Designation: E351 – 13

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

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

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

1. Scope

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

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

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

	Sections
Carbon, Graphitic, by the Direct Combustion Infrared Absorption Method (1 % to 3 %)	108
Carbon, Total by the Combustion Gravimetric Method (1.25 % to 4.50 %)—*Discontinued*	97
Cerium and Lanthanum by the Direct Current Plasma Atomic Emission Spectrometry Method (Ce: 0.003 % to 0.5 %; La: 0.001 % to 0.30 %)	237
Chromium by the Atomic Absorption Method (0.006 % to 1.00 %)	208
Chromium by the Peroxydisulfate Oxidation—Titration Method (0.006 % to 1.00 %)	218
Chromium by the Peroxydisulfate-Oxidation Titrimetric Method (0.05 % to 30.0 %)—*Discontinued*	
Cobalt by the Ion-Exchange—Potentiometric Titration Method (2.0 % to 4.5 %)	53
Cobalt by the Nitroso-R-Salt Spectrophotometric Method (0.01 % to 4.50 %)	61
Copper by the Neocuproine Spectrophotometric Method (0.03 % to 7.5 %)	116
Copper by the Sulfide Precipitation-Electrodeposition Gravimetric Method (0.03 % to 7.5 %)	81
Lead by the Ion-Exchange—Atomic Absorption Method (0.001 % to 0.15 %)	126
Magnesium by the Atomic Absorption Method (0.002 % to 0.10 %)	71
Manganese by the Periodate Spectrophotometric Method (0.10 % to 2.00 %)	8
Manganese by the Peroxydisulfate-Arsenite Titrimetric Method (0.10 % to 3.5 %)	152
Molybdenum by the Ion Exchange–8-Hydroxyquinoline Gravimetric Method	257
Molybdenum by the Spectrophotometric Method (0.01 % to 1.5 %)	196
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 % to 36.00 %)	168
Nickel by the Ion Exchange-Atomic Absorption Method (0.005 % to 1.00 %)	176
Phosphorus by the Alkalimetric Method (0.02 % to 0.90 %)	160
Phosphorus by the Molybdenum Blue Spectrophotometric Method (0.02 % to 0.90 %)	18
Silicon by the Gravimetric Method (0.1 % to 6.0 %)	46
Sulfur by the Gravimetric Method—*Discontinued*	30
Sulfur by the Combustion-Iodate Titration Method (0.005 % to 0.25 %)—*Discontinued*	37
Sulfur by the Chromatographic Gravimetric Method—*Discontinued*	
Tin by the Solvent Extraction-Atomic Absorption Method (0.002 % to 0.10 %)	186
Tin by the Sulfide-Iodometric Titration Method (0.01 % to 0.35 %)	89
Titanium, Total, by the Diantipyrylmethane Spectrophotometric Method (0.006 % to 0.35 %)	246
Vanadium by the Atomic Absorption Method (0.006 % to 0.15 %)	227

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

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

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

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

Current edition approved Feb. 1, 2013. Published May 2013. Originally approved in 1968. Last previous edition approved in 2006 as E351 – 93 (Reapproved 2006). DOI: 10.1520/E0351-13.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

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

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

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

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

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

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

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

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

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

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

E1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry (Withdrawn 2004)[3]

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

2.2 *Other Document:*[4]

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

3. Terminology

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

4. Significance and Use

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

5. Apparatus, Reagents, and Instrumental Practices

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

5.2 *Reagents:*

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

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

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

6. Hazards

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

7. Sampling

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

8. Interlaboratory Studies and Rounding Calculated Values

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

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

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

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

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

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

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

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

10. Summary of Method

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

11. Concentration Range

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

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

12. Stability of Color

12.1 The color is stable for at least 24 h.

13. Interferences

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

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

14. Reagents

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

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

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

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

15. Preparation of Calibration Curve

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

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

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

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

15.4 *Spectrophotometry:*

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

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

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

16. Procedure

16.1 *Test Solution:*

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

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

Transfer it to a 300-mL Erlenmeyer flask.

16.1.2 To dissolve samples that do not require HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO_3 as needed to

hasten dissolution, and then add 3 mL to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of $HClO_4$; evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, and digest if necessary to dissolve the salts. Cool and transfer the solution to either a 100-mL or 500-mL volumetric flask as indicated in 16.1.1. Proceed to 16.1.4.

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

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

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

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

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

16.4 *Reference Solutions:*

16.4.1 *Background Color Solution*—To one of the sample aliquots in a 50-mL volumetric flask, add 100 mL of HNO_3-H_3PO_4 mixture, and heat the solution at not less than 90 °C for 20 min to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

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

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

TABLE 1 Statistical Information—Manganese by the Metaperiodate Spectrophotometric Method

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

17. Calculation

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

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

where:

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

18. Precision and Bias

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

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

PHOSPHORUS BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD

19. Scope

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

20. Summary of Method

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

21. Concentration Range

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

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

22. Stability of Color

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

23. Interferences

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

24. Apparatus

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

25. Reagents

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

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

25.3 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ($(NH_2)_2\cdot H_2SO_4$) 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 *Test Solution:*

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

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

Transfer it to a 250-mL Erlenmeyer flask.

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

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

28.1.2.2 Cool the solution, add 60 mL of $HClO_4$ (1 + 5), and swirl to dissolve the salts. Transfer to a 100-mL volumetric flask, cool, dilute to volume, and mix. Allow insoluble matter to settle or dry filter the solution. Using a pipet, transfer 10-mL portions to two 100-mL borosilicate glass volumetric flasks; treat one in accordance with 28.3 and the other in accordance with 28.4.2.

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

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

28.1.3.2 Cool the solution, add 60 mL of $HClO_4$ (1 + 5), and swirl to dissolve the salts. Transfer to a 100-mL volumetric flask, cool, dilute to volume, and mix. Allow insoluble matter to settle or dry filter the solution. Using a pipet, transfer 10-mL portions to two 100-mL borosilicate glass volumetric flasks; treat one in accordance with 28.3 and the other in accordance with 28.4.2.

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

28.3 *Color Development*—Proceed with one of the 10-mL portions obtained in 28.1.2.2 or 28.1.3.2, in accordance with 26.3.

28.4 *Reference Solutions:*

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

28.4.2 *Background Color Reference Solution*—Add 15 mL of Na_2SO_3 solution to the second 10-mL portion obtained in 28.1.2.2 or 28.1.3.2. Boil gently for 30 s, add 50 mL of H_2SO_4 (3 + 37), cool, dilute to volume, and mix. Use this as the reference solution for the test solution.

TABLE 2 Statistical Information—Phosphorus

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

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

29. Calculation

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

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

where:

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

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

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

30. Precision and Bias

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

SULFUR BY THE GRAVIMETRIC METHOD

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

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

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

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

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

47. Summary of Test Method

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

48. Interferences

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

49. Reagents

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

49.2 *Perchloric Acid:*

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

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

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

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

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

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

49.2.6 Calculate the percent of silicon as follows:

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

where:

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

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

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

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

50. Procedure

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

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

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

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

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

50.2.2 *Sulfuric Acid Dehydration:*

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

50.2.3 *Perchloric Acid Dehydration:*

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

50.3 Add paper pulp and filter immediately, on a low-ash 11-cm medium-porosity filter paper. Collect the filtrate in a 600-mL beaker. Transfer the precipitate to the paper, and scrub the container thoroughly with a rubber-tipped rod. Wash the paper and precipitate alternately with 3-mL to 5-mL portions of hot HCl (1 + 19) and hot water until iron salts are removed but for not more than a total of ten washings. If the $HClO_4$ dehydration method was followed, wash the paper twice more with H_2SO_4 (1 + 49), but do not collect these washings in the filtrate; discard the washings. Transfer the paper to a platinum crucible and reserve.

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

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

TABLE 3 Statistical Information—Silicon

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

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

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

51. Calculation

51.1 Calculate the percent of silicon as follows:

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

where:

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

52. Precision

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

COBALT BY THE ION-EXCHANGE-POTENTIOMETRIC TITRATION METHOD

53. Scope

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

54. Summary of Method

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

55. Interferences

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

56. Apparatus

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

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

57. Reagents

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

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

57.2.1 *Preparation*—Dry a weighing bottle in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer 3.945 g of cobalt sulfate ($CoSO_4$)[25] that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in desiccator, stopper the bottle, and weigh. The difference in weight is the amount of $CoSO_4$ taken. Transfer the weighed $CoSO_4$ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 20 mL of HNO_3, and heat to dissolve the salts. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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

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

57.3 *Ion-Exchange Resin:*[6]

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

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

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

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

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

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

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

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

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

where:

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

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

58. Procedure

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

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

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

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

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

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

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

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

TABLE 4 Statistical Information—Cobalt

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

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

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

59. Calculation

59.1 Calculate the percentage of cobalt as follows:

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

where:

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

60. Precision

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

COBALT BY THE NITROSO-R-SALT SPECTROPHOTOMETRIC METHOD

61. Scope

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

62. Summary of Method

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

63. Concentration Range

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

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

64. Stability of Color

64.1 The color is stable for at least 3 h.

65. Interferences

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

66. Reagents

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

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

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

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

67. Preparation of Calibration Curve

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

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

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

67.4 *Spectrophotometry:*

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

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

path and using a light band centered at approximately 520 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions versus the reference solution (67.2).

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

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

68. Procedure

68.1 *Test Solution:*

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

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

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

68.1.2 Add 5 mL of a mixture of 1 volume of HNO_3 and 3 volumes of HCl. Heat gently until the sample is dissolved. Boil the solution until brown fumes have been expelled. Add 50 mL to 55 mL of water and cool.

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

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

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

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

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

TABLE 5 Statistical Information—Cobalt

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

69. Calculation

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

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

where:

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

70. Precision

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

MAGNESIUM BY THE ATOMIC ABSORPTION METHOD

71. Scope

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

72. Summary of Method

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

73. Concentration Range

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

74. Interferences

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

75. Apparatus

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

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

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

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

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

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

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

where:

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

76. Reagents

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

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

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

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

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

77. Preparation of Calibration Curves

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

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

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

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

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

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

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

77.3.3 Aspirate the magnesium solution used in 77.3.2 a sufficient number of times to establish that the absorbance reading is not drifting. Record six readings, and calculate the standard deviation, *s*, of the readings as follows:

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

where:

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

77.3.4 Beginning with the solution to which no magnesium was added in 77.1, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of the six values recorded in 77.3.3 by more than twice the standard deviation, *s*, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause (for

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

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

77.3.5 Proceed immediately as directed in 78.3.

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

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

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

77.5.2 Proceed immediately as directed in 78.3.

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

78. Procedure

78.1 *Test Solution:*

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

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

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

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

78.2 *Reagent Blank:*

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

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

TABLE 6 Statistical Information—Magnesium

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

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

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

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

79. Calculation

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

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

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

where:

A = absorbance found for solution prepared as directed in 78.2.1, and
B = absorbance found for solution prepared as directed in 78.2.2.

79.3 Calculate the percentage of magnesium as follows:

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

where:

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

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

80. Precision

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

COPPER BY THE SULFIDE PRECIPITATION-ELECTRODEPOSITION GRAVIMETRIC METHOD

81. Scope

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

82. Summary of Method

82.1 Copper is precipitated as the sulfide from dilute acid containing chloride and nitrate ions. After dissolution of the precipitate, iron is added and tin is separated from copper by double precipitation with ammonium hydroxide (Note 17). Chloride ions are removed from the filtrate, and copper, as the metal, is deposited on a platinum cathode.

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

83. Interferences

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

84. Apparatus

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

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

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

85. Reagents

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

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

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

86. Procedure

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

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

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

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

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

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