



# Standard Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys<sup>1</sup>

This standard is issued under the fixed designation E 354; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

<sup>ε1</sup> NOTE—Editorial changes were made in November 2000.

## 1. Scope

1.1 These test methods cover the chemical analysis of high-temperature, electrical, magnetic, and other similar iron, nickel, and cobalt alloys having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	0.005 to 18.00
Beryllium	0.001 to 0.05
Boron	0.001 to 1.00
Calcium	0.002 to 0.05
Carbon	0.001 to 1.10
Chromium	0.10 to 33.00
Cobalt	0.10 to 75.00
Columbium (Niobium)	0.01 to 6.0
Copper	0.01 to 10.00
Iron	0.01 to 85.00
Magnesium	0.001 to 0.05
Manganese	0.01 to 3.0
Molybdenum	0.01 to 30.0
Nickel	0.10 to 84.0
Nitrogen	0.001 to 0.20
Phosphorus	0.002 to 0.08
Silicon	0.01 to 5.00
Sulfur	0.002 to 0.10
Tantalum	0.005 to 10.0
Titanium	0.01 to 5.00
Tungsten	0.01 to 18.00
Vanadium	0.01 to 3.25
Zirconium	0.01 to 2.50

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

	Sections
Aluminum, Total, by the 8-Quinolinol Gravimetric Method (0.20 to 7.00 %)	100

Carbon, Total, by the Combustion-Thermal Conductivity Method	1 <sup>a</sup>
Carbon, Total, by the Combustion Gravimetric Method (0.05 to 1.10 %)	79
Chromium by the Atomic Absorption Method (0.006 to 1.00 %)	165
Chromium by the Peroxydisulfate Oxidation—Titration Method (0.10 to 33.00 %)	175
Chromium by the Peroxydisulfate-Oxidation Titrimetric Method	1 <sup>b</sup>
Cobalt by the Ion-Exchange-Potentiometric Titration Method (2 to 75 %)	53
Cobalt by the Nitroso-R-Salt Photometric Method (0.10 to 5.0 %)	61
Copper by Neocuproine Photometric Method (0.01 to 10.00 %)	90
Copper by the Sulfide Precipitation-Electrodeposition Gravimetric Method (0.01 to 10.00 %)	71
Iron by the Silver Reduction Titrimetric Method (1.0 to 50.0 %)	192
Manganese by the Periodate Photometric Method (0.05 to 2.00 %)	8
Molybdenum by the Ion Exchange—8-Hydroxyquinoline Gravimetric Method (1.5 to 30 %)	184
Molybdenum by the Photometric Method (0.01 to 1.50 %)	153
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 to 84.0 %)	135
Phosphorus by the Molybdenum Blue Photometric Method (0.002 to 0.08 %)	18
Silicon by the Gravimetric Method (0.05 to 5.00 %)	46
Sulfur by the Gravimetric Method	1 <sup>c</sup>
Sulfur by the Combustion-Iodate Titration Method (0.005 to 0.1 %)	37
Sulfur by the Chromatographic Gravimetric Method	1 <sup>b</sup>
Tin by the Solvent Extraction—Atomic Absorption Method (0.002 to 0.10 %)	143

1.3 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 method and therefore this standard contains multiple methods for some elements. The user must select the proper method by matching the information given in the Scope and Interference sections of each method with the composition of the alloy to be analyzed.

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

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Material and are the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferroalloys.

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<sup>1a</sup> Discontinued April 25, 1986. Its replacement appears as part of ASTM Test Methods E 1019, found in *Annual Book of ASTM Standards*, Vol 03.06.

<sup>1b</sup> Discontinued May 30, 1980.

<sup>1c</sup> Discontinued April 29, 1988.

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 Water<sup>2</sup>
  - E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>3</sup>
  - E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron<sup>4</sup>
  - E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals<sup>5</sup>
  - E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals<sup>5</sup>
  - E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals<sup>6</sup>
  - E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron<sup>5</sup>
  - E 351 Test Methods for Chemical Analysis of Cast Iron—All Types<sup>5</sup>
  - E 352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels<sup>5</sup>
  - E 353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys<sup>5</sup>
  - E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)<sup>7</sup>
  - E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory<sup>5</sup>
  - E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys<sup>5</sup>
  - E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry<sup>5</sup>
  - E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis<sup>5</sup>
  - E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition<sup>8</sup>
- 2.2 *Other Document:*
- ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests<sup>9</sup>

## 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 Com-

mittee 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 Practice

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.<sup>10</sup> 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 practice 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 METAPERIODATE PHOTOMETRIC METHOD

## 8. Scope

8.1 This method covers the determination of manganese in concentrations from 0.05 to 2.00 percent.

## 9. Summary of Method

9.1 Manganous ions are oxidized to permanganate ions by treatment with periodate. Tungsten when present at concentrations greater than 0.5 % is kept in solution with phosphoric

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

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

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 03.05.

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

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

<sup>8</sup> *Annual Book of ASTM Standards*, Vol 03.06.

<sup>9</sup> Available from American National Standards Institute, 11 West 42nd Street, 13th Floor, New York, NY 10036.

<sup>10</sup> “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.

acid. Solutions of the samples are fumed with perchloric acid so that the effect of periodate is limited to the oxidation of manganese. Photometric measurements are 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 (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 HNO<sub>3</sub> 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 HNO<sub>3</sub> and 400 mL of H<sub>3</sub>PO<sub>4</sub> 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 (KIO<sub>4</sub>) in 200 mL of hot HNO<sub>3</sub> (1 + 1), add 400 mL of H<sub>3</sub>PO<sub>4</sub>, cool, dilute to 1 L, and mix.

13.4 *Water, Pretreated with Metaperiodate*—Add 20 mL of KIO<sub>4</sub> 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 KIO<sub>4</sub> 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 KIO<sub>4</sub> 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 Solutions*—Select and weigh a sample in accordance with the following:

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

15.1.1 *For Samples Containing Not More Than 0.5 % Tungsten:*

15.1.1.1 To dissolve samples that do not require HF, add 8 to 10 mL of HCl (1+1), and heat. Add HNO<sub>3</sub> as needed to hasten dissolution, and then add 3 to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of HClO<sub>4</sub>; 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 a 100-mL volumetric flask. Proceed to 15.1.3.

15.1.1.2 For samples whose dissolution is hastened by HF, and 8 to 10 mL of HCl (1+1), and heat. Add HNO<sub>3</sub> and a few drops of HF as needed to hasten dissolution, and then add 3 to 4 mL of HNO<sub>3</sub>. When dissolution is complete, cool, then add 10 mL of HClO<sub>4</sub>, 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 15.1.5. Proceed to 15.1.3.

15.1.2 For Samples Containing More Than 0.5 % Tungsten:

15.1.2.1 To dissolve samples that do not require HF, add 8 to 10 mL of H<sub>3</sub>PO<sub>4</sub>, 10 mL of HClO<sub>4</sub>, 5 to 6 mL of H<sub>2</sub>SO<sub>4</sub>, and 3 to 4 mL of HNO<sub>3</sub>. 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 SO<sub>3</sub>. 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 15.1.3

15.1.2.2 For samples whose dissolution is hastened by HF: Add 8 to 10 mL of H<sub>3</sub>PO<sub>4</sub>, 10 mL of HClO<sub>4</sub>, 5 to 6 mL of H<sub>2</sub>SO<sub>4</sub>, 3 to 4 mL of HNO<sub>3</sub>, 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 of SO<sub>3</sub>. 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 15.1.3.

15.1.2.3 Cool the solution, 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.

15.1.3 Using a pipet, transfer 20-mL aliquots to two 50-mL borosilicate glass volumetric flasks; treat one as directed in 15.3 and the other as directed in 15.4.1.

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

15.3 Color Development—Proceed as directed in 14.3.

15.4 Reference Solutions:

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

15.4.2 Reagent Blank Reference Solution— Transfer the reagent blank solution (15.2) to the same size volumetric flask as used for the test solutions and transfer the same size aliquots as used for the test solutions to two 50-mL volumetric flasks. Treat one portion as directed in 15.3 and use as reference solution for test samples. Treat the other as directed in 15.4.1 and use as reference solution for Background Color Solutions.

15.5 Photometry—Establish the cell corrections with the Reagent Blank Reference solution to be used as a reference solution for Background Color solutions. Take the photometric readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference So-

lutions 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:

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

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 0.08 %.

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.

22. Interferences

22.1 See Section 22 of Test Methods E 352.

23. Apparatus

23.1 See Section 23 of Test Methods E 350.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Photometric Method

Test Specimen	Manganese Found, %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
1. Nickel alloy, 77Ni-20Cr (NIST 169, 0.073 Mn)	0.074	0.002	0.008
2. High-temperature alloy 68Ni-14Cr-7Al-6Mo (NIST 1205, 0.29 Mn)	0.289	0.007	0.026
3. Cobalt alloy 41Co-20Ni-20Cr-4Mo-4W (NIST 168, 1.50 Mn)	1.49	0.03	0.08
4. Stainless steel 18Cr-9Ni (NIST 101e, 1.77 Mn)	1.79	0.03	0.07



**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 and Less Than a Total of 1 % Columbium and Tantalum or 1 % of Either of the Latter Elements:*

27.1.1 *Test Solution:*

27.1.1.1 Proceed as directed in 27.1.1 through 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 and More Than a Total of 1 % Columbium and Tantalum or 1 % of Either of the Latter Elements:*

27.2.1 *Test Solution:*

27.2.1.1 Proceed as directed in 26.2.1.1 through 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 of Test Methods E 350.

**29. Precision**

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

**SULFUR BY THE GRAVIMETRIC METHOD**

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

**SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD**

**37. Scope**

37.1 This method covers the determination of sulfur in concentrations from 0.005 to 0.1 %.

**TABLE 2 Statistical Information—Phosphorus**

Test Specimen	Phosphorus Found, %	Repeatability ( $R_{11}$ , E 173)	Reproducibility ( $R_{21}$ , E 173)
1. Cobalt-base alloy 41Co-20-Ni-20Cr-4Mo-4W-3Nb (NBS 168, 0.008 P)	0.008	0.005	0.006

**38. Summary of Method**

38.1 See Section 38 of Test Methods E 350.

**39. Interferences**

39.1 The elements ordinarily 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 Although samples covered by this method with appropriate sulfur concentrations for evaluation of the method were not available, the precision data summarized in 45.1 of Test Methods E 353 should apply.

**SILICON BY THE GRAVIMETRIC METHOD**

**46. Scope**

46.1 This method covers the determination of silicon in concentrations from 0.05 to 5.00 % in alloys containing not more than 0.1 % boron.

**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. When boron is present in amounts greater than 0.1 %, the sample solution requires special treatment with methyl alcohol. (**Caution:** See 6.1.9.3 of Practices E 50) prior to acid dehydration. However, since no boron steels were tested, this special treatment was not evaluated.

**49. Reagents**

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

**50. Procedure**

50.1 Proceed as directed in 50.1 of Test Methods E 350.

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 SiO<sub>2</sub>.

**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 3. A sample with silicon concentration near the upper limit of the scope was 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 75 %.

**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**

58.1 Proceed as directed in 57.1 through 57.6 of Test Methods E 352, using 0.50-g samples for cobalt concentrations not greater than 25 %; at higher concentrations use samples

**TABLE 4 Statistical Information—Cobalt**

Test Specimen	Cobalt Found, %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
1. No. 1, E 352	1.86	0.05	0.12
2. No. 2, E 352	4.82	0.08	0.11
3. No. 3, E 352	8.46	0.03	0.07
4. High-temperature alloy 20Cr-13Ni-5Mo-2W-1Cb	11.27	0.06	0.16
5. Ni-base alloy 57Ni-14Cr (NBS 349, 13.95 Co)	13.88	0.09	0.18
6. High-temperature alloy 21Cr-20Ni-4Mo-3W	19.54	0.08	0.10
7. Co-base alloy 21Ni-20Cr-4Mo-5W-3Cb (NBS, 167, 42.90 Co)	42.91	0.18	0.15
8. Co-base alloy 28Cr-6Mo-3Ni	60.10	0.19	0.31

that represent between 100 and 125 mg of cobalt and weighed to the nearest 0.1 mg.

**59. Calculation**

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

**60. Precision**

60.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 4 for specimens 4 through 8. Although samples covered by this method with cobalt concentrations near the lower limit of the scope were not available for testing, the precision data obtained for specimens 1, 2, and 3 using the method indicated in Table 4 should apply.

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

**61. Scope**

61.1 This method covers the determination of cobalt in concentrations from 0.10 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.

**TABLE 3 Statistical Information—Silicon**

Test Specimen	Silicon Found, %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
HClO <sub>4</sub> Dehydration			
1. Ni-base alloy 75Ni-12Cr-6Al-4Mo-2Cb-0.7Ti	0.029	0.006	0.026
H <sub>2</sub> SO <sub>4</sub> Dehydration			
1. Ni-base alloy 75Ni-12Cr-6Al-4Mo-2Cb-0.7Ti	0.030	0.007	0.030
2. Co-base alloy 66Co-28Cr-4W-1.5Ni	1.01	0.03	0.06

**TABLE 5 Statistical Information—Cobalt**

Test Specimen	Cobalt Found, %	Repeatability ( $R_{11}$ , E 173)	Reproducibility ( $R_{21}$ , E 173)
1. Ni-base alloy, 36Ni (NBS 126b, 0.032 Co)	0.032	0.005	0.006
2. No. 2, E 353	0.094	0.006	0.013
3. No. 3, E 353	0.173	0.011	0.026
4. Ni-base alloy, 17Cr-15Fe (NBS 161, 0.47 Co)	0.468	0.020	0.028
5. No. 2, E 352	1.87	0.09	0.13
6. No. 3, E 352	4.94	0.08	0.17

## 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

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

## 70. Precision <sup>11</sup>

70.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 5 for specimens 1 and 4. Although samples covered by this method with cobalt concentration 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 5 should apply.

## COPPER BY THE SULFIDE PRECIPITATION-ELECTRODEPOSITION GRAVIMETRIC METHOD

## 71. Scope

71.1 This method covers the determination of copper in concentrations from 0.01 to 10.00 %.

## 72. Summary of Method

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

NOTE 3—This method describes the preliminary separations for the determination of tin by the sulfide-iodatimetric titration method.

## 73. Interferences

73.1 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 6).

## 74. Apparatus

74.1 Apparatus No. 9.

## 75. Reagents

75.1 *Ammonium Sulfate-Hydrogen Sulfide Solution*—Dissolve 50 g of ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) in about 800 mL of  $\text{H}_2\text{SO}_4$  (1+99), dilute to 1 L with  $\text{H}_2\text{SO}_4$  (1+99) and saturate with hydrogen sulfide ( $\text{H}_2\text{S}$ ).

75.2 *Ferric Chloride Solution* (2 g Fe/L)—Dissolve 10 g of ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) in about 800 mL of HCl (1+99) and dilute to 1 L with HCl (1+99).

75.3 *Sulfamic Acid* ( $\text{H}(\text{NH}_2)\text{SO}_3$ ).

## 76. Procedure

76.1 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
1.0 to 2.5	5	5
2.5 to 5.0	2	2
5.0 to 10.0	1	1

Transfer it to a 1-L Erlenmeyer flask.

76.2 If the sample type is other than cobalt base, proceed as directed in 76.3 through 76.22 of Test Methods E 350; treat cobalt base samples as directed in 76.2.1.

76.2.1 Add 30 mL of  $\text{HNO}_3$  and 10 mL of HBr. Heat cautiously to dissolve the sample. Evaporate the solution to a syrupy consistency and cool. Add 115 mL of HCl (1 + 2) and heat until salts are dissolved. Boil the solution 2 to 3 min. If the solution is clear, proceed as directed in 76.4 and 76.8 through 76.22 of Test Methods E 350. If the solution contains insoluble matter, proceed as directed in 76.4 through 76.22 of Test Methods E 350.

76.3 Add 115 mL of HCl (1+2) plus an additional 9 mL of HCl (1+2) and 1 mL of  $\text{HNO}_3$  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 76.4 and 76.9–76.22.

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

76.5 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 76.5.1 or 76.5.2 according to preference, bearing in mind that the latter procedure may be the easier to apply when copious amounts of insoluble matter are encountered.

76.5.1 Transfer the paper and precipitate to the original flask, add 20 mL of  $\text{HNO}_3$  and 10 mL of  $\text{HClO}_4$ , heat moderately to oxidize organic matter, and finally heat to mild fumes of  $\text{HClO}_4$ . Cool the solution, add 1 to 2 mL of HF, and repeat the fuming.

76.5.2 Transfer the paper and precipitate to a platinum

<sup>11</sup> Supporting data are available from ASTM Headquarters. Request RR: E03-1028.

crucible. Dry the paper and heat at 600°C until the carbon is removed. Finally ignite for 30 min at 1100°C. Cool, add 3 drops of HNO<sub>3</sub> and 1 to 2 mL of HF, and evaporate to dryness. Add 10 mL of HNO<sub>3</sub> (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 HClO<sub>4</sub>, and heat to mild fumes of HClO<sub>4</sub>.

76.6 Cool the solution from 76.5.1 or 76.5.2, add 100 mL of water and digest at or near boiling for about 45 min.

76.7 If tungsten is present, as indicated by the presence of a bright yellow precipitate of tungstic acid, add a slight excess of NH<sub>4</sub>OH and 20 g of tartaric acid. When the tartaric acid has dissolved, again add a slight excess of NH<sub>4</sub>OH and digest near the boiling point until dissolution is complete, or nearly so.

76.8 Add 5 mL of H<sub>2</sub>SO<sub>4</sub> and heat at 85 to 95°C for 30 min. If insoluble matter persists, repeat the steps as directed in 76.5–76.8. When dissolution is complete, combine the solution with the filtrate reserved in 76.5.

76.9 If the volume is less than 600 mL, dilute the solution approximately to that volume and treat with H<sub>2</sub>S; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 to 15 h.

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

76.11 Transfer the filter paper and precipitate to the original flask, add 12 mL of H<sub>2</sub>SO<sub>4</sub>, and heat to char the paper. Add 20 mL of HNO<sub>3</sub>, and evaporate to fumes to destroy organic matter. Add HNO<sub>3</sub> in 1-mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

76.12 Cool the solution, rinse the sides of the flask, and repeat the fuming to ensure the complete removal of HNO<sub>3</sub>.

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

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

76.15 Add 10 mL of FeCl<sub>3</sub> solution to the filtrate. Add just enough NH<sub>4</sub>OH (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 NH<sub>4</sub>OH (1+99) and water into an 800-mL beaker. Reserve the filter and the filtrate. Dissolve the precipitate by washing the filter alternately with hot HCl (1+1) and hot water, and reserve the filter paper. Precipitate the iron, tin, and chromium as before. Wash the reserved filter paper three times with hot NH<sub>4</sub>OH (1+99) and then filter the hot solution into the 800-mL beaker reserved from the first filtration: wash alternately five times each with hot NH<sub>4</sub>OH (1+99) and water.

NOTE 4—If tin is to be determined by using the same sample, reserve the precipitate and proceed as directed in 100.5 through 100.8.

76.16 Acidify the combined filtrates with HNO<sub>3</sub>, and evaporate at low heat until salts begin to appear. Remove the beaker from the hot plate and while the solution is still hot add 5 mL

of HNO<sub>3</sub>. When the reaction has subsided, add another 5 mL of HNO<sub>3</sub> and again wait until the reaction subsides. Continue adding 5-mL increments of HNO<sub>3</sub> in this manner until there is no further reaction with the chloride ions. Cover the beaker with a ribbed cover glass and warm gently until the vigorous evolution of gas ceases. Evaporate to fumes of SO<sub>3</sub>. Cool, add 25 mL of water, and heat to dissolve the salts. Cool, transfer to a 250-mL beaker, add 3 mL of HNO<sub>3</sub>, and dilute to 175 mL.

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

76.18 Stir the solution with an automatic stirrer, start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1 A/dm<sup>2</sup>. Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 to 3 A/dm<sup>2</sup>. (Note 5). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 5—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm<sup>2</sup>, and 2 to 3 h should be allowed for complete deposition.

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

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

76.21 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 6—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of HNO<sub>3</sub> and 5 mL of H<sub>2</sub>SO<sub>4</sub> in 175 mL of water contained in a 300-mL tail-form beaker. Reverse the polarity of the electrodes, and electrolyze with a current density of 3 A/dm<sup>2</sup> 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 76.19 and 76.20.

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

NOTE 7—To prepare the electrode for reuse, immerse it in HNO<sub>3</sub>(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.

## 77. Calculation

77.1 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.

**78. Precision**

78.1 Six laboratories cooperated in testing this method and obtained eight sets of data summarized in Table 6. Although samples covered by this method were not available for testing, the precision data obtained for specimens using the method indicated should apply.

**TOTAL CARBON BY THE COMBUSTION GRAVIMETRIC METHOD**

**79. Scope**

79.1 This method covers the determination of carbon in concentrations from 0.05 to 1.10 %.

**80. Summary of Test Method**

80.1 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.

80.2 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.

**81. Interferences**

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

**82. Apparatus**

82.1 *Apparatus No. 1.*

NOTE 8—The induction furnace must be equipped with suitable controls to regulate the power input to the induction coil.

NOTE 9—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.

82.2 *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.

**TABLE 6 Statistical Information—Copper**

Test Specimen	Copper Found, %	Repeatability ( <i>R</i> <sub>1</sub> , E 173)	Reproducibility ( <i>R</i> <sub>2</sub> , E 173)
1. Low-alloy steel (NBS 152a, 0.023 Cu)	0.020	0.005	0.006
2. No. 2, E 352	0.079	0.003	0.006
3. No. 3, E 353	0.364	0.009	0.010
4. No. 3, E 351	0.678	0.037	0.041
5. No. 4, E 351	5.49	0.10	0.10

NOTE 10—For precision-testing this balance see 7.4 of Methods E 319, or its equivalent.

**83. Reagents**

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

83.2 *Iron (Low-Carbon) Accelerator*—Iron chips (Note 11).

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

83.4 *Tin (Low-Carbon) Accelerator*, granular (Note 11).

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

NOTE 11—Prior to use, all accelerators should be washed three times with acetone by decantation until free of organic contaminants and then dried.

**84. Preparation of Apparatus—Induction Furnace**

84.1 The train of the induction furnace shall include an oxygen purifier, catalyst heater (Note 12), 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 12—The catalyst heater contains copper oxide heater to about 300°C to ensure complete conversion of CO to CO<sub>2</sub>.

84.2 *Conditioning of Apparatus:*

84.2.1 Transfer 1 g of a sample containing approximately 0.5 % carbon and 1 g of the accelerators (see Section 83) to a cupelet, crucible, or boat.

84.2.2 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.

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

NOTE 13—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.

84.2.4 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 14—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.

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

NOTE 15—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.

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

**85. Preparation of Apparatus—Resistance Furnace**

85.1 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.

*85.2 Conditioning of Apparatus:*

85.2.1 Fill the boat with Alundum bedding material (Note 16). 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 83).

NOTE 16—The Alundum bedding material should be previously heated in oxygen at 1325°C for 15 min, cooled, and stored under cover.

85.2.2 Open the stopcock(s) of the absorption bulb (Note 13) and connect it to the carbon train.

85.2.3 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 14).

NOTE 17—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.

85.2.4 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.

**86. Blank Procedure**

*86.1 Induction Furnace:*

86.1.1 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 84.2.

86.1.2 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 cupellet, crucible, or boat. Proceed as directed in 84.2.2–84.2.6.

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

86.1.4 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.

86.1.5 Proceed as directed in Section 87.

*86.2 Resistance Furnace:*

86.2.1 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 85.2.

86.2.2 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 16). Proceed as directed in 85.2.2–85.2.4.

86.2.3 Proceed as directed in 86.1.3 and 86.1.4.

86.2.4 Proceed as directed in Section 87.

**87. Procedure**

87.1 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 87.2–87.5.

NOTE 18—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 19—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 CO<sub>2</sub> absorbent. High results may be due to inadequate purification of the oxygen or failure to remove oxides of sulfur.

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

87.3 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, cupellet, or boat containing Alundum (Note 16).

87.4 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 84.2.2–84.2.6 and 85.2.2–85.2.4.

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

**88. Calculation**

88.1 Calculate the percent of carbon as follows:

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

where:

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

**89. Precision**

89.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 7. Repeatability (R<sub>1</sub>)

**TABLE 7 Statistical Information—Carbon**

Test Specimen	Carbon Found, <sup>A</sup> %	Repeat-ability (R <sub>1</sub> , E 173)	Reproduc-ibility (R <sub>2</sub> , E 173)
1. Monel-type alloy 64Ni-31Cu (NBS 162a, 0.079 C)	0.080	0.005	0.006
2. High-speed steel 8Mo-2W-4Cr-1V (NBS 134a, 0.808 C)	0.81	0.01	0.03
3. Nickel-base alloy 60Ni-18Cr-1.8Mo	1.49	0.06	0.09

<sup>A</sup> All values based on duplicate determinations by each laboratory.

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

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

where  $\sigma_a$  is the among laboratories standard deviation, both  $S$  and  $\sigma_w$  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.

89.1.1 The repeatability is related to and can be estimated from  $\sigma_w$  as follows: Let  $X_1$  and  $X_2$  be the difference between two values obtained within a laboratory. The standard deviation  $\sigma_d$  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  $\sigma_d$ , is then

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

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

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

### COPPER BY THE NEOCUPROINE PHOTOMETRIC METHOD

#### 90. Scope

90.1 This method covers the determination of copper in concentrations from 0.01 to 10.00 %.

#### 91. Summary of Method

91.1 See Section 115 of Test Methods E 350.

#### 92. Concentration Range

92.1 See Section 116 of Test Methods E 350.

#### 93. Stability of Color

93.1 See Section 117 of Test Methods E 350.

#### 94. Interferences

94.1 See Section 118 of Test Methods E 350.

#### 95. Reagents

95.1 See Section 119 of Test Methods E 350.

#### 96. Preparation of Calibration Curve

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

#### 97. Procedure

97.1 *Test Solution:*

97.1.1 Select a sample in accordance with the following:

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.01 to 0.15	1.00	1.0	100	20
0.10 to 0.25	1.00	1.0	250	30
0.20 to 0.50	1.00	0.5	250	15
0.40 to 1.00	0.50	0.5	250	15
0.80 to 1.50	0.50	0.1	250	10
1.40 to 3.00	1.00	0.1	1000	10
2.80 to 5.00	0.60	0.1	1000	10
4.80 to 7.50	0.80	0.1	1000	5
7.25 to 10.00	0.60	0.1	1000	5

Transfer it to a 250-mL Erlenmeyer flask.

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

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

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

#### 98. Calculation

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

#### 99. Precision

99.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 8. Although samples only in the lower part of the scope of this method were available for testing, the precision data obtained for specimens in the remainder of the scope using the methods indicated should apply.

### TOTAL ALUMINUM BY THE 8-QUINOLINOL GRAVIMETRIC METHOD

#### 100. Scope

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

#### 101. Summary of Method

101.1 See Section 125 of Test Methods E 350.

#### 102. Interferences

TABLE 8 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability, ( $R_1$ , E 173)	Reproducibility, ( $R_2$ , E 173)
1. Nickel-base alloy, 57Ni-14Cr (NBS 349, 0.006 Cu)	0.006	0.001	0.004
2. Nickel-base alloy, 77Ni-20Cr (NBS 169, 0.015 Cu)	0.014	0.002	0.006
3. Cobalt-base alloy 41Co-20Ni (NBS 168, 0.035 Cu)	0.033	0.005	0.004
4. No. 5, E 352	0.078	0.005	0.010
5. No. 6, E 352	0.118	0.007	0.016
6. No. 6, E 353	0.176	0.019	0.021
7. No. 7, E 353	0.200	0.012	0.018
8. No. 8, E 353	0.221	0.013	0.022
9. No. 9, E 353	0.361	0.015	0.036
10. No. 5, E 351	1.51	0.04	0.05
11. No. 6, E 351	5.53	0.19	0.18

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

**103. Apparatus**

103.1 See Section 127 of Test Methods E 350.

**104. Reagents**

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

**105. Procedure**

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

105.2 Proceed as directed in 124.2 of Test Methods E 353.

**106. Calculation**

106.1 Proceed as directed in 125.1 of Test Methods E 353.

**107. Precision**<sup>5</sup>

107.1 Eight laboratories cooperated in testing this method using test specimens 3 and 6, nine using test specimens 4 and 5, with one laboratory reporting a second pair of values in each instance; the data are summarized in Table 9. Although samples covered by this method with aluminum concentrations at the upper limit and at the lower limit of the scope were not available for testing, the precision data obtained using the methods indicated in Table 9 should apply.

**SULFUR BY THE CHROMATOGRAPHIC GRAVIMETRIC METHOD**

(This method, which consisted of Sections 108 through 115 of this standard, was discontinued in 1980.)

**CHROMIUM BY THE PEROXYDISULFATE-OXIDATION TITRIMETRIC METHOD**

(This method, which consisted of Sections 116 through 123 of this standard, was discontinued in 1980.)

**TOTAL CARBON BY THE COMBUSTION-THERMAL CONDUCTIVITY METHOD**

(This method, which consisted of Sections 124 through 134 of this standard, was discontinued in 1986.)

**NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD**

**135. Scope**

135.1 This method covers the determination of nickel in concentrations from 0.1 to 84.0 %.

**136. Summary of Method**

136.1 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.

136.2 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.

**137. Interferences**

137.1 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.

**138. Apparatus**

138.1 *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.

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

138.3 *pH Meter*—Apparatus No. 3A.

**139. Reagents**

139.1 *Ammonium Citrate Solution (200 g/L)*—Dissolve 200 g of diammonium hydrogen citrate [(NH<sub>4</sub>)<sub>2</sub>HC<sub>6</sub>H<sub>5</sub>O<sub>7</sub>] in 600 mL of water. Filter and dilute to 1 L.

139.2 *Anion Exchange Resin*:

139.2.1 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.<sup>12</sup> 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

**TABLE 9 Statistical Information—Aluminum**

Test Specimen	Aluminum Found, %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
1. No. 1, E 353	0.232	0.036	0.041
2. No. 2, E 353	1.16	0.06	0.10
3. Nickel-base alloy 57Ni-14Cr (NBS 349, 1.23 A1)	1.21	0.02	0.08
4. No. 4, E 350	1.44	0.07	0.16
5. Nickel-base alloy 19Cr-19Co-4Mo-3Ti	2.88	0.06	0.12
6. Nickel-base alloy 13Cr-4.5Mo-2.2Cb	5.84	0.16	0.26

<sup>12</sup> Dowex 1, manufactured by the Dow Chemical Co., Midland, MI, has been found satisfactory for this purpose.



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.

139.2.2 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.

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

## 140. Procedure

### 140.1 Double Precipitation:

140.1.1 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
48.0 to 84.0	0.5	0.2

Transfer it to a 600-mL beaker.

140.1.2 Add 60 mL of HCl (1 + 1) and 10 mL of HNO<sub>3</sub>. Heat to dissolve the sample and boil to expel oxides of nitrogen. Cool the solution and add 30 mL of HClO<sub>4</sub>. Heat to strong fumes of HClO<sub>4</sub> and continue fuming for 5 min. Cool and dilute to 100 mL with water.

140.1.3 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 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.

140.1.4 Add 200 mL of water and 30 mL of ammonium citrate solution. Using a pH meter, adjust the pH to at least 7.5 with NH<sub>4</sub>OH. Acidify the solution with HCl to pH 6.3 ± 0.1.

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

140.1.6 Using a pH meter, adjust the pH to 7.4 ± 0.1 with NH<sub>4</sub>OH. 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.

140.1.7 Filter using a 12.5-cm coarse paper. Wash five to seven 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.

140.1.8 Add 30 mL of HNO<sub>3</sub> and 15 mL of HClO<sub>4</sub>. Evaporate to strong fumes and continue fuming for 5 min. Cool and add 50 mL of water.

140.1.9 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 140.3–140.7.

### 140.2 Anion-Exchange Separation:

140.2.1 Proceed as directed in 140.1.1.

140.2.2 Proceed as directed in 140.1.2, but dilute with only 50 mL of water.

140.2.3 Filter the solution obtained in 140.2.2 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 three times with 5-mL portions of hot water. Discard the residue.

140.2.4 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.

140.2.5 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.

140.2.6 Place a clean 600-mL beaker under the ion-exchange column and open the bottom stopcock. Transfer the solution from 140.2.4 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 three 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.

140.2.7 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 140.2.5.

140.2.8 Heat the solution reserved in 140.2.6 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.

140.3 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<sub>4</sub>OH. Remove and rinse the electrodes with water collecting the rinsings in the original beaker.

140.4 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.

140.5 Using a pH meter, adjust the pH to 7.4 ± 0.1 with NH<sub>4</sub>OH. 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.

140.6 With the aid of suction, filter using a weighed (Note 20) fritted glass crucible. Wash the beaker and precipitate 6 times with cold water.

NOTE 20—Heat the crucible at 150°C and cool in a desiccator before weighing.

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

#### 141. Calculation

141.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} [((A - B) \times 0.2032)/C] \times 100 \quad (9)$$

where:

A = weight of crucible and precipitate, g,

B = weight of crucible, g, and

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

#### 142. Precision<sup>3</sup>

142.1 Ten laboratories cooperated in the testing of this method and obtained the data summarized in Table 10. Although a sample covered by this method near the lower end of the scope was not tested, the data obtained for other types of alloys using the methods indicated in Table 10 should apply.

### TIN BY THE SOLVENT EXTRACTION—ATOMIC ABSORPTION METHOD

TABLE 10 Statistical Information—Nickel

Test Specimen	Nickel Found %	Repeatability (R <sub>1</sub> , E 173)	Reproducibility (R <sub>2</sub> , E 173)
1. No. 1, E 352	0.135	0.012	0.015
2. No. 2, E 352	1.81	0.09	0.08
3. Nickel-chrome steel 16 Cr-4 Ni-3 Cu (NBS 345, 4.24 Ni)	4.22	0.06	0.05
4. Cobalt alloy 41 Co-20 Ni-20 Cr-4 Mo-4W (NBS 168, 20.25 Ni)	20.26	0.23	0.17
5. Nickel alloy 77 Ni-20 Cr (NBS 169, 77.26 Ni)	77.13	0.56	0.55

#### 143. Scope

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

#### 144. Summary of Method

144.1 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.

#### 145. Concentration Range

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

#### 146. Interferences

146.1 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.

#### 147. Apparatus

147.1 *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 149.4.

#### 148. Reagents

148.1 *Ascorbic Acid*.

148.2 *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.

148.3 *Methyl Isobutyl Ketone (MIBK)*.

148.4 *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.

148.5 *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.

148.6 *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.

#### 149. Preparation of Calibration Curve

149.1 *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 21—Volumetric flasks with ground glass stoppers must be used.

#### 149.2 Extraction:

149.2.1 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.

149.2.2 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 22—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

#### 149.3 Photometry:

149.3.1 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.

149.3.2 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 23—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 149.3.1.

149.3.3 Aspirate the solution with the highest concentration (40 µg Sn/mL) from the series prepared in 149.1 a sufficient number of times to establish that the absorbance is not drifting.

NOTE 24—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 25—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.

149.3.4 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 149.3.3 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 149.3.1–149.3.4.

149.3.5 Proceed immediately as directed in 150.3.

149.4 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:

$$\text{Deviation from linearity} = (A - B)/C \quad (10)$$

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.

## 150. Procedure

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

### 150.2 Test Solution:

150.2.1 Select and weigh a sample (Note 26) 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.

NOTE 26—Select a sample that will pass through a No. 20 (850-µm) sieve.

150.2.2 Add 100 mL of HCl, 20 drops of 30 % H<sub>2</sub>O<sub>2</sub>, and 5 drops of HF. Cover the beaker with a poly (tetrafluoroethylene) cover and heat at a low temperature (approximately 90°C). At 20-min intervals, remove the cover with platinum-tipped tongs and cautiously add an additional 20 drops of 30 % H<sub>2</sub>O<sub>2</sub>. Repeat this step until dissolution is complete.

NOTE 27—If silicon is above 0.5 %, use 10 to 12 drops of HF. If dissolution is very slow, add an additional 50 mL of HCl and heat at approximately 90°C overnight.

150.2.3 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.

NOTE 28—If niobium, tantalum, tungsten, or certain other elements are present in sufficiently high concentration, they will precipitate. Extract such samples as directed with minimal delay.

150.2.4 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.

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

150.2.6 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.

150.3 *Photometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 24) and record the absorbance values. Take three readings on each solution (Note 25). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drift as in 149.3.4 and 149.3.5.

**151. Calculation**

151.1 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:

$$\text{Tin, \%} = [(D - E)/(F \times 1000)] \tag{11}$$

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.

**152. Precision and Bias <sup>13</sup>**

152.1 *Precision*—Eleven laboratories cooperated in testing this method and obtained the precision listed for No. 1, 2, 4, and 6 in Table 11. This method differs only slightly from the method for tin, Test Methods E 350, in that the reagents used for sample dissolution were slightly modified. The fact that the precision obtained for No. 2, 4, and 6 of Table 11, corresponds closely to that obtained for samples of similar tin content in Test Methods E 350, suggests that the precision of the two methods is the same.

152.2 *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.

**MOLYBDENUM BY THE PHOTOMETRIC METHOD**

<sup>13</sup> Supporting data are available from ASTM Headquarters. Request RR: E03-1022.

**TABLE 11 Statistical Information—Tin**

Test Specimen	Tin Found, %	Repeat-ability (R <sub>1</sub> , E 173)	Repro-ducibility (R <sub>2</sub> , E 173)
1. Cobalt-alloy (49 Co-balance Fe), 0.001 Sn (not certified)	0.0017	0.0002	0.0004
2. Nickel-base alloy (74 Ni-15 Cr), 0.002 Sn (not certified)	0.0021	0.0005	0.0006
3. No. 1, E 350	0.0034	0.0009	0.0014
4. Nickel-base alloy (74 Ni-15 Cr), 0.008 Sn (not certified)	0.0076	0.0013	0.0017
5. No. 2, E 350	0.0079	0.0009	0.0014
6. Nickel-base alloy (74 Ni-15 Cr), 0.017 Sn (not certified)	0.015	0.002	0.003
7. No. 4, E 350	0.031	0.003	0.004
8. No. 6, E 350	0.097	0.011	0.011

**153. Scope**

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

**154. Summary of Method**

154.1 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.

**155. Concentration Range**

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

NOTE 29—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.

**156. Stability of Color**

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

**157. Interferences**

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

**158. Reagents**

158.1 *Butyl Acetate*:

NOTE 30—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.

158.2 *Dissolving Solution*—While stirring, add 300 mL of H<sub>3</sub>PO<sub>4</sub> and 300 mL of HNO<sub>3</sub> to 1400 mL of HClO<sub>4</sub>.

158.3 *Iron<sup>14</sup>*—Purity: 99.8 % minimum, molybdenum 0.001 % max.

158.4 *Iron Solution A* (1 mL = 70 mg Fe)—Dissolve 25 g of ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O) in 75 mL of hot water. Cool and add 10 mL of H<sub>2</sub>SO<sub>4</sub>. Cool, and dilute to 100 mL.

158.5 *Iron Solution B* (1 mL = 0.84 mg Fe)—Add 12 mL of iron Solution A to 175 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1), and dilute to 1 L.

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

158.7 *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.

158.8 *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.

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

<sup>14</sup> Johnson-Matthey JMC 847 sponge iron has been found suitable for this purpose.



158.10 *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 31—This solution is used for color development in 159.3, 160.3, 161.3, and 162.3. 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.

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

#### 159.1 Calibration Solutions:

159.1.1 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.

159.1.2 Increase the temperature and evaporate to  $\text{HClO}_4$  fumes. Cool, add 50 mL of water and 70 mL of  $\text{H}_2\text{SO}_4$  (1 + 1). Heat to boiling and cool in a water bath.

159.1.3 Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 159.3.

159.2 *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 159.1.2, 159.1.3, and 159.3.

159.3 *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  $\text{SnCl}_2$  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  $\text{H}_2\text{SO}_4$  (1 + 6), 5 mL of NaSCN solution, and 5 mL of  $\text{SnCl}_2$  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 32—This funnel should be cleaned thoroughly after each filtration to avoid development of a pink color that would contaminate the filtrate.

159.4 *Reference Solution*—Butyl acetate.

#### 159.5 Photometry:

159.5.1 *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.

159.5.2 *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.

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

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

#### 160.1 Calibration Solutions:

160.1.1 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.

160.1.2 Increase the temperature and evaporate to  $\text{HClO}_4$  fumes. Cool, add 50 mL of water, and 70 mL of  $\text{H}_2\text{SO}_4$  (1 + 1). Heat to boiling and cool in a water bath.

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

160.2 *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 160.1.2, 160.1.3, and 160.3.

160.3 *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  $\text{SnCl}_2$  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  $\text{H}_2\text{SO}_4$  (1 + 6), 5 mL of NaSCN solution, and 5 mL of  $\text{SnCl}_2$  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 32.)

160.4 *Reference Solution*—Butyl acetate.

#### 160.5 Photometry:

160.5.1 *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.

160.5.2 *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.

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

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

#### 161.1 Calibration Solutions:

161.1.1 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.

161.1.2 Increase the temperature and evaporate to HClO<sub>4</sub> fumes. Cool, add 30 mL of water and 70 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1). Heat to boiling and cool in a water bath.

161.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 161.3.

161.2 *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 161.1.2, 161.1.3, and 161.3.

161.3 *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<sub>2</sub> 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<sub>2</sub>SO<sub>4</sub> (1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl<sub>2</sub> 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 32.)

161.4 *Reference Solution*—Butyl acetate.

161.5 *Photometry*:

161.5.1 *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.

161.5.2 *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.

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

## 162. Procedure

162.1 *Test Solution*:

162.1.1 Transfer 0.3-g sample, weighed to the nearest 1 mg, to a 250-mL Erlenmeyer flask. If the alloy contains tungsten, add 30 mL of dissolving acid. Add HCl, or HNO<sub>3</sub>, or mixtures and dilutions of these acids, or bromine and HCl in a ratio of 1:3 (plus a few drops of HF), and heat until dissolution is complete.

162.1.2 Increase the temperature and heat to HClO<sub>4</sub> fumes. Continue fuming until chromium, if present, is oxidized and the white HClO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> (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 162.1.3. Wash the paper with five 5-mL portions of H<sub>2</sub>SO<sub>4</sub> (1 + 99), collecting these in the same volumetric flask. Proceed as directed in 162.3. If the solution is clear, proceed to 162.1.3.

162.1.3 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 162.3.

162.2 *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 162.1.2, 162.1.3, and 162.3, using the same dilution and aliquots used for the test solution.

162.3 *Color Development*—Using a pipet, transfer the appropriate aliquot to a 250-mL separatory funnel containing the appropriate amount of iron solution for the specified aliquot. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of SnCl<sub>2</sub> solution, and, measured with a pipet, the amount of butyl acetate specified in the aliquot guide. Stopper the separatory funnel and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl<sub>2</sub> 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 32.)

162.4 *Reference Solution*—Butyl acetate.

162.5 *Photometry*—Take the photometric reading of the test solution and of the reagent blank solution as directed in 160.5.

## 163. Calculation

163.1 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:

$$\text{Molybdenum, \%} = \frac{A}{B \times 10} \quad (12)$$

TABLE 12 Statistical Information—Molybdenum

Test Specimen	Molybdenum Found, %	Repeatability R <sub>1</sub> , F173	Reproducibility R <sub>2</sub> , E 173
1. No. 1, E 350	0.012	0.002	0.006
2. No. 3, E 353	0.432	0.010	0.017
3. No. 4, E 353	1.34	0.032	0.092

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 162.1.3).

#### 164. Precision and Bias<sup>15</sup>

164.1 *Precision*—No data are presently available to determine the precision of this method. However, the difference between this method and molybdenum Test Methods E 350, E 351, E 352, and E 353 are minor and will not affect the precision of the results (see Table 12.). This fact suggests that the precision for these methods is the same.

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

### CHROMIUM BY THE ATOMIC ABSORPTION METHOD

#### 165. Scope

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

#### 166. Summary of Method

166.1 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.

#### 167. Concentration Range

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

#### 168. Interferences

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

#### 169. Apparatus

169.1 *Atomic Absorption Spectrophotometer*, capable of 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 171.4. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this method.

#### 170. Reagents

170.1 *Chromium, Standard Solution* (1 mL = 0.1 mg Cr)—Transfer 2.8290 g of potassium dichromate ( $K_2Cr_2O_7$ ) (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  $H_2SO_4$  and, while stirring, add 10 mL of  $H_2O_2$  (30 %). Heat at near boiling for 5 min to remove excess  $H_2O_2$ . Cool, transfer the solution to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask, dilute to volume, and mix.

170.2 *Iron*,<sup>16</sup> *Low Chromium*—Cr <0.0001 %.

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

#### 171. Preparation of Calibration Curves

171.1 *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  $HNO_3$  and heat gently until dissolution is complete. Evaporate to dryness on a hot plate and cool. Add 10 mL of HCl and warm to dissolve salts. Dilute to about 50 mL and transfer to 100-mL volumetric flasks. Add 10 mL of  $K_2CO_3$  solution to each of 7 flasks. Using pipets, transfer 1, 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.

171.2 *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  $HNO_3$ . Warm as necessary to dissolve the sample. Evaporate just to dryness on a hot plate and cool. Add 20 mL of HCl and warm to dissolve salts. Dilute to about 100 mL and add 20 mL of  $K_2CO_3$  solution. Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Transfer 10-mL aliquots to each of seven 100-mL volumetric flasks and add 9 mL of HCl to each flask. Using pipets, transfer 1, 3, 5, 7, 10, and 15 mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium concentration. Dilute to volume and mix.

171.3 *Photometry*:

171.3.1 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.

171.3.2 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 171.1, 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.

171.3.3 Aspirate the chromium solutions used in 171.3.2 to assure that the absorbance reading is repeatable. Record 6 readings, and calculate the standard deviation, *s*, of the readings as follows:

<sup>15</sup> Supporting data are available from ASTM Headquarters. Request RR: E03-1023.

<sup>16</sup> Johnson-Matthey sponge iron or Spex iron has been found suitable for this purpose.



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

where:

*A* = the highest of 6 values found, and  
*B* = the lowest of the 6 values found.<sup>17</sup>

171.3.4 Using water as a reference solution, and beginning with the solution to which no addition of chromium was made in 171.1 and 171.2, 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 171.3.3 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 171.3.1–171.3.4.

171.3.5 Proceed immediately as directed in Section 172.

171.4 *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:

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

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.

171.5 *Calibration for Concentrations from 0.10 to 1.00 %*—Proceed as directed in 171.4.

## 172. Procedure

### 172.1 Test Solution:

172.1.1 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.

172.1.2 Add 20 mL HCl, 10 mL HNO<sub>3</sub>, and 5 drops of HF. Heat to dissolve. Remove from the hot plate and dilute to approximately 50 mL. Add a small amount of filter pulp and filter the solution through 11-cm fine filter paper into a 250-mL borosilicate beaker. Wash the paper 5 times with HCl (1 + 99), and reserve the filtrate.

172.1.3 Transfer the paper and contents to a platinum crucible. Dry on a hot plate, and transfer to a muffle furnace that is less than 400°C. Gradually heat to 600°C and hold at this temperature for 1 h. Cool, add 0.5 g of K<sub>2</sub>CO<sub>3</sub>, and carefully fuse over a free flame until a clear melt is obtained

(see Note 33). 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 33—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.

172.1.4 Transfer this solution to the filtrate from 172.1.2 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 172.3. 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.

172.2 Prepare for each concentration range a reagent blank by treating the same amount of all reagents as directed in 172.1.1–172.1.4, including the low chromium iron. Use reagents from the same lots for blank and test solutions.

172.3 *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 171.3.4, 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 171.3.3, 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.

## 173. Calculation

173.1 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:

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (15)$$

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.

TABLE 13 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability ( <i>R</i> <sub>1</sub> , E 173)	Reproducibility ( <i>R</i> <sub>2</sub> , E 173)
1. 40 Ni 0.2 Si 0.5 Mn 0.02 C Steel	0.072	0.007	0.009
2. No. 1, E 352	0.149	0.028	0.025
3. 18 Ni 9 Co 5 Mo 0.5 Ti Steel	0.961	0.036	0.093

<sup>17</sup> 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, 1957, Table 8b, (1), p. 404.



## 174. Precision and Bias<sup>18</sup>

174.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 13.

174.2 *Bias*—The accuracy can be inferred from the data in Table 13 by comparing the certified values for chromium with the average value obtained by using this method.

### CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

## 175. Scope

175.1 This method covers the determination of chromium in concentrations from 0.10 to 33.00 %.

## 176. Summary of Method

176.1 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 34—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.

## 177. Interferences

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

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

$$(2.6A + 0.05B + 0.01C) D \quad (16)$$

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.

## 178. Apparatus

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

## 179. Reagents

179.1 *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.

179.2 *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 180.1, 180.2, or 180.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

179.3 *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.

179.4 *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.

179.5 *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.

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

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

179.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 *M*)—Reagent No. 122 (Practices E 50).

## 180. Standardization of Ferrous Ammonium Sulfate Solution

180.1 *Against Potassium Permanganate Solution:*

180.1.1 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 (179.2) 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 (179.5) 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.

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

$$\text{Normality} = AB/C \quad (17)$$

where:

*A* = normality of  $KMnO_4$  solution (179.5),

*B* =  $KMnO_4$  solution, mL, and

*C* =  $Fe(NH_4)_2(SO_4)_2$  solution, mL.

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

<sup>18</sup> Supporting data are available from ASTM Headquarters. Request RR: E03-1030.

180.2.1 Transfer 180 mL of water, 12 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1), and 5 mL of H<sub>3</sub>PO<sub>4</sub> into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 or 0.10 N Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> (179.2) 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, while swirling the flask. As the end point is approached, add the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution as before, and again titrate with either 0.05 or 0.10 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution to the blue end point. Subtract this volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution from the volume recorded for the first titration and record the difference as the indicator blank.

180.2.2 Calculate the normality of the Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution as follows:

$$\text{Normality} = (0.05 \text{ or } 0.10 (A - B))/C \quad (18)$$

where:

A = 0.05 or 0.10 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, mL, used in the first titration,

B = mL equivalent to the indicator blank, and

C = Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution, mL, used in the first titration.

180.3 *Against Potassium Dichromate Using Potentiometric End Point:*

180.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 or 0.10 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution into a 600-mL beaker. Reserve the remaining 0.05 or 0.10 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution in the buret for the back-titration. Add 150 mL of water, 10 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 1), and 5 mL of H<sub>3</sub>PO<sub>4</sub>. 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<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> until the dichromate ion yellow color disappears and then a slight excess. Record the volume of the Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution to the nearest 0.01 mL. Back-titrate with the remaining 0.05 or 0.10 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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 <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> Back Titrant (mL)	Voltage (mV)	Δ Voltage (mV)	Difference Before and After Maximum
20.80	555		
20.90	570		
21.00	620	50	50
21.10	720	100	20
21.20	800	80	
21.30	835		
21.40	854		

Maximum voltage change occurred between 21.00 and 21.10 mL of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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.

180.3.2 Calculate the normality of the Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution as follows:

$$\text{Normality} = 0.05 \text{ or } 0.10 A/B \quad (19)$$

where:

A = 0.05 or 0.10 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution, mL, and

B = Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution, mL.

## 181. Procedure

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Normality of Titrants
0.10 to 0.50	3.50	2.0	0.05
0.40 to 1.00	2.00	1.0	0.05
0.80 to 1.60	1.25	0.3	0.05
1.50 to 3.50	0.50	0.1	0.05
3.30 to 8.00	0.25	0.1	0.05
8.00 to 14.00 <sup>A</sup>	0.50	0.1	0.10
13.00 to 20.00 <sup>A</sup>	0.40	0.1	0.10
18.00 to 30.00 <sup>A</sup>	0.20	0.1	0.10
28.00 to 33.00 <sup>A</sup>	0.15	0.1	0.10

<sup>A</sup> 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.

181.2 Add 80 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 5) and 5 mL of H<sub>3</sub>PO<sub>4</sub>. Cover the beaker with a ribbed cover glass and heat at 85 to 100°C until the sample is decomposed. Add sufficient HNO<sub>3</sub> in small increments to oxidize iron. Boil 2 min to expel oxides of nitrogen. Proceed as directed in 181.4.

181.3 If the alloy does not dissolve in the acids specified in 181.2, add amounts of HCl or HNO<sub>3</sub>, 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 H<sub>2</sub>SO<sub>4</sub> (1 + 5), 5 mL of H<sub>3</sub>PO<sub>4</sub>, 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.

181.4 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.

181.5 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 H<sub>2</sub>SO<sub>4</sub> (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 H<sub>2</sub>SO<sub>4</sub> is removed. Fuse the residue with a minimum amount of either fused sodium hydrogen sulfate (sodium pyrosulfate—Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub>) or potassium pyrosulfate (K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>). Cool the crucible, place in a 250-mL beaker, and dissolve the melt in 20 mL of H<sub>2</sub>SO<sub>4</sub> (1 + 10). Remove the crucible, rinse with water, transfer the solution to the reserved filtrate (181.4), and dilute to 200 mL.

181.6 Add 5 mL of AgNO<sub>3</sub> solution and 20 mL of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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 KMnO<sub>4</sub> solution (179.4), 5 mL more of AgNO<sub>3</sub> solution, 20 mL more of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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 181.7.

181.7 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 MnO<sub>2</sub> 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 181.9. If vanadium is absent and the criteria of 177.2 are met, proceed as directed in 181.9. If vanadium is absent and the criteria of 177.2 are not met, or if potentiometric titration is preferred and vanadium is absent, proceed as directed in 181.10.

181.8 *Titration With Potassium Permanganate*—While swirling the flask, add 1 to 2 drops of 1,10 phenanthroline indicator solution and then add sufficient Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> 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 KMnO<sub>4</sub> standard solution. Add KMnO<sub>4</sub> 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.

181.9 *Titration with Potassium Dichromate to the Diphenylamine Sulfonate End Point*—While swirling the flask, add Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution. Add the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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.

181.10 *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<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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 180.3). 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 180.3.

## 182. Calculations

182.1 If KMnO<sub>4</sub> was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (20)$$

where:

- A = Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution, mL
- B = normality of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution,
- C = KMnO<sub>4</sub> solution used, mL
- D = normality of the KMnO<sub>4</sub> solution, and
- E = sample taken, g.

182.2 If K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (21)$$

**TABLE 14 Statistical Information—Chromium**

Test Specimen	Chromium Found, %	Repeatability ( $R_1$ , E 173)	Reproducibility ( $R_2$ , E 173)
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. High-Temperature Alloy Waspalloy (NBS 349, 19.50Cr)	19.46	0.25	0.49
5. High-Temperature Alloy 41Co, 20Ni, 20Cr (NBS 168, 20.33Cr)	20.26	0.35	0.57

where:

- A** =  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution, mL  
**B** = normality of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  solution,  
**C** =  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, mL  
**D** = normality of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, and  
**E** = sample taken, g.

### 183. Precision and Bias<sup>19</sup>

183.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 14. 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 14 should apply.

183.2 *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 14).

## MOLYBDENUM BY THE ION EXCHANGE— 8-HYDROXYQUINOLINE GRAVIMETRIC METHOD

### 184. Scope

184.1 This method covers the determination of molybdenum in concentrations from 1.5 to 30 %.

### 185. Summary of Method

185.1 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.

### 186. Interferences

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

### 187. Apparatus

187.1 *Ion Exchange Column, Polystyrene*,<sup>20</sup> 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 35).

NOTE 35—The ion exchange column system must be carefully assembled and checked to avoid possible leakage of solutions containing HF.

### 188. Reagents

188.1 *Ammonium Chloride Solution* (240 g/L)—Dissolve 240 g of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) in 800 mL of water. Warm to room temperature, dilute to 1 L and mix.

188.2 *Ammonium Fluoride* ( $\text{NH}_4\text{F}$ ).

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

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

188.5 *Eluent Solutions*— **WARNING**—See Note 36.

NOTE 36—**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.

188.5.1 *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.

188.5.2 *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.

188.5.3 *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.

188.5.4 *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  $\text{NH}_4\text{Cl}$  on a weight/volume basis.)

188.5.5 *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  $\text{NH}_4\text{F}$ . 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  $\text{NH}_4\text{OH}$ . Store in an HF-resistant plastic bottle. (This solution is 14.4 % in  $\text{NH}_4\text{Cl}$  and 4.1 % in  $\text{NH}_4\text{F}$  on a weight/volume basis.)

188.6 *8-Hydroxyquinoline Solution* (30 g/L)—Dissolve 30 g of 8-hydroxyquinoline in 120 mL of glacial acetic acid ( $\text{CH}_3\text{COOH}$ ). Cautiously add water, with stirring to a total solution volume of 600 mL. Warm to 40°C. Add  $\text{NH}_4\text{OH}$  (1+1) dropwise with stirring until a slight permanent precipitate is formed. Carefully add glacial  $\text{CH}_3\text{COOH}$  with stirring until the precipitate first dissolves. Dilute to 1 L.

188.7 *Ion-Exchange Resin:*

188.7.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads

<sup>19</sup> Supporting data are available from ASTM Headquarters. Request RR:E03-1036.

<sup>20</sup> Columns available from Ledoux & Co., Inc., Teaneck, NJ have been found satisfactory.



having a cross-linkage of 8 % and of 200 to 400 nominal U.S. mesh size.<sup>21</sup> To remove those beads greater than about 180  $\mu\text{m}$  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- $\mu\text{m}$ ) 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.

188.7.2 Prepare the column as follows: Place a 10 to 20-mm layer of poly (vinyl chloride) plastic fiber<sup>22</sup> 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.

188.8 *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.

188.9 *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.

## 189. Procedure

189.1 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  $\text{HNO}_3$  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.

189.2 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 37). Cool

to room temperature and dilute to 100 mL with water.

NOTE 37—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

189.3 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.

189.4 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 38).

NOTE 38—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 ( $\text{Na}_2\text{CO}_3$ ) 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.

189.5 Continue to add HF/HCl/water (4+1+95) until 650 mL have been collected in the 800 mL plastic beaker (Note 39). Drain solution to the top of the resin bed. Cautiously discard this solution.

NOTE 39—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper, and manganese.

189.6 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 40).

NOTE 40—This solution contains all the tungsten, titanium, zirconium, and hafnium.

189.7 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 162.11.

189.8 Place an 800-mL plastic beaker under the column and elute 300 mL of HF/ $\text{NH}_4\text{Cl}$ /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 41).

NOTE 41—This solution contains all the niobium.

189.9 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 42).

NOTE 42—This solution contains all the tantalum.

<sup>21</sup> AG1-X8, 200 to 400 mesh, chloride form, available from Bio-Rad Laboratories, Richmond, CA, has been found satisfactory.

<sup>22</sup> Dynel plastic wool available from Union Carbide Corp., Chemical Division, Textile Fibers Department, Needham Heights, MA, has been found satisfactory.

189.10 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 (189.3).

189.11 To the eluent containing the molybdenum (from 189.7) cautiously add 15 mL of H<sub>2</sub>SO<sub>4</sub> (1+1) and evaporate to light fumes on a sandbath or other carefully controlled heat source. (**WARNING**—See Note 43.) Cool and cautiously rinse into a 400-mL borosilicate glass beaker. Heat to low volume (about 10 mL), cool, add 2 mL of HNO<sub>3</sub>, and evaporate to strong fumes of SO<sub>3</sub>.

NOTE 43—**Warning:** Ensure that the applied temperature does not exceed the softening point of polytetrafluoroethylene.

189.12 Cool to room temperature, dilute to about 30 mL with water, add 5 mL of HNO<sub>3</sub> and 5 mL of HCl. Cover and heat for 10 min.

189.13 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 189.14.

189.14 —If the molybdenum content of the solution or filtrate obtained in 189.13 is known to be less than 125 mg proceed to paragraph 189.15. If the molybdenum content of the solution or filtrate obtained in 189.13 is known to be greater than 125 mg, transfer the solution to a 250-mL volumetric flask, cool to room temperature, dilute to volume, and mix. Transfer a 100 mL aliquot by pipet to a 400-mL borosilicate beaker (**PRECAUTION**—Note 44).

NOTE 44—**Precaution:** Minimize contact time of caustic solutions in volumetric glassware; wash glassware thoroughly immediately after use.

189.15 Adjust the volume of the solution in the 400-mL beaker to approximately 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).

189.16 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.

189.17 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.

189.18 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.

**190. Calculation**

190.1 Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, \%} = [(A - B) \times C \times 23.05]/D \quad (22)$$

where:

- A = weight of crucible plus precipitate, in g,
- B = weight of crucible, in g,
- C = aliquot factor (direct: C = 1, aliquot: C = 2.5), and
- D = sample weight, in g.

**191. Precision and Bias**

191.1 *Precision*—Seven laboratories cooperated in testing this method and obtained the data summarized in Table 15. The unavailability of appropriate test specimens at the upper limit of the Scope necessitated the inclusion of Test Material 5 which is a different class of material. While the testing range exceeds the upper limit of the Scope, the data for Test Material 5 suggests the precision at upper limit of the Scope is adequate.

191.2 *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.

**IRON BY THE SILVER REDUCTION TITRIMETRIC METHOD**

**192. Scope**

192.1 This method covers the determination of iron in concentrations from 1.0 to 50.0 %.

**193. Summary of Method**

193.1 The sample is dissolved in HCl and HNO<sub>3</sub> and fumed in HClO<sub>4</sub>. Iron is precipitated with NH<sub>4</sub>OH in the presence of ammonium peroxydisulfate. The precipitate is dissolved in HCl. The resulting solution is adjusted to dilute acidity and passed through a silver reductor. After addition of a mixture of H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> and sodium diphenylaminesulfonate indicator the sample is titrated with standard potassium dichromate solution.

**194. Interferences**

194.1 The elements normally present do not interfere if their concentrations are less than the maximum amounts shown in 1.1.

**195. Apparatus**

**TABLE 15 Statistical Information—Molybdenum Ion Exchange—8-Hydroxyquinoline Gravimetric Method**

Test Material	Molybdenum Found, %	Repeatability, (R <sub>r</sub> , E 173 <sup>A</sup> )	Reproducibility, (R <sub>2</sub> , E 173 <sup>A</sup> )
1. No. 1, E 351	1.48	0.070	0.086
2. Co-base alloy 43Co-21Ni-20Cr-5W-3Nb-2Fe-2Mn (NBS 167, 3.90 Mo-prov.)	3.92	0.219	0.250
3. No. 3, E 352	8.85	0.180	0.188
4. Ni-base alloy 16Cr-5Fe-4W-Bal. Ni (AMS 5388, 17 Mo—not cert.)	17.49	0.285	0.641
5. Ferromolybdenum Balance Fe (FeMo-2, 53.20 Mo)	52.70	1.21	2.34

<sup>A</sup> This test was performed in accordance with the 1980 version of Practice E 173.

### 195.1 Silver Reductor Column:

195.1.1 *Preparation*—Use a glass column (2-cm diameter and 25-cm length) fitted with a stopcock and a reservoir cup (approximately 100-mL capacity). Lightly insert a glass wool plug above the stopper. Fill the column with a slurry of silver powder in HCl (1+11) and drain the acid solution to within 1 cm of the top of the column to produce a silver metal column of 17-cm length. Wash the column with 150 mL of HCl (1+11), allowing the acid solution to drain at a rate of about 30 mL/min. Store the column with 1 to 2 cm of HCl (1+11) above the top of the metal.

195.1.2 *Regeneration*—When a dark grey area extends down 10 cm from the top of the metal column, the column must be regenerated as follows. Pass 150 mL of H<sub>2</sub>SO<sub>4</sub>(1+99) through the column at a rate of about 30 mL/min. Leave 1 cm of solution above the metal. Lower two zinc rods (15 cm long) attached to cotton strings until they contact the silver metal and let stand overnight. Pass 50 mL of H<sub>2</sub>SO<sub>4</sub> (1+1) through the column. Remove the zinc rods. Pass 150 mL of HCl (1+11) through the column at a rate of 30 mL/min. The column is now ready for reuse. Store the column with 1 to 2 cm of HCl (1+11) above the top of the metal.

NOTE 45—If the flow from the column slows significantly in use or if the liquid layer falls below the metal, the metal and glass wool must be removed and the column repacked. For this reason some laboratories may find it convenient to maintain two silver reductor columns.

## 196. Reagents

196.1 *Ammonium Peroxydisulfate*, [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>].

196.2 *Potassium Dichromate, Standard Solution* (0.10N)—Dissolve 4.9032 g of National Bureau of Standards standard potassium dichromate in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

196.3 *Silver Powder*:

196.3.1 Use high purity (99.9 % minimum purity) silver powder, 40 to 60 mesh.

196.3.2 *Alternate*:

Dissolve 100 g silver nitrate (AgNO<sub>3</sub>) in 400 mL of water in a 600-mL beaker. Add 10 mL of HNO<sub>3</sub>. Place two zinc rods (15 cm in length) crosswise in the solution and let stand overnight. Remove the rods, washing them into the solution. Decant the supernatant solution and discard it. Add 400 mL H<sub>2</sub>SO<sub>4</sub> (1+99) to the precipitated silver metal, stir well, allow to settle, and discard the supernatant solution. Repeat the decantation until the supernatant solution is clear. The precipitated silver may be transferred to the glass column in this form, then washed with HCl (1+11), as described in 195.1.1.

196.4 *Sodium Diphenylaminesulfonate Indicator Solution* (2 g/L)—Dissolve 0.20 g of sodium diphenylaminesulfonate in 100 mL of water. Store in a dark glass bottle.

196.5 *Sulfuric Acid—Phosphoric Acid Mixture*—Add 150 mL of H<sub>3</sub>PO<sub>4</sub> to 400 mL of water, stirring well. Cool in a water bath and cautiously add 150 mL of H<sub>2</sub>SO<sub>4</sub> while stirring well. Cool to room temperature and dilute to 1 L while cautiously cooling and stirring. Cool again to room temperature.

196.6 *Zinc Metal Rods* (approximately 8 mm in diameter and 150 mm in length), 99.9 % purity.

## 197. Procedure

197.1 Select a sample weight which is expected to contain 60 to 100 mg of iron (but not exceeding 3.0 g). Weigh the sample to the nearest 0.2 mg and transfer it to a 400-mL beaker. Add 25 mL of HCl and 25 mL of HNO<sub>3</sub> and heat to dissolve. Add 4 drops of HF to remove SiO<sub>2</sub>. Cool and cautiously add 20 mL HClO<sub>4</sub>. Heat to dense white fumes. Continue heating for 5 min to fully oxidize chromium.

197.2 Cool and dilute to 200 mL with water. Add NH<sub>4</sub>OH slowly, while stirring, until the precipitate redissolves slowly, then add 25 mL additional NH<sub>4</sub>OH and 2 g of ammonium peroxydisulfate. Boil carefully for 2 min and filter through a high-porosity filter paper,<sup>23</sup> wash 5 times with NH<sub>4</sub>OH (1+50). Discard the filtrate.

197.3 Place the original beaker under the funnel and dissolve the precipitate in 50 mL hot HCl (1+3). Wash the paper alternately with hot water and with hot HCl (1+3) until it is free of yellow iron color. Discard the paper.

NOTE 46—Several drops of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 30 %, added to the hot HCl (1+3) in the funnel will aid in dissolving the precipitate if a large amount of manganese is present.

197.4 Dilute the solution to 150 mL. Add NH<sub>4</sub>OH cautiously, while stirring, until the precipitate redissolves slowly, then add 25 mL additional NH<sub>4</sub>OH and 2 g ammonium peroxydisulfate. Boil carefully for 2 min and filter through a high-porosity filter paper,<sup>19</sup> wash 5 times with NH<sub>4</sub>OH (1+50). Discard the filtrate.

197.5 Place the original beaker under the funnel and dissolve the precipitate in 50 mL hot HCl (1+3). Wash the paper alternately with hot water and with hot HCl (1+3) until it is free of yellow iron color. Discard the paper.

197.6 Boil the solution to reduce the volume to approximately 10 mL. Cool, dilute to 100 mL with water. Place a 600-mL beaker under the silver reductor column. Pass the solution through the column at a rate of approximately 35 mL/min. Rinse the 400 mL beaker 3 times with HCl (1+11) and add the rinsings to the column. Drain the solution to within 1 cm of the top of the silver metal, then add 150 mL of HCl (1+11) to the column, collecting all the eluent at approximately 35 mL/min in the 600-mL beaker. Retain a 1 cm layer of HCl (1+11) above the silver.

197.7 Add 25 mL of the sulfuric acid-phosphoric acid mixture to the 600-mL beaker, then add 5 to 6 drops of sodium diphenylaminesulfonate indicator solution. Titrate immediately with potassium dichromate standard solution (0.10N) to a permanent purple end point.

## 198. Calculation

198.1 Calculate the percentage of iron as follows:

$$\text{Iron, \%} = [(0.55847) \times (A)/(B)] \quad (23)$$

where:

A = K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standard solution (0.1000N), mL, and

B = sample taken, g.

<sup>23</sup> Whatman No. 541 has been found acceptable.

**TABLE 16 Statistical Information—Iron by the Silver Reduction Titrmetric Method**

Sample	Cert, %	Iron Found %	Repeatability, ( $R_{11}$ , E 173 <sup>A</sup> )	Reproducibility, ( $R_{21}$ , E 173 <sup>A</sup> )
NBS 169 Ni Base	0.54	0.54	0.0179	0.0186
NBS 162a Cu-Ni	2.19	2.19	0.0317	0.0331
NBS 864 Inconel 600	9.6	9.62	0.0289	0.0688
NBS 161 Ni Base	15.01	15.00	0.1152	0.1260
NBS 348 A286	53.3	53.25	0.1653	0.2952

<sup>A</sup> This test was performed in accordance with the 1980 version of Practice E 173.

## 199. Precision and Bias

199.1 *Precision*—Six laboratories co-operated in testing this

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method and obtained data summarized in Table 16. The precision data demonstrates that the method is applicable between 0.5 to 53 % iron well within the stated concentration range, in the scope.

199.2 *Bias*—No information on the accuracy of this method is known. The accuracy of this method may be judged by the agreement between the certified reference values and the corresponding arithmetic average obtained by interlaboratory testing (see Table 16).

## 200. Keywords

200.1 aluminum; chromium; cobalt; cobalt alloys; combustion analysis; copper; high temperature alloys; induction furnace; infrared absorption; iron; manganese; magnetic alloys; molybdenum; nickel; nickel alloys; phosphorus; silicon; sulfur; tin; total carbon