Designation: E354 – 14

Standard Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys[1]

This standard is issued under the fixed designation E354; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

1. Scope

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

Element	Composition 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	Discontinued
Carbon, Total, by the Combustion Gravimetric Method (0.05 % to 1.10 %)	Discontinued
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	Discontinued
Cobalt by the Ion-Exchange-Potentiometric Titration Method (2 % to 75 %)	53
Cobalt by the Nitroso-R-Salt Spectrophotometric Method (0.10 % to 5.0 %)	61
Copper by Neocuproine Spectrophotometric 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 ReductionTitrimetric Method (1.0 % to 50.0 %)	192
Manganese by the Periodate Spectrophotometric Method (0.05 % to 2.00 %)	9
Molybdenum by the Ion Exchange—8-Hydroxyquinoline Gravimetric Method (1.5 % to 30 %)	184
Molybdenum by the Spectrophotometric Method (0.01 % to 1.50 %)	153
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 % to 84.0 %)	135
Phosphorus by the Molybdenum Blue Spectrophotometric Method (0.002 % to 0.08 %)	19
Silicon by the Gravimetric Method (0.05 % to 5.00 %)	46
Sulfur by the Gravimetric Method	Discontinued
Sulfur by the Combustion-Iodate Titration Method (0.005 % to 0.1 %)	Discontinued
Sulfur by the Chromatographic Gravimetric Method	
Tin by the Solvent Extraction–Atomic Absorption Method (0.002 % to 0.10 %)	143

1.3 Methods for the determination of carbon and sulfur not included in this standard can be found in Test Methods E1019.

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

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

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 6 and in special "Warning" paragraphs throughout these test methods.

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

Current edition approved Sept. 15, 2014. Published November 2014. Originally approved in 1968. Last previous edition approved in 2006 as E354 – 93 (2006). DOI: 10.1520/E0354-14.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

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

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

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

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

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

E351 Test Methods for Chemical Analysis of Cast Iron—All Types

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

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

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

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

2.2 *Other Document:*

ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests[4]

3. Terminology

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

4. Significance and Use

4.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with compositional specifications, particularly those under the jurisdiction of the ASTM Committee 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 E882.

5. Apparatus, Reagents, and Instrumental Practice

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

5.2 *Reagents:*

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

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

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

6. Hazards

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

7. Sampling

7.1 For procedures for sampling the material, reference shall be made to Practice E1806.

8. Interlaboratory Studies and Rounding Calculated Values

8.1 These test methods have been evaluated in accordance with Practice E173 (withdrawn 1997) or ISO 5725. The Reproducibility R2 of Practice E173 corresponds to the Reproducibility Index R of Practice E1601. The Repeatability R1 of Practice E173 corresponds to the Repeatability Index r of Practice E1601

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

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

9.1 This method covers the determination of manganese in compositions from 0.05 % to 2.00 %.

10. Summary of Method

10.1 Manganous ions are oxidized to permanganate ions by treatment with periodate. Tungsten when present at compositions greater than 0.5 % is kept in solution with H_3PO_4.

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

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

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

Solutions of the samples are fumed with $HClO_4$ so that the effect of periodate is limited to the oxidation of manganese. Spectrophotometric measurements are made at approximately 545 nm.

11. Concentration Range

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

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

12. Stability of Color

12.1 The color is stable for at least 24 h.

13. Interferences

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

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

13.3 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.

14. Reagents

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

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

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

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

15. Preparation of Calibration Curve

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

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

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

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

15.4 *Spectrophotometry:*

15.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using the Reference Solution (15.2) in absorption cells with a 1-cm light path and using a light band centered at approximately 545 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions versus the Reference Solution (15.2)

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

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

16. Procedure

16.1 *Test 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

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

16.1.1.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO_3 as needed to hasten dissolution, and then add 3 mL to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of $HClO_4$; evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool,

add 50 mL of water, and digest if necessary to dissolve the salts. Cool and transfer the solution to a 100-mL volumetric flask. Proceed to 16.1.3.

16.1.1.2 For samples whose dissolution is hastened by HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO_3 and a few drops of HF as needed to hasten dissolution, and then add 3 mL to 4 mL of HNO_3. When dissolution is complete, cool, then add 10 mL or $HClO_4$, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to either a 100-mL or 500-mL volumetric flask as indicated in 16.1. Proceed to 16.1.3.

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

16.1.2.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of H_3PO_4, 10 mL of $HClO_4$, 5 mL to 6 mL of H_2SO_4, and 3 mL to 4 mL of HNO_3. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 min to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO_3. Cool, add 50 mL of water, and digest, if necessary, to dissolve the salts. Transfer the solution to either a 100-mL or 500-mL volumetric flask as directed in 16.1. Proceed to 16.1.3.

16.1.2.2 For samples whose dissolution is hastened by HF: Add 8 mL to 10 mL of H_3PO_4, 10 mL of $HClO_4$, 5 mL to 6 mL of H_2SO_4, 3 mL to 4 mL of HNO_3, and a few drops of HF. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 min to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO_3. Cool, add 50 mL of water, digest, if necessary, to dissolve the salts, cool, and transfer the solution to a 100-mL or 500-mL volumetric flask as directed in 16.1. Proceed to 16.1.3.

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

16.1.3 Using a pipet, transfer 20-mL aliquots to two 50-mL borosilicate glass volumetric flasks; treat one as directed in 16.3 and the other as directed in 16.4.1.

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

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

16.4 *Reference Solutions:*

16.4.1 *Background Color Solution*—To one of the sample aliquots in a 50-mL volumetric flask, add 10 mL of HNO_3-H_3PO_4 mixture, and heat the solution at not less than 90 °C for 20 min to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

16.4.2 *Reagent Blank Reference Solution*—Transfer the reagent blank solution (16.2) to the same size volumetric flask as used for the test solutions and transfer the same size aliquots as used for the test solutions to two 50-mL volumetric flasks. Treat one portion as directed in 16.3 and use as reference solution for test samples. Treat the other as directed in 16.4.1 and use as reference solution for Background Color Solutions.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Spectrophotometric Method

Test Specimen	Manganese Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
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

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

17. Calculation

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

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

where:

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

B = apparent manganese, mg, found in 50 mL of the final background color solution, and

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

18. Precision and Bias

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

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

PHOSPHORUS BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD

19. Scope

19.1 This method covers the determination of phosphorus in compositions from 0.002 % to 0.08 %.

20. Summary of Method

20.1 The sample is dissolved in mixed acids and the solution is fumed with $HClO_4$. Ammonium molybdate is added to react with the phosphorus to form the heteropoly phosphomolybdate. This species is then reduced with hydrazine sulfate

to form the molybdenum blue complex. Spectrophotometric measurement is made at 650 nm or 825 nm, depending upon the concentration.

21. Concentration Range

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

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

22. Stability of Color

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

23. Interferences

23.1 None of the elements usually present interfere. The interference of tungsten at compositions greater than 0.5 % is avoided by proceeding directly with a small sample weight rather than an aliquot portion of a larger sample.

24. Apparatus

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

25. Reagents

25.1 *Ammonium Molybdate Solution* (20 g/L)—Cautiously, while stirring and cooling, add 300 mL of H_2SO_4 to 500 mL of water and cool. Add 20 g of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4\ H_2O$), cautiously dilute to 1 L, and mix.

25.2 *Ammonium Molybdate-Hydrazine Sulfate Solution*—Dilute 250 mL of the ammonium molybdate solution to 600 mL, add 100 mL of the hydrazine sulfate solution, dilute to 1 L, and mix. Do not use a solution that has stood for more than 1 h.

25.3 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ($(NH_2)_2{\cdot}H_2SO_4$) in water, dilute to 1 L, and mix. Discard any unused solution after 24 h.

25.4 *Phosphorus Standard Solution A* (1 mL = 1.0 mg P)—Transfer 2.292 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4), previously dried to constant weight at 105 °C, to a 500-mL volumetric flask; dissolve in about 100 mL of water, dilute to volume, and mix.

25.5 *Phosphorus Standard Solution B* (1 mL = 0.01 mg P)—Using a pipet, transfer 10 mL of Solution A (1 mL = 1.0 mg P) to a 1-L volumetric flask, add 50 mL of $HClO_4$ (1 + 5), dilute to volume, and mix.

25.6 *Phosphorus Standard Solution C* (1 mL = 0.10 mg P)—Using a pipet, transfer 50 mL of Solution A (1 mL = 1.0 mg P) to a 500-mL volumetric flask, add 50 mL of $HClO_4$ (1 + 5), dilute to volume, and mix.

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

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

26.1 *Calibration Solutions*—Using pipets, transfer 5 mL, 10 mL, 15 mL, 25 mL, and 50 mL of Phosphorus Standard Solution B (1 mL = 0.01 mg P) to 100-mL volumetric flasks. Add 20 mL of $HClO_4$, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 100-mL borosilicate glass volumetric flask. Proceed in accordance with 26.3.

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

26.3 *Color Development:*

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

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

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

26.4 *Reference Solution*—Water.

26.5 *Spectrophotometry:*

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

26.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (26.4) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting using a light band centered at approximately 825 nm. While maintaining this adjustment, take the spectrophotometric readings of the reagent blank solution and of the calibration solutions.

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

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

27.1 *Calibration Solutions*—Using pipets, transfer 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 30 mL of Phosphorus Standard Solution C (1 mL = 0.10 mg P) to 100-mL volumetric flasks. Add 20 mL of $HClO_4$, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 100-mL borosilicate glass volumetric flask.

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

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

27.4 *Reference Solution*—Water.

27.5 *Spectrophotometry:*

27.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) versus the reference solution (27.4) using absorption cells with a 1-cm light path and a light band centered at approximately 650 nm.

Using the test cell, take the spectrophotometric readings of the calibration solutions versus the reference solution.

27.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (27.4) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting using a light band (no change) centered at approximately 650 nm. While maintaining this adjustment, take the spectrophotometric readings of the reagent blank solution and of the calibration solutions.

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

28. Procedure

28.1 *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:*

28.1.1 *Test Solution:*

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

28.1.1.2 Add 15 mL of a freshly prepared mixture of 1 volume of HNO_3 and 3 volumes of HCl, slowly and in small portions. When the reaction has ceased, add 10 mL of $HClO_4$ and evaporate to fumes. Remove the flask immediately to avoid undue loss of $HClO_4$, cool, and add 20 mL of HBr (1 + 4). Evaporate the solution to copious white fumes and then, without delay, fume strongly enough to cause the white fumes to clear the neck of the flask, and continue at this rate for 1 min.

28.1.1.3 Cool the solution, add 60 mL of $HClO_4$ (1 + 5), and swirl to dissolve the salts. Transfer to a 100-mL volumetric flask, cool, dilute to volume, and mix. Allow insoluble matter to settle or dry filter the solution. Using a pipet, transfer 10-mL portions to two 100-mL borosilicate glass volumetric flasks; treat one in accordance with 28.1.3 and the other in accordance with 28.1.4.2.

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

28.1.3 *Color Development*—Proceed with one of the 10-mL portions obtained in 28.1.1.3, in accordance with 26.3.

28.1.4 *Reference Solutions:*

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

28.1.4.2 *Background Color Reference Solution*—Add 15 mL of Na_2SO_3 solution to the second 10-mL portion obtained in 28.1.1.3. Boil gently for 30 s, add 50 mL of H_2SO_4 (3 + 37), cool, dilute to volume, and mix. Use this as the reference solution for the test solution.

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

28.2 *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:*

28.2.1 *Test Solution:*

28.2.1.1 Transfer 0.100-g samples, weighed to the nearest 0.1 mg, to two 100-mL Erlenmeyer flasks.

28.2.1.2 Add 5 mL of a mixture of 1 volume of HNO_3 and 3 volumes of HCl. When the reaction has ceased, add 2.5 mL of $HClO_4$ and 5 mL of HBr (1 + 4). Evaporate the solutions to copious white fumes; then, without delay, fume strongly enough to cause the white fumes to clear the neck of the flasks, and continue at this rate for 1 min.

28.2.1.3 Cool the solutions, and add 10 mL of water. Filter through a 9-cm fine paper collecting the filtrate in a 100-mL borosilicate glass volumetric flask. Wash the paper and insoluble matter 5 times with 3-mL portions of water. Treat one solution as directed in 28.2.3 and the other as directed in 28.2.4.

28.2.2 *Reagent Blank Solution*—Proceed as directed in 28.2.1.2 and 28.2.1.3.

28.2.3 *Color Development*—Proceed as directed in 26.3.

28.2.4 *Reference Solutions:*

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

28.2.4.2 *Background Color Reference Solution*—Add 15 mL of Na_2SO_3 solution to the second 10-mL portion obtained in 28.2.1.3. Boil gently for 30 s, add 50 mL of H_2SO_4 (3 + 37), cool, dilute to volume, and mix. Use this as the reference solution for the test solution.

28.2.5 *Spectrophotometry*—Proceed as directed in 28.1.5.

29. Calculation

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

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

where:

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

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

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

TABLE 2 Statistical Information—Phosphorus

	Test Specimen	Phosphorus Found,%	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	Cobalt-base alloy 41Co-20-Ni-20Cr-4Mo-4W-3Nb (NIST 168, 0.008 P)	0.008	0.005	0.006

30. Precision

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

(This method, which consisted of Sections 37 through 45, was discontinued in 2014.)

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

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

47. Summary of Test Method

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

48. Interferences

48.1 The elements normally present do not interfere. When boron is present in amounts greater than 0.1 %, the sample solution requires special treatment with methyl alcohol.

49. Reagents

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

49.2 *Perchloric Acid:*

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

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

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

49.2.3 Add paper pulp and filter immediately, using low-ash 11-cm medium-porosity filter papers. Transfer the precipitates to the papers, and scrub the beakers thoroughly with a rubber-tipped rod. Wash the papers and precipitates alternately with 3-mL to 5-mL portions of hot HCl (1 + 19) and hot water, for a total of 6 times. Finally wash the papers twice with H_2SO_4 (1 + 49). Transfer the papers to platinum crucibles.

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

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

49.2.6 Calculate the percent of silicon as follows:

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

where:

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

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

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

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

50. Procedure

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

Silicon, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dehydrating Acid, mL H_2SO_4 (1 + 4)	Dehydrating Acid, mL $HClO_4$
0.05 to 0.10	5.0	5	150	75
0.10 to 1.0	4.0	4	100	60
1.0 to 2.0	3.0	3	100	50
2.0 to 5.0	2.0	2	100	40

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

50.2 *Sulfuric Acid Dehydration*—if tungsten is greater than 0.5 %.

50.2.1 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, that are sufficient to dissolve the sample; and then add the H_2SO_4 (1 + 4) as specified in 50.1, and cover. Heat until dissolution is complete. Remove and rinse the cover glass; substitute a ribbed cover glass.

50.2.2 Evaporate until salts begin to separate; at this point evaporate the solution rapidly to the first appearance of fumes and fume strongly for 2 min to 3 min. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat, if necessary, but do not boil. Proceed immediately in accordance with 50.4.

50.3 *Perchloric Acid Dehydration*—if tungsten is less than 0.5 % or use 50.2.

50.3.1 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample, and cover. Heat until dissolution is complete. Add HNO_3 to provide a total of 35 mL to 40 mL, followed by $HClO_4$ as specified in the table in 50.1. Remove and rinse the cover glass; substitute a ribbed cover glass.

50.3.2 Evaporate the solution to fumes and heat for 15 min to 20 min at such a rate that the $HClO_4$ refluxes on the sides of the container. Cool sufficiently and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat to boiling. If the sample solution contains more than 100 mg of chromium, add, while stirring, 1 mL of tartaric acid solution for each 25 mg of chromium.

50.4 Add paper pulp and filter immediately, on a low-ash 11-cm medium-porosity filter paper. Collect the filtrate in a 600-mL beaker. Transfer the precipitate to the paper, and scrub the container thoroughly with a rubber-tipped rod. Wash the paper and precipitate alternately with 3-mL to 5-mL portions of hot HCl (1 + 19) and hot water until iron salts are removed but for not more than a total of ten washings. If the perchloric acid dehydration method was followed, wash the paper twice more with H_2SO_4 (1 + 49), but do not collect these washings in the filtrate; discard the washings. Transfer the paper to a platinum crucible and reserve.

50.5 Add 15 mL of HNO_3 to the filtrate, stir, and evaporate in accordance with either 50.2 or 50.3, depending upon the dehydrating acid used. Filter immediately, using a low-ash, 9-cm-100-porosity filter paper, and wash in accordance with 50.4.

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

50.7 Add enough H_2SO_4 (1 + 1) to moisten the impure SiO_2, and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Ignite at 1100 °C to 1150 °C for 15 min, cool in a desiccator, and weigh. If the sample contains more than 0.5 % tungsten, ignite at 750 °C instead of 1100 °C to 1150 °C after volatilization of SiO_2.

TABLE 3 Statistical Information—Silicon

	Test Specimen	Silicon Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
	$HClO_4$ Dehydration			
1.	Ni-base alloy 75Ni-12Cr-6A1-4Mo-2Cb-0.7Ti	0.029	0.006	0.026
	H_2SO_4 Dehydration			
1.	Ni-base alloy 75Ni-12Cr-6A1-4Mo-2Cb-0.7Ti	0.030	0.007	0.030
2.	Co-base alloy 66Co-28Cr-4W-1.5Ni	1.01	0.03	0.06

51. Calculation

51.1 Calculate the percent of silicon as follows:

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

where:

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

52. Precision

52.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 3. A sample with silicon composition 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 compositions from 2 % to 75 %.

54. Summary of Test Method

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

55. Interferences

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

56. Apparatus

56.1 *Ion-Exchange Column,* approximately 25 mm in diameter and 300 mm in length, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. A Jones Reductor (Fig. 1), may be adapted to this method. A reservoir for the eluants may be added at the top of the column.

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

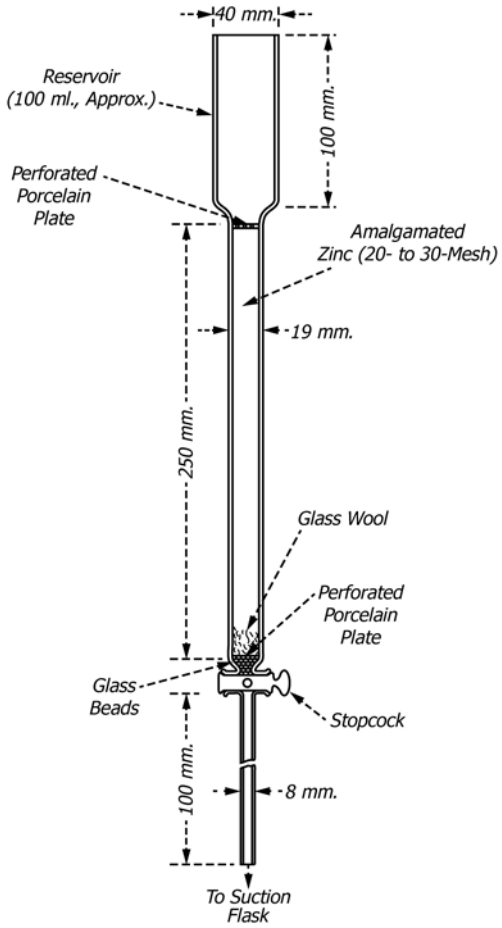

FIG. 1 Jones Reductor

57. Reagents

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

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

57.2.1 *Preparation*—Dry a weighing bottle in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer 3.945 g of cobalt sulfate ($CoSO_4$)[5] that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in desiccator, stopper the bottle, and weigh. The difference in weight is the amount of $CoSO_4$ taken. Transfer the weighed $CoSO_4$ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 20 mL of HNO_3, and heat to dissolve the salts. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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

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

57.3 *Ion-Exchange Resin*[6]:

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

57.3.2 Prepare the column as follows: Place a 10-mm to 20-mm layer of glass wool or polyvinyl chloride plastic fiber in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 140 mm. Place a 20-mm layer of glass wool or polyvinyl chloride plastic fiber at the top of the resin bed to protect it from being carried into suspension when the solutions are added. While passing a minimum of 35 mL of HCl (7 + 5) through the column, with the hydrostatic head 100 mm above the top of the resin bed, adjust the flow rate to not more than 3.0 mL per min. Drain to 10 mm to 20 mm above the top of the resin bed and then close the lower stopcock.

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

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

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

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

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

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

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

where:

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

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

58. Procedure

58.1 Proceed as directed in 58.2 through 58.7, using 0.50 g samples for cobalt concentrations not greater than 25 %; at higher concentrations use samples that represent between 100 mg and 125 mg of cobalt and weighed to the nearest 0.1 mg.

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

NOTE 8—Some alloys are decomposed more readily by a mixture of 5 mL of bromine, 15 mL of HCl, and 1 drop to 2 drops of HF.

58.3 Cool to room temperature and transfer the solution to the ion-exchange column. Place a beaker under the column and open the lower stopcock. When the solution reaches a level 10 mm to 20 mm above the resin bed, rinse the original beaker with 5 mL to 6 mL of HCl (7 + 5) and transfer the rinsings to the column. Repeat this at 2-min intervals until the beaker has been rinsed four times. Wash the upper part of the column with HCl (7 + 5) 2 times or 3 times and allow the level to drop to 10 mm to 20 mm above the resin bed each time. Maintain the flow rate at not more than 3.0 mL/min and add HCL (7 + 5) to the column until a total of 175 mL to 185 mL of solution (sample solution and washings) containing mainly chromium, manganese, and nickel is collected (Note 9). When the solution in the column reaches a level 10 mm to 20 mm above the resin bed, discard the eluate and then use a 400-mL beaker for the collection of the cobalt eluate.

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

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

TABLE 4 Statistical Information—Cobalt

	Test Specimen	Cobalt Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	No. 1, E352	1.86	0.05	0.12
2.	No. 2, E352	4.82	0.08	0.11
3.	No. 3, E352	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 (NIST 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 (NIST, 167, 42.90 Co)	42.91	0.18	0.15
8.	Co-base alloy 28Cr-6Mo-3Ni	60.10	0.19	0.31

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

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

58.7 While stirring, add the sample solution to the solution from 58.6, rinse the beaker with water, and add the rinsings to the solution (Note 10). Using a 50-mL buret, titrate the excess $K_3Fe(CN)_6$ with the cobalt solution (1 mL = 1.5 mg Co), at a fairly rapid rate until the end point is approached, and then add the titrant in 1-drop increments through the end point. After the addition of each increment, record the buret reading and voltage when equilibrium is reached. Estimate the buret reading at the end point to the nearest 0.01 mL by interpolation.

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

59. Calculation

59.1 Calculate the percentage of cobalt as follows:

$$\text{Cobalt},\% = [(A\,B - C\,D) / E] \times 100 \quad (7)$$

where:

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

60. Precision

60.1 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 compositions 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 SPECTROPHOTOMETRIC METHOD

61. Scope

61.1 This method covers the determination of cobalt in compositions from 0.10 % to 5.0 %.

62. Summary of Test Method

62.1 The sample solution is treated with zinc oxide to remove iron, chromium, and vanadium. Nitroso-R-salt solution is added to a portion of the filtrate which has been buffered with sodium acetate to produce an orange-colored complex with cobalt. The addition of HNO_3 stabilizes the cobalt complex and also destroys certain interfering complexes. Spectrophotometric measurement is made at approximately 520 nm.

63. Concentration Range

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

NOTE 11—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

64. Stability of Color

64.1 The color is stable for at least 3 h.

65. Interferences

65.1 Nickel, manganese, and copper form complexes with nitroso-R-salt that deplete the reagent and inhibit the formation of the colored cobalt complex. A sufficient amount of nitroso-R-salt is used to provide full color development with 0.15 mg of cobalt in the presence of 41 mg of nickel, 1.5 mg of manganese, and 5 mg of copper, or 48 mg of nickel only. Colored complexes of nickel, manganese, and copper are destroyed by treating the hot solution with HNO_3.

66. Reagents

66.1 *Cobalt, Standard Solution* (1 mL = 0.06 mg Co)—Dry a weighing bottle and stopper in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer approximately 0.789 g of cobalt sulfate ($CoSO_4$)[7] that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in a desiccator, stopper the bottle, and weigh. The difference in weight is the exact amount of $CoSO_4$ taken. Transfer the weighed $CoSO_4$ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 10 mL of HCl, and heat to dissolve the salts. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix. By means of a pipet, transfer a 50-mL aliquot of this solution to a 500-mL volumetric flask, dilute to volume, and mix. The exact concentration (in milligrams of cobalt per millilitre) of the final solution is the exact weight of $CoSO_4$ taken multiplied by 0.076046.

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

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

66.3 *Sodium Acetate Solution* (500 g/L)—Dissolve 500 g of sodium acetate trihydrate ($CH_3COONa{\cdot}3H_2O$) in about 600 mL of water, filter, and dilute to 1 L.

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

67. Preparation of Calibration Curve

67.1 *Calibration Solutions*—Using pipets, transfer 2 mL, 5 mL, 10 mL, 15 mL, 20 mL, and 25 mL of cobalt standard solution (1 mL = 0.06 mg Co) to six 100-mL volumetric flasks, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 50-mL borosilicate glass volumetric flask. Proceed in acordance with 67.3.

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

67.3 *Color Development*—Add 5 mL of sodium acetate solution, and mix. Using a pipet, add 10 mL of nitroso-R-salt solution, and mix. Place the flask in a boiling water bath. After 6 min to 10 min, add 5 mL of HNO_3 (1 + 2), and mix. Continue the heating for 2 min to 4 min. Cool the solution to room temperature, dilute to volume, and mix.

67.4 *Spectrophotometry:*

67.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction with water using absorption cells with a 1-cm light path and using a light band centered at approximately 520 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions versus the reference solution (67.2).

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

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

68. Procedure

68.1 *Test Solution:*

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

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

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

68.1.2 Add 5 mL of a mixture of 1 volume of HNO_3 and 3 volumes of HCl. Heat gently until the sample is dissolved. Boil

TABLE 5 Statistical Information—Cobalt

	Test Specimen	Cobalt Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	Ni-base alloy, 36Ni (NIST 126b, 0.032 Co)	0.032	0.005	0.006
2.	No. 2, E353	0.094	0.006	0.013
3.	No. 3, E353	0.173	0.011	0.026
4.	Ni-base alloy, 17Cr-15Fe (NIST 161, 0.47 Co)	0.468	0.020	0.028
5.	No. 2, E352	1.87	0.09	0.13
6.	No. 3, E352	4.94	0.08	0.17

the solution until brown fumes have been expelled. Add 50 mL to 55 mL of water and cool.

68.1.3 Add ZnO suspension in portions of about 5 mL until the iron is precipitated and a slight excess of ZnO is present. Shake thoroughly after each addition of the precipitant and avoid a large excess (Note 12). Dilute to volume, and mix. Allow the precipitate to settle; filter a portion of the solution through a dry, fine-porosity filter paper and collect it in a dry, 150-mL beaker after having discarded the first 10 mL to 20 mL. Using a pipet, transfer 10 mL of the filtrate to a 50-mL borosilicate glass volumetric flask. Proceed as in accordance with 68.3.

NOTE 12—When sufficient ZnO has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is indicated by a slightly white and milky supernatant liquid.

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

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

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

69. Calculation

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

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

where:

A = cobalt found in 50 mL of the final test solution, mg, and
B = sample represented in 50 mL of the final test solution, g.

70. Precision[8]

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 composition 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.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E03-1028. Contact ASTM Customer Service at service@astm.org.

COPPER BY THE SULFIDE PRECIPITATION-ELECTRODEPOSITION GRAVIMETRIC METHOD

71. Scope

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

72. Summary of Test 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 NH_4OH (Note 13). Chloride ions are removed from the filtrate, and copper, as the metal, is deposited on a platinum cathode.

NOTE 13—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 15).

74. Apparatus

74.1 *Electrodes*—Platinum electrodes of the stationary type are recommended as described in 74.1.1 and 74.1.2, but strict adherence to the exact size and shape of the electrodes is not mandatory. When agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes, generally available, may be employed. The surface of the platinum electrodes should be smooth, clean, and bright to promote uniform deposition and good adherence. Sandblasting is not recommended.

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

74.1.2 *Anodes*—Platinum anodes may be of the spiral type when anodic deposits are not being determined, or if the deposits are small (as in the electrolytic determination of lead when it is present in amounts not over 0.2 %). When used in analyses where both cathodic and anodic plates are to be determined, the anodes should be of wire gauze. Spiral anodes should be made from 1.00-mm or larger platinum wire formed into a spiral of seven turns having a height of approximately 50 mm and a diameter of 12 mm, the over-all height being

approximately 130 mm. A spiral anode of this description will have a surface area of 9 cm^2. Platinum gauze anodes should be made of the same material and of the same general design as platinum gauze cathodes. The anode cylinder should be approximately 12 mm in diameter and 50 mm in height and the over-all height of the anode should be approximately 130 mm. A gauze anode of these dimensions will have a surface area of 54 cm2. Both areas are exclusive of the stem.

75. Reagents

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

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

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

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; treat cobalt base samples as directed in 76.2.1.

76.2.1 Add 30 mL of 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 min to 3 min. If the solution is clear, proceed as directed in 76.4 and 76.8 through 76.22. If the solution contains insoluble matter, proceed as directed in 76.4 through 76.22.

76.3 Add 115 mL of HCl (1 + 2) plus an additional 9 mL of HCl (1 + 2) and 1 mL of HNO_3 for each gram of sample. Heat until dissolution is complete, and then boil the solution for 2 min to 3 min. If the solution is clear, proceed as directed in 76.4 and 76.9 through 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 min to 20 min, and then filter through medium filter paper into a 1-L Erlenmeyer flask. Suction may be used if necessary. Wash the filter 4 times or 5 times with water. Reserve the filtrate. Proceed as directed in 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 HNO_3 and 10 mL of $HClO_4$, heat moderately to oxidize organic matter, and finally heat to mild fumes of $HClO_4$. Cool the solution, add 1 mL to 2 mL of HF, and repeat the fuming.

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

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_4OH and 20 g of tartaric acid. When the tartaric acid has dissolved, again add a slight excess of NH_4OH and digest near the boiling point until dissolution is complete, or nearly so.

76.8 Add 5 mL of H_2SO_4 and heat at 85 °C to 95 °C for 30 min. If insoluble matter persists, repeat the steps as directed in 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_2S; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 h to 15 h.

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_2SO_4, and heat to char the paper. Add 20 mL of HNO_3, and evaporate to fumes to destroy organic matter. Add HNO_3 in 1-mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

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

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

NH_4OH (1 + 99) and then filter the hot solution into the 800-mL beaker reserved from the first filtration: wash alternately five times each with hot NH_4OH (1 + 99) and water.

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

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^2. Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 to 3 A/dm^2 (Note 14). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 14—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm^2, and 2 h to 3 h should be allowed for complete deposition.

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 min 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 °C to 110 °C for 2 min to 3 min.

NOTE 15—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of HNO_3 and 5 mL of H_2SO_4 in 175 mL of water contained in a 300-mL tall-form beaker. Reverse the polarity of the electrodes, and electrolyze with a current density of 3 A/dm^2 until the copper has been removed from the original electrode. Reverse the polarity and redeposit the copper on the original electrode as directed in 76.17 and 76.18. Proceed as directed in 76.19 and 76.20.

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

NOTE 16—To prepare the electrode for reuse, immerse it in HNO_3 (1 + 1) to dissolve the deposit of copper, rinse thoroughly with water and then with acetone or ethanol. Dry in an oven, cool to room temperature, and weigh.

77. Calculation

77.1 Calculate the percentage of copper as follows:

$$\text{Copper, } \% = [((A - B) - (C - D))/E] \times 100 \quad (9)$$

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.

TABLE 6 Statistical Information—Copper

	Test Specimen	Copper Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	Low-alloy steel (NIST 152a, 0.023 Cu)	0.020	0.005	0.006
2.	No. 2, E352	0.079	0.003	0.006
3.	No. 3, E353	0.364	0.009	0.010
4.	No. 3, E351	0.678	0.037	0.041
5.	No. 4, E351	5.49	0.10	0.10

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

(This method, which consisted of Sections 79 through 89 of this standard, was discontinued in 2014.)

COPPER BY THE NEOCUPROINE SPECTROPHOTOMETRIC METHOD

90. Scope

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

91. Summary of Test Method

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

92. Concentration Range

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

NOTE 17—This test method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

93. Stability of Color

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

94. Interferences

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

95. Reagents

95.1 *Chloroform* ($CHCl_3$).

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

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

95.4 *2,9-Dimethyl-1,10-Phenanthroline (Neocuproine) Solution* (1 g/L)—Dissolve 0.1 g of neocuproine in 100 mL of absolute ethanol.

NOTE 18—In addition to absolute ethanol, 95 % ethanol or denatured ethanol have been found suitable for preparing this solution.

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

96. Preparation of Calibration Curve

96.1 *Calibration Solutions*—Using pipets, transfer 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 30 mL of copper solution (1 mL = 0.01 mg Cu) to 150-mL beakers, and dilute to 50 mL. Proceed in accordance with 96.3.

96.2 *Reagent Blank Solution*—Transfer 50 mL of water to a 150-mL beaker. Proceed in accordance with 96.3.

96.3 *Color Development:*

96.3.1 Add 5 mL of $NH_2OH·HCl$ solution and 10 mL of citric acid solution. Stir for 30 s. Using a pH meter (Note 19), adjust the pH to 5.0 ± 1.0 with NH_4OH (1 + 1). Add 10 mL of neocuproine solution.

NOTE 19—Test paper may be used, except for highly colored solutions, by affixing it to the inner wall of the beaker, and rinsing it with water before removing it.

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

96.4 *Reference Solution*—$CHCl_3$.

96.5 *Spectrophotometry:*

96.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at approximately 455 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

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

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

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 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample (Note 20). Heat as required to hasten dissolution. Add HNO_3 to provide an excess of 3 mL to 4 mL, a sufficient amount of HF to volatilize the silica, and 15 mL of $HClO_4$.

NOTE 20—Some alloys are more readily decomposed by a mixture of 5 mL of bromine, 15 mL of HCl, and 1 drop to 2 drops of HF.

97.1.3 Heat to fumes, and continue fuming until chromium, if present, is oxidized and the white $HClO_4$ vapors are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming the solution until the volume has been reduced to about 10 mL. Cool, add 7 mL of water, and digest if necessary to dissolve the salts. Cool to room temperature, add 1 mL of HCl, and transfer the solution (Note 21) to a volumetric flask that provides for the dilution in accordance with 97.1.1. Dilute to volume and mix.

NOTE 21—If silver is present in the alloy it must be removed by filtration at this point.

97.1.4 Allow insoluble matter to settle, or dry-filter through a coarse paper and discard the first 15 mL to 20 mL of the filtrate before taking the aliquot. Using a pipet, transfer a portion as specified in 97.1.1 to a 150-mL beaker, and dilute to 50 mL. Proceed as directed in 97.4.

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

TABLE 7 Statistical Information—Copper

	Test Specimen	Copper Found, %	Repeatability, (R_1, E173)	Reproducibility, (R_2, E173)
1.	Nickel-base alloy, 57Ni-14Cr (NIST 349, 0.006 Cu)	0.006	0.001	0.004
2.	Nickel-base alloy, 77Ni-20Cr (NIST 169, 0.015 Cu)	0.014	0.002	0.006
3.	Cobalt-base alloy 41Co-20Ni (NIST 168, 0.035 Cu)	0.033	0.005	0.004
4.	No. 5, E352	0.078	0.005	0.010
5.	No. 6, E352	0.118	0.007	0.016
6.	No. 6, E353	0.176	0.019	0.021
7.	No. 7, E353	0.200	0.012	0.018
8.	No. 8, E353	0.221	0.013	0.022
9.	No. 9, E353	0.361	0.015	0.036
10.	No. 5, E351	1.51	0.04	0.05
11.	No. 6, E351	5.53	0.19	0.18

97.3 *Reference Solution*—$CHCl_3$.

97.4 *Color Development*—Proceed in accordance with 96.3.

97.5 *Spectrophotometry*—Take the spectrophotometric reading of the test solution in accordance with 96.5.

98. Calculation

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

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

where:

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

99. Precision

99.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 7. 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 compositions from 0.20 % to 7.00 %.

101. Summary of Test Method

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

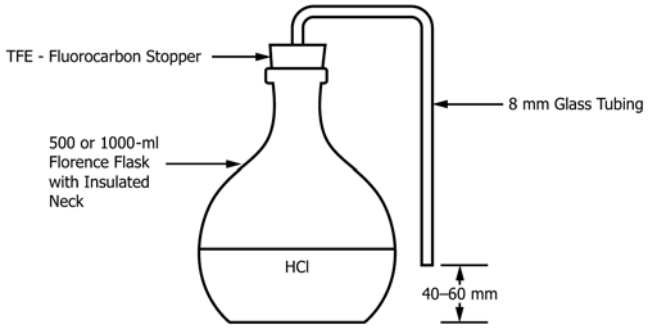

FIG. 2 HCl Gas Generator

102. Interferences

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

103. Apparatus

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

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

103.3 *HCl Gas Generator* (Fig. 2)—A simple HCl gas generator constructed from a stoppered wash bottle and glass tubing.

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

103.5 *pH Meter.*

104. Reagents

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

104.2 *Chloroform* ($CHCl_3$).

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

104.4 *8-Quinolinol Solution* (25 g/L)—Dissolve 25 g of 8-quinolinol in 50 mL of acetic acid, dilute to 300 mL with warm water, filter through a medium paper, and dilute to 1 L. Store in an amber bottle away from direct sunlight. Do not use a solution that has stood more than 1 month.

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

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

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

105. Procedure

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

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

105.3 Add 30 mL of HCl and 10 mL of HNO_3 and digest at a low temperature until dissolution is complete. Add 30 mL of $HClO_4$, heat to fumes, and continue fuming until chromium, if present, is oxidized. If chromium is present, position the gas generator containing boiling HCl (use a fresh portion of HCl for each sample), so that the tube extends into the beaker and the HCl gas is delivered 20 mm to 30 mm above the surface of the fuming $HClO_4$ Continue boiling the HCl and fuming the sample solution until there is no evidence of yellow chromyl chloride in the fumes. Remove the generator and continue fuming the solution until the volume is reduced to 10 mL. Remove from the hot plate and cool. Add 25 mL of water to dissolve the salts. If iron hydrolyzes, indicating that the sample was fumed too long, add 1 mL to 2 mL of HCl and 5 mL of $HClO_4$ and again take to fumes. Dilute to 75 mL with water and boil to remove chlorine.

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

105.5 Transfer the paper to a platinum crucible, dry it, and then heat at about 600 °C until the carbon has been removed. Finally ignite at 1100 °C, cool, and add a few drops of H_2SO_4 (1 + 1) and 4 mL to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until the H_2SO_4 has been removed. Cool, add 2 g to 3 g of sodium hydrogen sulfate, fused, and heat until a clear melt is obtained. Cool the crucible, transfer it to a 250-mL beaker, add 50 mL of water, and then digest until the melt is dissolved. Remove and rinse the crucible with water.

105.6 If the solution is clear, add it to the filtrate reserved in 105.4. If the solution is turbid, filter through an 11-cm fine paper containing paper pulp into the beaker containing the reserved filtrate. Wash the paper 3 times or 4 times with hot H_2SO_4 (3 + 97). Discard the paper and residue.

105.7 Evaporate to approximately 100 mL, and cool. Transfer the solution to a mercury cathode cell. Dilute to 150 mL to 200 mL and electrolyze at 15 A (Note 22) until the iron has been removed (Note 23). Without interrupting the current, transfer the solution from the cell to a 400-mL beaker. Thoroughly rinse the cell and electrodes several times with water and add the rinsings to the solution.

NOTE 22—Contact between the mercury pool and the platinum cathode may be broken intermittently due to stirring the mercury too rapidly. Since this will cause arcing which will result in the dissolution of some mercury in the electrolyte, it should be avoided by adding more mercury to the cell, using less current, or by proper adjustment of the cathode lead wire so that contact will be ensured.

NOTE 23—The completeness of the removal of iron, which usually requires 1 h to 3 h, can be determined by the following test: Transfer 1 drop of the electrolyte to a watch glass or spot test plate. Add 1 drop of H_2SO_4 (1 + 1), 1 drop of saturated potassium permanganate ($KMnO_4$) solution, and 1 drop of sodium thiocyanate (NaSCN) solution (500 g/L). When only a faint pink color is observed, the electrolysis may be considered complete.

105.8 Filter the solution through a 12.5-cm medium paper containing paper pulp (Note 24) into a 600-mL beaker, and wash 3 times or 4 times with hot water. To the filtrate add 10 mL of H_2SO_4 (1 + 1) and 10 mL of $(NH_4)_2S_2O_8$ solution. Heat to boiling and evaporate to about 75 mL. Cool in an ice bath to below 10 °C.

NOTE 24—This filtration removes any mercurous chloride that may have formed and any metallic mercury that may have been transferred from the cell.

105.9 Transfer the solution to a 250-mL conical separatory funnel, and without delay add 15 mL of cupferron solution. Reserve the beaker. Shake for 30 s and allow the precipitate to settle. Add 20 mL of $CHCl_3$ and shake for 1 min. Allow the layers to separate. Draw off and discard the $CHCl_3$ layer. Repeat the extraction with 20-mL portions of $CHCl_3$ until the extract is colorless. Transfer the aqueous solution to the reserved 600-mL beaker and evaporate to 35 mL to 40 mL. Add 25 mL of HNO_3, cover with a ribbed cover glass, evaporate to fumes of H_2SO_4, and cool. Dilute to 50 mL, heat to boiling, and cool.

105.10 Transfer the solution to a platinum, quartz or high-silica glass, or poly(tetrafluoroethylene) beaker. Police thoroughly (Note 25), rinse the beaker, and add the rinsings to the main solution. Neutralize to litmus with sodium hydroxide (NaOH) solution (Note 26), and add a 10-mL excess. Add 1 mL of H_2O_2, digest near the boiling point for 5 min to 7 min, and finally boil for 1 min to 2 min to coagulate the manganese precipitate. Cool, and filter through a 12.5-cm medium paper containing paper pulp previously washed 3 times with hot dilute NaOH solution (20 g/L), into a 600-mL beaker. Wash the paper and precipitate 4 times or 5 times with hot water. Immediately add HCl (1 + 1) to the filtrate until acidic to litmus paper, and then add 3 mL to 4 mL in excess.

NOTE 25—This step is necessary whether or not a precipitate is visible.

NOTE 26—Approximately 70 mL will be required.

105.11 If the aluminum composition is less than 1.50 %, proceed as directed in 105.12 through 105.14.

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

105.13 Add 10 mL of H_2O_2 (Note 27), heat to 55 °C, and while stirring add 15 mL of 8-quinolinol solution. Add 5 mL of NH_4OH, and stir continuously for 1 min and then for 5 s to 10 s once a minute for 9 more min while maintaining the temperature at 50 °C to 55 °C.

TABLE 8 Statistical Information—Aluminum

	Test Specimen	Aluminum Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	No. 1, E353	0.232	0.036	0.041
2.	No. 2, E353	1.16	0.06	0.10
3.	Nickel-base alloy 57Ni-14Cr (NIST 349, 1.23 Al)	1.21	0.02	0.08
4.	No. 4, E350	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

NOTE 27—Precipitate aluminum in only one sample at a time. A motor-driven stirrer operating continuously for 10 min may be used.

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

105.15 If the aluminum composition is greater than 1.50 %, transfer the solution to a 250-mL volumetric flask, dilute to volume, and mix. Select the proper aliquot in accordance with the following:

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

Using a pipet, transfer it to a 600-mL beaker. Proceed as directed in 105.12 through 105.14.

106. Calculation

106.1 Calculate the percentage of total aluminum as follows:

$$\text{Total aluminum, \%} = [((A - B) \times 0.0587)/C] \times 100 \quad (11)$$

where:

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

107. Precision

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 8. Although samples covered by this method with aluminum compositions 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 8 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 compositions from 0.1 % to 84.0 %.

136. Summary of Test 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 HCl to eliminate the need for the first precipitation with dimethylglyoxime. This separation must be used when cobalt is present in compositions greater than 0.5 % and may be used for all other samples. Nickel 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 in length, tapered at one end, and

provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. The Jones Reductor, Figure 1 may be adapted 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.*

139. Reagents

139.1 *Ammonium Citrate Solution* (200 g/L)—Dissolve 200 g of diammonium hydrogen citrate [$(NH_4)2HC_6H_5O_7$] in 600 mL of water. Filter and dilute to 1 L.

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-nominal to 400-nominal mesh size.[9] To remove those beads greater than 180 µm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a No. 80 (180-µm) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 min to 6 min, decant 150 mL to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

139.2.2 Prepare the column as follows: Place a 10-mm to 20-mm layer of glass wool or polyvinyl chloride plastic fiber in the bottom of the column and add a sufficient amount of the prepared resin to fill the column to a height of approximately 140 mm. Place a 20-mm layer of glass wool or polyvinyl chloride plastic fiber at the top of the resin bed to protect it from being carried into suspension when the solutions are added. While passing a minimum of 100 mL of HCl (3 + 1) through the column with the hydrostatic head 100 mm above the top of the resin bed, adjust the flow rate to not more than 3.0 mL/min. Drain 10 mm to 20 mm above the top of the resin bed and then close the lower stopcock.

139.3 *Dimethylglyoxime Solution in Ethanol (10 g/L)*—Dissolve 10 g of dimethylglyoxime in ethanol, methanol, denatured ethanol and dilute to 1 L with ethanol. Filter before using. This solution keeps almost indefinitely.

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_3. Heat to dissolve the sample and boil to expel oxides of nitrogen. Cool the solution and add 30 mL of $HClO_4$. Heat to strong fumes of $HClO_4$ and continue fuming for 5 min. Cool and dilute to 100 mL with water.

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_4OH. 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_4OH. Remove the electrode and rinse with water. Heat at 50 °C to 70 °C for 30 min. Let stand for at least 4 h at 20 °C to 25 °C.

140.1.7 Filter using a 12.5-cm coarse paper. Wash five times 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_3 and 15 mL of $HClO_4$. 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

[9] Dowex 1, manufactured by the Dow Chemical Co., Midland, MI, has been found satisfactory for this purpose.

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

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 mm to 10 mm from the top of the resin bed. Add HCl (1 + 19) in 50-mL increments until iron has been eluted and the eluate is visibly free of color (approximately 300-mL). Drain the solution to 5 mm to 10 mm from the top of the resin bed and close the lower stopcock. If the column is not to be used immediately, cover and store. If another sample solution is to be put through the column, proceed as directed in 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_4OH. 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_4OH. Remove and rinse the electrodes with water. Heat at 50 °C to 70 °C for 30 min and allow to stand for at least 4 h at 20 °C to 25 °C.

140.6 With the aid of suction, filter using a weighed fritted glass crucible. Heat the crucible at 150 °C and cool in a desiccator before weighing. Wash the beaker and precipitate 6 times with cold water.

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

TABLE 9 Statistical Information—Nickel

	Test Specimen	Nickel Found %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	No. 1, E352	0.135	0.012	0.015
2.	No. 2, E352	1.81	0.09	0.08
3.	Nickel-chrome steel 16 Cr-4 Ni-3 Cu (NIST 345, 4.24 Ni)	4.22	0.06	0.05
4.	Cobalt alloy 41 Co-20 Ni-20 Cr-4 Mo-4W (NIST 168, 20.25 Ni)	20.26	0.23	0.17
5.	Nickel alloy 77 Ni-20 Cr (NIST 169, 77.26 Ni)	77.13	0.56	0.55

141. Calculation

141.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} \left[\left((A - B) \times 0.2032\right)/C\right] \times 100 \quad (12)$$

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

142.1 Ten laboratories cooperated in the testing of this method and obtained the data summarized in Table 9. 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 9 should apply.

TIN BY THE SOLVENT EXTRACTION—ATOMIC ABSORPTION METHOD

143. Scope

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

144. Summary of Test Method

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

145. Concentration Range

145.1 The recommended concentration range is from 4 µg 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 Spectrometer,* capable of resolving the 286.3 nm line, equipped with a tin hollow-cathode lamp or tin electrodeless discharge lamp whose radiant energy is modulated, with a detector system tuned to the same frequency and a premix nitrous oxide-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (40 µg/mL) produces an absorbance of 0.15 or higher, and a calibration curve whose deviation from linearity is within the limits specified in 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 mL, 1 mL, 2 mL, 4 mL, 6 mL, and 8 mL of solution B (1 mL = 50 µg Sn) to 100-mL volumetric flask. 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.

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

149.3 *Spectrometry:*

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 286.3 nm.

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

149.3.3 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 149.3.2.

149.3.4 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. Ensure that the capillary end does not enter the aqueous (bottom) layer at any time. Due to the small amount of extract available for conducting this test, the number of readings and the time between readings must be kept to a minimum.

149.3.5 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 – 149.3.5.

149.3.6 Proceed immediately as directed in 150.3.

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

$$\text{Deviation from linearity} = (A - B)/C \quad (13)$$

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 28) 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 polytetrafluoroethylene beaker.

NOTE 28—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_2O_2, and 5 drops of HF. Cover the beaker with a polytetrafluoro-ethylene 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_2O_2. Repeat this step until dissolution is complete. If silicon is above 0.5 %, use 10 drops 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 29—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 *Spectrometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution and record the absorbance values. Ensure that the capillary end does not enter the aqueous (bottom) layer at any time. Take three readings on each solution. Due to the small amount of extract available for conducting this test, the number of readings and the time between readings must be kept to a minimum. Measure the absorbance of the calibration solution with the highest concentration of tin to check for drift as in 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:

$$\text{Tin, \%} = [(D - E)/(F \times 1000)] \quad (14)$$

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.

TABLE 10 Statistical Information—Tin

	Test Specimen	Tin Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
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, E350	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, E350	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, E350	0.031	0.003	0.004
8.	No. 6, E350	0.097	0.011	0.011

152. Precision and Bias[10]

152.1 *Precision*—Eleven laboratories cooperated in testing this method and obtained the precision listed for No. 1, 2, 4, and 6 in Table 10. This method differs only slightly from the method for tin in Test Methods E350, 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 10, corresponds closely to that obtained for samples of similar tin content in Test Methods E350, 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 SPECTROPHOTOMETRIC METHOD

153. Scope

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

154. Summary of Test 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. Spectrophotometric measurement is made at approximately 475 nm.

155. Concentration Range

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

[10] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E03-1022. Contact ASTM Customer Service at service@astm.org.

NOTE 30—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, spectrophotometric 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 compositions are under the maximum limits shown in 1.1.

158. Reagents

158.1 *Butyl Acetate.*

NOTE 31—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_3PO_4 and 300 mL of HNO_3 to 1400 mL of $HClO_4$.

158.3 *Iron*[11]—Purity: 99.8 % minimum, molybdenum 0.001 % max.

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

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

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

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

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

NOTE 32—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 spectrophotometric 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.

[11] Johnson-Matthey JMC 847 sponge iron has been found suitable for this purpose.

159. Preparation of Calibration Curve for Compositions 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 mL, 5 mL, 10 mL, and 15 mL of molybdenum solution C (1 mL = 0.01 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

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

159.1.3 Transfer to a 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 $SNCl_2$ solution, and 25 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel, containing a dry filter paper, to fill an absorption cell.

NOTE 33—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 *Spectrophotometry:*

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

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

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

160. Preparation of Calibration Curve for Compositions from 0.05 % 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 mL, 5 mL, 10 mL, and 15 mL of molybdenum solution B (1 mL = 0.1 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

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

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 $SnCl_2$ solution, and 50 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 33.)

160.4 *Reference Solution*—Butyl acetate.

160.5 *Spectrophotometry:*

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

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

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

161. Preparation of Calibration Curve for Compositions 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 mL, 10 mL, 15 mL, 20 mL, and 25 mL of molybdenum solution A (1 mL = 0.2 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

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

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 $SnCl_2$ solution, and 100 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 33.)

161.4 *Reference Solution*—Butyl acetate.

161.5 *Spectrophotometry:*

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

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

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

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_3, 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 $HClO_4$ fumes. Continue fuming until chromium, if present, is oxidized and the white $HClO_4$ fumes are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl, allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been volatilized. Continue fuming the solution until the volume has been reduced to about 15 mL. Cool, add 50 mL of water and 70 mL of H_2SO_4 (1 + 1), heat to boiling, and cool in a water bath. 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_2SO_4 (1 + 99), collecting these in the same volumetric flask. 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 $SnCl_2$ solution, and, measured with a pipet, the amount of butyl acetate specified in the aliquot guide. Stopper the separatory funnel and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously 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 33.)

162.4 *Reference Solution*—Butyl acetate.

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

163. Calculation

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

$$\text{Molybdenum, \%} = \frac{A}{B \times 10} \quad (15)$$

where:

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

B = sample, g, represented in 25 mL, 50 mL, or 100 mL, as appropriate, of butyl acetate and the aliquot used (see aliquot guide 162.1.3).

164. Precision and Bias[12]

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 E350, E351, E352, and E353 are minor and will not affect the precision of the results (see Table 11). This fact suggests that the precision for these methods is the same.

TABLE 11 Statistical Information—Molybdenum

	Test Specimen	Molybdenum Found, %	Repeatability R_1, E173	Reproducibility R_2, E173
1.	No. 1, E350	0.012	0.002	0.006
2.	No. 3, E353	0.432	0.010	0.017
3.	No. 4, E353	1.34	0.032	0.092

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 compositions from 0.006 % to 1.00 %.

166. Summary of Test 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 spectrometer. Spectral energy at approximately 357.9 nm from a chromium hollow-cathode lamp is passed through the flame, and the absorbance is measured. The spectrometer is calibrated with solutions of known chromium concentrations.

167. Concentration Range

167.1 The recommended concentration range is 0.001 mg 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 Spectrometer,* capable of resolving the 357.9 nm line, equipped with a chromium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it meets the limits defined in 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 ($K_2Cr_2O_7$) (NIST 136 or equivalent) to an 800-mL borosilicate beaker, add 500 mL of water, and mix. When dissolution is complete, add 5 mL of H_2SO_4 and, while stirring, add 10 mL of H_2O_2 (30 %). Heat at near boiling for 5 min to remove excess H_2O_2. Cool, transfer the solution to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask, dilute to volume, and mix.

[12] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E03-1023. Contact ASTM Customer Service at service@astm.org.

170.2 *Iron,*[13] 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 Compositions 0.005 % to 0.10 %*—To each of seven 250-mL borosilicate beakers, transfer 1.0 g of low chromium iron weighed to the nearest 1 mg. Add to each beaker 20 mL of HCl and 10 mL of HNO_3 and heat gently until dissolution is complete. Evaporate to dryness on a hot plate and cool. Add 10 mL of HCl and warm to dissolve salts. Dilute to about 50 mL and transfer to 100-mL volumetric flasks. Add 10 mL of K_2CO_3 solution to each of 7 flasks. Using pipets, transfer 1 mL, 3 mL, 5 mL, 7 mL, 10 mL, and 15 mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium concentration. Dilute to volume and mix.

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

171.3 *Spectrometry:*

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

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:

$$s = (A - B) \times 0.40 \quad (16)$$

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

171.3.4 Using water as a reference, 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 Compositions from 0.005 % to 0.10 %*—Follow the instrument manufacturer's instructions for generating the calibration curve. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \quad (17)$$

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 Compositions 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 dissolution, mL	Aliquot Required, mL	HCl to be added to Aliquot, mL	Final Dilution, mL
0.005–0.10	1	0.10	100	0	0	100
0.10–1.00	1	0.10	100	10	9	100

Transfer it to a 250-mL borosilicate beaker.

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

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_2CO_3, and carefully fuse over a free flame until a clear melt is obtained (see Note 34). 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 34—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

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

TABLE 12 Statistical Information—Chromium

	Test Specimen	Chromium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	40 Ni 0.2 Si 0.5 Mn 0.02 C Steel	0.072	0.007	0.009
2.	No. 1, E352	0.149	0.028	0.025
3.	18 Ni 9 Co 5 Mo 0.5 Ti Steel	0.961	0.036	0.093

chromium compositions less than 0.10 %, proceed as directed in 172.3. For samples with expected chromium compositions greater than 0.10 %, transfer by pipet 10 mL to a 100-mL volumetric flask, add 9 mL of HCl, dilute to volume, and mix.

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 *Spectrometry*—Using water as a reference solution, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of 4 or fewer test solutions and reagent blank solutions has been aspirated, apply the test using the standard solution as directed in 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:

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (18)$$

where:

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

174. Precision and Bias[14]

174.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 12.

174.2 *Bias*—The accuracy can be inferred from the data in Table 12 by comparing the certified values for chromium with the average value obtained by using this method.

[14] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E03-1030. Contact ASTM Customer Service at service@astm.org.

CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

175. Scope

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

176. Summary of Test 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 35—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 compositions 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:

$$(2.6A + 0.05B + 0.01C)\, D \quad (19)$$

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*—pH meter 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*)—Dissolve 20 g and 40 g of ferrous ammonium sulfate ($Fe(NH_4)2(SO_4)_2{\cdot}6H_2O$) in 500 mL of cold H_2SO_4 (5 + 95) and dilute to 1 L with H_2SO_4 (5 + 95). Standardize the

solution as directed in 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*)—Dissolve 2.4518 g and 4.9036 g of NIST 136c standard potassium dichromate ($K_2Cr_2O_7$) or equivalent primary standard grade in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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*):

179.5.1 *Preparation*—Dissolve 1.6 g and 3.2 g of potassium permanganate ($KMnO_4$) in 1 L of water. Let stand in the dark for 2 weeks. Filter, without washing, through a Gooch crucible or a fine porosity fritted-glass crucible. Avoid contact with rubber or other organic material. Store in a dark-colored glass-stoppered bottle.

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

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

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

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

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

179.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 *M*)—Dissolve 1.485 g of 1,10-phenanthroline monohydrate in 100 mL of ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$).

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 *N* or 0.10 *N* $Fe(NH_4)_2(SO_4)_2$ (179.2) with either 0.05 *N* or 0.10 *N* $KMnO_4$ solution (179.5) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 1 drop to 2 drops of 1,10 phenanthroline indicator solution. Using a 25-mL buret, titrate the ferrous ions with 0.05 *N* $KMnO_4$ standard solution (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:

$$\text{Normality} = AB/C \tag{20}$$

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:*

180.2.1 Transfer 180 mL of water, 12 mL of H_2SO_4 (1 + 1), and 5 mL of H_3PO_4 into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 *N* or 0.10 *N* $Fe(NH_4)_2(SO_4)_2$ (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 *N* or 0.10 *N* $K_2Cr_2O_7$ solution, while swirling the flask. As the end point is approached, add the $K_2Cr_2O_7$ titrant dropwise. Continue until a blue color appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL. Refill the burets, add the same volume of $Fe(NH_4)_2(SO_4)_2$ solution as before, and again titrate with either 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution to the blue end point. Subtract this volume of $K_2Cr_2O_7$ solution from the volume recorded for the first titration and record the difference as the indicator blank.

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

$$\text{Normality} = \left(0.05 \text{ or } 0.10\,(A - B)\right)/C \tag{21}$$

where:

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

180.3 *Against Potassium Dichromate Using Potentiometric End Point:*

180.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution into a 600-mL beaker. Reserve the remaining 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution in the buret for the back-titration. Add 150 mL of water, 10 mL of H_2SO_4 (1 + 1), and 5 mL of H_3PO_4. Insert the saturated calomel reference electrode and the platinum indicator electrode into the beaker and connect them to the potentiometer apparatus. While stirring the solution, add $Fe(NH_4)_2(SO_4)_2$ until the dichromate ion yellow color disappears and then a slight excess. Record the volume of the $Fe(NH_4)_2(SO_4)_2$ solution to the nearest 0.01 mL. Back-titrate with the remaining 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution by adding the solution in 0.1-mL increments as the end point is approached. Record the voltage when equilibrium is reached after each 0.1-mL increment. Inspect the data for the

maximum voltage change per 0.1-mL increment. Determine the voltage change for the 0.1-mL increments before and after this maximum change. Determine the two differences between the three voltage readings corresponding to the volume (0.1-mL) increment before the maximum, the maximum, and after the maximum. This is a very close approximation of the second derivative of the volume versus change in voltage curve corresponding to the maximum inflection if this curve were plotted. Sum the two voltage differences. Determine the ratio of the first of these two differences to the sum and multiply 0.1 mL by this ratio to obtain the volume to be added to the smaller volume between the two incremental additions that the maximum change in voltage occurred. See the following example:

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

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

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

$$\text{Normality} = 0.05 \text{ or } 0.10\,A/B \tag{22}$$

where:

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

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[A]	0.50	0.1	0.10
13.00 to 20.00[A]	0.40	0.1	0.10
18.00 to 30.00[A]	0.20	0.1	0.10
28.00 to 33.00[A]	0.15	0.1	0.10

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

Transfer it to a 600-mL beaker.

181.2 Add 80 mL of H_2SO_4 (1 + 5) and 5 mL of H_3PO_4. Cover the beaker with a ribbed cover glass and heat at 85 °C to 100 °C until the sample is decomposed. Add sufficient HNO_3 in small increments to oxidize iron. Boil 2 min to expel oxides of nitrogen. 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_3, or mixtures and dilutions of these acids, or bromine and HCl in a ratio of 1 to 3 plus a few drops of HF, which are sufficient to dissolve the sample. When dissolution is complete, add 80 mL of H_2SO_4 (1 + 5), 5 mL of H_3PO_4, and evaporate to light fumes. Rinse the cover and walls of the beaker. Again evaporate to fumes and fume for 1 min. Cool, add 100 mL of water, and heat at 85 °C 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 times 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 °C to 900 °C for 15 min. Cool, add sufficient H_2SO_4 (1 + 1) to moisten the residue, and then 3 mL to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue with a minimum amount of either fused sodium hydrogen sulfate (sodium pyrosulfate—$Na_2S_2O_7$) or potassium pyrosulfate ($K_2S_2O_7$). Cool the crucible, place in a 250-mL beaker, and dissolve the melt in 20 mL of H_2SO_4 (1 + 10). Remove the crucible, rinse with water, transfer the solution to the reserved filtrate (181.4), and dilute to 200 mL.

181.6 Add 5 mL of $AgNO_3$ solution and 20 mL of $(NH_4)_2S_2O_8$ solution. If a beaker is used, cover it with a ribbed cover glass. Boil the solution 8 min to 10 min, maintaining the volume at 200 mL by additions of hot water. If the color due to permanganate ions does not develop, or develops but does not persist, add 2 drops of $KMnO_4$ solution (179.4), 5 mL more of $AgNO_3$ solution, 20 mL more of $(NH_4)_2S_2O_8$ solution, and boil for an additional 8 min to 10 min. Add hot water to maintain the volume at 200 mL during this operation and the operations that follow in 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_2 is present, add 2 mL of HCl (1 + 3) and boil again for 10 min. Repeat the addition of HCl and boiling until all manganese is present as colorless manganous ions. Cool to room temperature and dilute to 200 mL. If vanadium is present or its absence has not been confirmed, proceed as directed in 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 drop to 2 drops of 1,10 phenanthroline indicator solution and then add sufficient $Fe(NH_4)_2(SO_4)_2$ solution to effect a change in color from clear green to pink. Add 1 mL to 2 mL more and record the buret reading to the

nearest 0.01 mL. Using a 25-mL buret, back-titrate the excess ferrous ions with 0.05 *N* $KMnO_4$ standard solution. Add $KMnO_4$ dropwise as the end point is approached. Continue the titration until the pink color has changed to clear green which persists for 60 s. Record the buret reading to the nearest 0.01 mL.

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

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 $Fe(NH_4)_2(SO_4)_2$ solution while stirring until the yellow color disappears. Then add 1 mL to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Using another 25-mL buret add 0.05 *N* $K_2Cr_2O_7$ standard 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. Calculation

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

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (23)$$

where:

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

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

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

where:

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

TABLE 13 Statistical Information—Chromium

	Test Specimen	Chromium Found, %	Repeatability (R_1, E173)	Reproducibility (R_2, E173)
1.	No. 2, E350	0.481	0.015	0.053
2.	No. 2, E351	1.96	0.10	0.16
3.	No. 3, E352	3.68	0.16	0.48
4.	High-Temperature Alloy Waspalloy (NIST 349, 19.50Cr)	19.46	0.25	0.49
5.	High-Temperature Alloy 41Co, 20Ni, 20Cr (NIST 168, 20.33Cr)	20.26	0.35	0.57

183. Precision and Bias[15]

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

MOLYBDENUM BY THE ION EXCHANGE—8-HYDROXYQUINOLINE GRAVIMETRIC METHOD

184. Scope

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

185. Summary of Test Method

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

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,* approximately 400 mm in length and 25 mm in inside diameter, the bottom tapered to a 2-mm bore outlet, fitted with a hosecock or stopcock to control the liquid flow. All parts of the apparatus must be constructed of HF-resistant plastic, such as polytetrafluoroethylene, polyethylene, or polyvinyl chloride (Note 36).

[15] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E03-1036. Contact ASTM Customer Service at service@astm.org.

NOTE 36—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 (NH_4Cl) in 800 mL of water. Warm to room temperature, dilute to 1 L and mix.

188.2 *Ammonium Fluoride* (NH_4F).

188.3 *Ammonium Oxalate*—($NH_4OCOCOONH_4H_2O$).

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 37.

NOTE 37—**Warning:** HF causes serious burns which may not be immediately painful; read the paragraph about HF in the Hazards section of Practices E50.

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/Hydrochloride 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 NH_4Cl 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 NH_4F. Add water to the 900 mL mark and stir to dissolve. Dilute to 1 L and mix. With narrow-range pH paper, verify that the pH is between 5.6 and 5.8. If it is above this range, adjust the solution with dropwise additions of HF; if it is below this range, adjust the solution with dropwise additions of NH_4OH. Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH_4Cl and 4.1 % in NH_4F on a weight/volume basis.)

188.6 *8-Hydroxyquinoline Solution* (30 g/L)—Dissolve 30 g of 8-hydroxyquinoline in 120 mL of glacial acetic acid (CH_3COOH). Cautiously add water, with stirring to a total solution volume of 600 mL. Warm to 40 °C. Add NH_4OH (1 + 1) dropwise with stirring until a slight permanent precipitate is formed. Carefully add glacial CH_3COOH with stirring until the precipitate first dissolves. Dilute to 1 L.

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 having a cross-linkage of 8 % and of 200-nominal to 400-nominal U.S. mesh size.[16] To remove those beads greater than about 180 µm in diameter, as well as the very small diameter beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow at least 30 min for the beads to undergo maximum swelling. Place a No. 80 (180-µm) screen, 150 mm in diameter, over a 2-L beaker. Prepare a thin slurry of the resin and pour it into the screen. Wash the fine beads through the screen using a small stream of water. Discard the beads retained on the screen periodically to avoid undue clogging of the openings. When the bulk of the resin has settled in the 2-L beaker, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19) and stir vigorously. Allow the resin to settle for 4 min to 6 min, decant 150 mL to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

188.7.2 Prepare the column as follows: Place a 10-mm to 20-mm layer of polyvinyl chloride plastic fiber in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 150 mm to 175 mm. Place a 20-mm layer of polyvinyl chloride plastic fiber on the top of the resin surface to protect it from being carried into suspension when the solutions are added. Add 100 mL to 125 mL of HCl (3 + 1) to the column. When the solution level is 5 mm to 10 mm above the top of the resin bed add 100 mL of HCl (1 + 9) to the column. Repeat this cycle twice more and finally wash the resin bed with 200 mL HCl (1 + 3) turning off the stopcock when the solution level is 10 mm to 20 mm above the top of the resin bed.

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 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 38). Cool to room temperature and dilute to 100 mL with water.

[16] AG1-X8 (catalog number 140-1451), 200 mesh to 400 mesh, chloride form, available from Bio-Rad Laboratories, Hercules, CA, 94547, has been found satisfactory (www.bio-rad.com).

NOTE 38—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. If insoluble molybdenum compounds are suspected or known to be present, halt the flow from the column when the washing of the paper is complete. Cautiously transfer the paper to a platinum crucible and ignite at 500 °C (no higher) in a muffle furnace. Cool in a desiccator, add 1 g anhydrous sodium carbonate powder (Na_2CO_3) and fuse over a burner. Cool, add 20 mL water and heat to dissolve the melt. Carefully acidify with dropwise additions of HCl (1 + 4) until effervescence ceases plus 10 drops excess. Evaporate to dryness, cool, add 20 mL HF/HCl/water (4 + 1 + 95), heat to dissolve, cool, and transfer this solution to the column. Resume the 2 mL/min flow from the column.

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 189.11.

189.8 Place an 800-mL plastic beaker under the column and elute 300 mL of HF/NH_4Cl/water (4 + 60 + 36) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 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 NH_4F/NH_4Cl solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 42).

NOTE 42—This solution contains all the tantalum.

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 mm to 20 mm above the resin bed. Cautiously discard the solution. The column is now ready to be stored for future use or to be preconditioned for another sample (189.3).

189.11 To the eluent containing the molybdenum (from 189.7) cautiously add 15 mL of H_2SO_4 (1 + 1) and evaporate to light fumes on a steambath or other carefully controlled heat source. Ensure that the applied temperature does not exceed the softening point of polytetrafluoroethylene. Cool and cautiously rinse into a 400-mL borosilicate glass beaker. Heat to low volume (about 10 mL), cool, add 2 mL of HNO_3, and evaporate to strong fumes of SO_3.

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

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 43).

NOTE 43—**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.

TABLE 14 Statistical Information—Molybdenum Ion Exchange—8-Hydroxyquinoline Gravimetric Method

Test Material	Molybdenum Found, %	Repeatability, (R_1, E173[A])	Reproducibility, (R_2, E173[A])
1. No. 1, E351	1.48	0.070	0.086
2. Co-base alloy 43Co-21Ni-20Cr-5W-3Nb-2Fe-2Mn (NIST 167, 3.90 Mo-prov.)	3.92	0.219	0.250
3. No. 3, E352	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

[A] This test was performed in accordance with the 1980 version of Practice E173.

190. Calculation

190.1 Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, \%} = [(A - B) \times C \times 23.05]/D \quad (25)$$

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 14. 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 compositions from 1.0 % to 50.0 %.

193. Summary of Test Method

193.1 The sample is dissolved in HCl and $HNO_3$and fumed in $HClO_4$. Iron is precipitated with NH_4OH 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_3PO_4 and H_2SO_4 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 compositions are less than the maximum amounts shown in 1.1.

195. Apparatus

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 cm 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_2SO_4 (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_2SO_4 (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 cm to 2 cm of HCl (1 + 11) above the top of the metal.

NOTE 44—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,* $[(NH_4)_2S_2O_8]$.

196.2 *Potassium Dichromate, Standard Solution* (0.10N)—Dissolve 4.9032 g of NIST standard potassium dichromate or equivalent 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 mesh to 60 mesh.

196.3.2 *Alternate*—Dissolve 100 g silver nitrate ($AgNO_3$) in 400 mL of water in a 600-mL beaker. Add 10 mL of HNO_3. 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_2SO_4 (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_3PO_4 to 400 mL of water, stirring well. Cool in a water bath and cautiously add 150 mL of H_2SO_4 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 mg 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_3 and heat to dissolve. Add 4 drops of HF to remove SiO_2. Cool and cautiously add 20 mL $HClO_4$. 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_4OH slowly, while stirring, until the precipitate redissolves slowly, then add 25 mL additional NH_4OH and 2 g of ammonium peroxydisulfate. Boil carefully for 2 min and filter through a high-porosity filter paper,[17] wash 5 times with NH_4OH (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 45—Several drops of hydrogen peroxide (H_2O_2), 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_4OH cautiously, while stirring, until the precipitate redissolves slowly, then add 25 mL additional NH_4OH and 2 g ammonium peroxydisulfate. Boil carefully for 2 min and filter through a high-porosity filter paper,[17] wash 5 times with NH_4OH (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 drops to 6 drops of sodium diphenylaminesulfonate indicator solution. Titrate immediately with potassium dichromate standard solution (0.10 N) to a permanent purple end point.

[17] Whatman No. 541 has been found acceptable.

TABLE 15 Statistical Information—Iron by the Silver Reduction Titrimetric Method

Sample	Cert, %	Iron Found %	Repeatability, (R_1, E173[A])	Reproducibility, (R_2, E173[A])
NIST 169 Ni Base	0.54	0.54	0.0179	0.0186
NIST 162a Cu-Ni	2.19	2.19	0.0317	0.0331
NIST 864 Inconel 600	9.6	9.62	0.0289	0.0688
NIST 161 Ni Base	15.01	15.00	0.1152	0.1260
NIST 348 A286	53.3	53.25	0.1653	0.2952

[A] This test was performed in accordance with the 1980 version of Practice E173.

198. Calculation

198.1 Calculate the percentage of iron as follows:

$$\text{Iron, \%} = [(0.55847) \times (A)/(B)] \quad (26)$$

where:

A = $K_2Cr_2O_7$ standard solution (0.1000N), mL, and
B = sample taken, g.

199. Precision and Bias

199.1 *Precision*—Six laboratories co-operated in testing this method and obtained data summarized in Table 15. The precision data demonstrates that the method is applicable between 0.5 % to 53 % iron well within the stated composition 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 15).

200. Keywords

200.1 aluminum; atomic absorption; chromium; cobalt; cobalt alloys; copper; high temperature alloys; ion exchange; iron; magnetic alloys; manganese; molybdenum; nickel; nickel alloys; phosphorus; silicon; spectrophotometric; tin; titrimetric