeatability (R ₁ , E173 ^A)	Reproducibility (R ₂ , E173 ^A)
Stainless Steel (JSS 652-7, 0.038 V)	0.038	0.003	0.005
No. 1, E350	0.107	0.008	0.014
No. 1, E351	0.008	0.002	0.003
No. 1, E352	0.032	0.002	0.004
No. 2, E352	0.161	0.007	0.011

^A This test was performed in accordance with the 1980 version of Practice E 173.

229. Calculation

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

$$\text{Vanadium, \%} = ((A - B) \times 10)/C \quad (27)$$

where:

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

230. Precision and Bias²²

²² Supporting data are available from ASTM Headquarters. Request RR:E03-1040.

230.1 *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 20. All testing meets the requirements of Practice E 173.

230.2 *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.

**TOTAL TITANIUM BY THE
DIANTIPYRYLMETHANE
SPECTROPHOTOMETRIC METHOD**

231. Scope

231.1 This method covers the determination of titanium in concentrations from 0.01 to 0.35 %.

232. Summary of Method

232.1 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.

233. Concentration Range

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

234. Stability of Color

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

235. Interferences

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

236. Apparatus

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

237. Reagents

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

237.2 *Diantipyrylmethane (DAPM)* (20 g/L)—Dissolve 5 g of 4,4'-diantipyrylmethane monohydrate (C₂₃H₂₄N₄O₂H₂O) in HCl (1 + 9) and dilute to 250 mL with the dilute hydrochloric acid. Prepare as needed.

237.3 *Potassium Hydrogen Sulfate, Fused*—(a mixture of K₂S₂O₇ and KHSO₄).

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

237.5 *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 H₂SO₄ (1 + 3) and dissolve at less than 150°C. Oxidize the titanium by adding HNO₃ dropwise (Note 39). Cool, dilute to volume with H₂SO₄ (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 39—An excess of HNO₃ should be avoided. Two to three drops of HNO₃ should be sufficient to oxidize the titanium sulfate solution and discharge the blue color.

238. Preparation of Calibration Curve

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

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

NOTE 40—Take spectrophotometric readings of the calibration solutions containing 0.5, 1, 2, 4, and 6 mL of titanium solution using a 2-cm light path. Use a 1-cm light path for the remaining solutions.

238.3 *Reference Solution*—Water.

238.4 *Reagent Blank*—Transfer 10 mL of water to a 50-mL volumetric flask and proceed as directed in 238.5.

238.5 *Color Development:*

238.5.1 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.

238.6 *Spectrophotometry:*

238.6.1 *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.

238.6.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1- 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.

238.7 *Calibration Curve*—Subtract the reagent blank reading from each of the calibration solution readings. Plot the blank-corrected spectrophotometric readings of the calibration solutions against milligrams of titanium per 50 mL of solution. Prepare separate curves for 1 and 2-cm light path cells.

239. Procedure

239.1 *Test Solution:*

239.1.1 Select a sample weight in accordance with the following:

Titanium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Final Volume, mL	Aliquot Volume, mL	Cell Size, cm
0.01 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 0.4 100 10.00 1

Transfer it to a 250-mL beaker.

239.1.2 Add 20 mL of HCl and bring to boil. Remove from hot plate and add 5 mL of HNO₃. Sample should dissolve without any additional heat. After sample has dissolved, evaporate the solution to dryness.

NOTE 41—The use of a coarse screen of 3-mm (1/8-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 to 100°C and then add 5 mL of water.

239.1.3 Filter through an 11-cm medium-porosity filter paper containing paper pulp into a 100-mL volumetric flask 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.

NOTE 42—If more than 2 mg of tungsten is present in aliquot volume, remove soluble portion of sample from under filter funnel and wash papers several times with NH₄OH (1 + 1). Discard washings.

239.1.4 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 H₂SO₄ (1 + 1) followed by 2 mL of HF. Evaporate to dryness, and then heat at a gradually increasing rate until the H₂SO₄ 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 to 100°C, and when the melt is dissolved, add this solution to the reserved filtrate in the volumetric flask (239.1.3). Dilute to volume, and mix.

239.1.5 Using a pipet, transfer a 10-mL portion to a 50-mL volumetric flask and treat as directed in 238.5.1 using 1 mL of HCl (1 + 1).

239.2 *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 239.1.5 and 238.5.1, omitting the addition of DAPM.

239.3 *Reagent Blank Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with the sample omitted (239.1.1 through 239.1.5).

239.4 *Reference Solutions*—Water and the sample blank solution, as described in 239.5.

239.5 *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 238.6.

240. Calculation

240.1 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:

$$\text{Titanium, \%} = (A - B)/(C \times 100) \times 100 \quad (28)$$

TABLE 21 Statistical Information—Titanium

Test Material	Titanium Found, %	Repeatability, % (R ₁ , E173 ^A)	Reproducibility, % (R ₂ , E173 ^A)
1. Low Alloy (NBS 170a, 0.281 Ti)	0.282	0.0097	0.0228
2. Cast Iron (NBS 122d, 0.007 Ti)	0.006	0.0019	0.0037
3. Blast Furnace Iron (NBS 1144a, 0.32 Ti)	0.33	0.0118	0.0168
4. High Alloy (NBS 344, 0.076 Ti)	0.079	0.0022	0.0065
5. Specialty Steel (NBS 1156, 0.21 Ti)	0.20	0.0054	0.0143

^A This test was performed in accordance with the 1980 version of Practice E 173.

where:

- A = titanium found, mg, in the final color development solution,
- B = titanium found, mg, in the reagent blank,
- C = original sample weight, g, as determined in 239.1.1.

241. Precision and Bias

241.1 *Precision*—Eight laboratories cooperated in testing this method and obtained data summarized in Table 21.

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

242. Scope

242.1 This method covers the determination of molybdenum in concentrations from 1.5 to 7.0 %.

243. Summary of Method

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

244. Interferences

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

245. Apparatus

245.1 *Ion Exchange Column, Polystyrene*,²¹ approximately 400 mm long 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 poly (vinyl chloride) (Note 43).²³

²³ Columns available from Ledoux & Co., Inc., Teaneck, NJ, have been found satisfactory.

NOTE 43—The ion exchange column system must be carefully assembled and checked to avoid possible leakage of solutions containing HF.

246. Reagents

246.1 *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.

246.2 *Ammonium Fluoride* (NH_4F).

246.3 *Ammonium Oxalate*—($\text{NH}_4\text{OCOCOONH}_4\text{H}_2\text{O}$).

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

246.5 *Eluent Solutions*—See Note 44.

NOTE 44—**Warning:** HF causes serious burns which may not be immediately painful; read the paragraph about HF in the Safety Precautions section of Practices E 50.

246.5.1 *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.

246.5.2 *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.

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

246.5.4 *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.)

246.5.5 *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; if 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.)

246.6 *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.

246.7 *Ion-Exchange Resin*:

246.7.1 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 to 400 nominal U.S.

mesh size.²⁴ 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 to 6 min, decant 150 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.

246.7.2 Prepare the column as follows: Place a 10 to 20-mm layer of poly (vinyl chloride) plastic fiber²⁵ 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 to 175 mm. Place a 20-mm layer of poly (vinyl 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 to 125 mL of HCl (3+1) to the column. When the solution level is 5 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 to 20 mm above the top of the resin bed.

246.8 *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 a 1 L. Store in a plastic bottle.

246.9 *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.

247. Procedure

247.1 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.

247.2 Over a steambath or 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 HF and 25 mL water. Warm over low heat until all salts are dissolved (Note 45). Cool to room temperature and dilute to 100 mL with water.

²⁴ AG1-X8, 200–400 mesh, chloride form, which is available from Bio-Rad Laboratories, Richmond, CA, has been found satisfactory.

²⁵ Dynel plastic wool available from Union Carbide Corp., Chemical Division, Textile Fibers Department, Needham Heights, MA, has been found satisfactory.

NOTE 45—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

247.3 Drain the solution in the ion exchange column by passing 100 mL of HF/HCl/water (4+1+95) through it at a rate 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.

247.4 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 46).

NOTE 46—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.

247.5 Continue to add HF/HCl/water (4+1+95) until 650 mL have been collected in the 800 mL plastic beaker (Note 47). Drain solution to the top of the resin bed. Cautiously discard this solution.

NOTE 47—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper, and manganese.

247.6 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 48).

NOTE 48—This solution contains all the tungsten, titanium, zirconium, and hafnium.

247.7 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 described in 247.11.

247.8 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 49).

NOTE 49—This solution contains all the niobium.

247.9 Place an 800-mL plastic beaker under the column and elute 350 mL of $\text{NH}_4\text{F}/\text{NH}_4\text{Cl}$ solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 50).

NOTE 50—This solution contains all the tantalum.

247.10 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 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 (247.3).

247.11 To the eluent containing the molybdenum (from 247.7) cautiously add 15 mL of H_2SO_4 (1+1) and evaporate to light fumes on a sandbath or other carefully controlled heat source. (See Note 51.) Cool and cautiously rinse into a 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 .

NOTE 51—**Warning:** Ensure that the applied temperature does not exceed the softening point of polytetrafluoroethylene.

247.12 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.

247.13 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 247.14.

247.14 Adjust the volume of the solution or filtrate obtained in 247.13 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).

247.15 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.

247.16 Filter through a tared medium-porosity 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 volume of about 100 mL.

247.17 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.

248. Calculation

248.1 Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, \%} = [(A - B) \times 23.05]/C \quad (29)$$

where:

A = weight of crucible plus precipitate, in g,

B = weight of crucible, in g, and

C = sample weight, in g.

249. Precision and Bias

249.1 *Precision*—Seven laboratories cooperated in testing this method and obtained the data summarized in Table 22. As indicated, no data are presently available to determine the precision of this method. However, this method is identical to

TABLE 22 Statistical Information—Molybdenum Ion Exchange—8-Hydroxyquinoline Gravimetric Method

Test Material	Molybdenum Found, %	Repeatability (R_1 , E173 ^A)	Reproducibility (R_2 , E173 ^A)
1. No. 1, E351	1.48	0.070	0.086
2. No. 2, E354	3.92	0.219	0.250
3. No. 3, E352	8.85	0.180	0.188

^AThis test was performed in accordance with the 1980 version of Practice E 173.

the ion-exchange—8-hydroxyquinoline gravimetric procedure in Test Methods E 351, E 352, and E 354. This fact suggests that the precision for this method is the same. 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.

249.2 *Bias*—No data are presently available to determine the accuracy of this method.

250. Keywords

250.1 aluminum; chromium; chromium-nickel-iron alloys; cobalt; combustion analysis; copper; gravimetric; induction furnace; infrared absorption; lead; manganese; molybdenum; nickel; phosphorus; silicon; stainless steel; sulfur; tin; titanium; total carbon; vanadium

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