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Standard Test Methods for Chemical Analysis of Cast Iron—All Types¹

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

1. Scope

1.1 These test methods² cover the chemical analysis of pig iron, gray cast iron (including alloy and austenitic), white cast iron, malleable cast iron, and ductile (nodular³) iron having chemical compositions within the following limits:

| Element | Concentration Range, % |
|------------------------|------------------------|
| Aluminum ⁴ | 0.003 to 0.50 |
| Antimony | 0.005 to 0.03 |
| Arsenic ⁴ | 0.02 to 0.10 |
| Bismuth ⁴ | 0.001 to 0.03 |
| Boron ⁴ | 0.001 to 0.10 |
| Cadmium ⁴ | 0.001 to 0.005 |
| Carbon | 1.25 to 4.50 |
| Cerium ⁴ | 0.005 to 0.05 |
| Chromium | 0.01 to 30.00 |
| Cobalt ⁴ | 0.01 to 4.50 |
| Copper | 0.03 to 7.50 |
| Lead ⁴ | 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 ⁴ | 0.001 to 0.06 |
| Silicon | 0.10 to 6.0 |
| Sulfur | 0.005 to 0.25 |
| Tellurium ⁴ | 0.001 to 0.35 |
| Tin ⁴ | 0.001 to 0.35 |
| Titanium ⁴ | 0.001 to 0.20 |
| Tungsten ⁴ | 0.001 to 0.20 |
| Vanadium ⁴ | 0.005 to 0.50 |
| Zinc ⁴ | 0.005 to 0.20 |

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

Sections

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

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² These test methods represent revisions of methods covered by Test Methods E30, which appear in this publication. Typical alloy specification numbers for this category are listed in the Appendix.

³ As typified by compositions listed in *Cast Metals Handbook*, 1957, pp. 196–197.

| | |
|--|-----|
| Carbon, Graphitic, by the Direct Combustion Gravimetric Method (1 to 3 %) | 108 |
| Carbon, Total by the Combustion Gravimetric Method (1.25 to 4.50 %) | 97 |
| Cerium and Lanthanum by the D-C Plasma Optical Emission 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—Titrimetric Method (0.006 to 1.00 %) | 218 |
| Chromium by the Peroxydisulfate-Oxidation Titrimetric Method (0.05 to 30.0 %) | 4 a |
| Cobalt by the Ion-Exchange—Potentiometric Titration Method (2.0 to 4.5 %) | 53 |
| Cobalt by the Nitroso-R-Salt Photometric Method (0.01 to 4.50 %) | 61 |
| Copper by the Neocuproine Photometric 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 Photometric 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 Photometric 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 Photometric Method (0.02 to 0.90 %) | 18 |
| Silicon by the Gravimetric Method (0.1 to 6.0 %) | 46 |
| Sulfur by the Gravimetric Method | 30 |
| Sulfur by the Combustion-Iodate Titration Method (0.005 to 0.25 %) | 37 |
| Sulfur by the Chromatographic Gravimetric Method | 4 b |
| 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 several elements not included in these test methods can be found in Test Methods E30 and Test Methods E1019.

1.4 Some of the concentration ranges given in 1.1 are too broad to be covered by a single method and therefore this standard contains multiple methods for some elements. The

user must select the proper method by matching the information given in the Scope and Interference sections of each method with the composition of the alloy to be analyzed.

1.5 The values stated in SI units are to be regarded as standard. In some cases, exceptions allowed in Practice E380 are also used.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazards statements are given in Section 5 and in special “Warning” paragraphs throughout these Methods.

2. Referenced Documents

2.1 ASTM Standards:⁴

D1193 Specification for Reagent Water

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

E30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron.⁵

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

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁵

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) (Modernized Metric System)⁵

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)⁶

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

2.2 Other Document:⁷

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

3. Significance and Use

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

4. Apparatus, Reagents, and Instrumental Practices

4.1 *Apparatus*—Specialized apparatus requirements are listed in the Apparatus section in each method. In some cases reference may be made to Practices E50.

4.2 Reagents:

4.2.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the Reagent Grade Specifications of the American Chemical Society.⁸ Other chemicals may be used, provided it is first ascertained that they are of sufficiently high purity to permit their use without adversely affecting the expected performance of the determination, as indicated in the section on “Precision and Bias.”

4.2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

4.3 *Photometric Practice*—Photometric practice prescribed in these test methods shall conform to Practice E60.

5. Hazards

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

6. Sampling

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

7. Interlaboratory Studies and Rounding Calculated Values

7.1 These test methods have been evaluated using Practice E173 or ISO 5725.

⁴ 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.

⁵ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.⁶

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

⁷ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

⁸ *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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.2 Calculated values shall be rounded to the desired number of places as directed in 3.4 to 3.6 of Practice E29.

MANGANESE BY THE METAPERIODATE PHOTOMETRIC METHOD

8. Scope

8.1 This test method covers the determination of manganese in concentrations from 0.10 to 2.00 %.

9. Summary of Method

9.1 Manganous ions are oxidized to permanganate ions by reaction with metaperiodate ions. Solutions of the samples are fumed with perchloric acid so that the effect of metaperiodate ion is limited to the oxidation of manganese. Photometric measurement is made at approximately 545 nm.

10. Concentration Range

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

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

11. Stability of Color

11.1 The color is stable for at least 24 h.

12. Interferences

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

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

13. Reagents

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

Cool, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 500-mL volumetric flask, dilute to volume, and mix.

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

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

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

14. Preparation of Calibration Curve

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

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

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

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

14.4 *Photometry*: <https://standards.astro.org/standards/3a9f2b140/astm-e351-932006>

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

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

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

15. Procedure

15.1 *Test Solution*:

15.1.1 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.

15.1.2 To dissolve samples that do not require HF, add 8 to 10 mL of HCl (1 + 1), and heat. Add HNO₃ as needed to hasten dissolution, and then add 3 to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of HClO₄; evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, and digest if necessary to dissolve the salts. Cool and transfer the solution to either a 100- or 500-mL volumetric flask as indicated in 15.1.1. Proceed to 15.1.4.

15.1.3 For samples whose dissolution is hastened by HF, treat them by adding 8 to 10 mL of HCl (1 + 1), and heating. Add HNO₃ and a few drops of HF as needed to hasten dissolution, and then add 3 to 4 mL of HNO₃. When dissolution is complete, cool, then add 10 mL of HClO₄, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to either a 100- or 500-mL volumetric flask as indicated in 15.1.1.

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

15.1.5 Using a pipet, transfer 20 mL aliquots, to two 50-mL borosilicate glass volumetric flasks. Treat one portion as directed in 15.3. Treat the other portion as directed in 15.4.1.

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

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

15.4 *Reference Solutions:*

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

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

15.5 *Photometry*—Establish the cell corrections with the Reagent Blank Reference solution to be used as a reference solution for Background Color solutions. Take the photometric readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference Solutions as directed in 14.4.

16. Calculation

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

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

where:

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

17. Precision and Bias

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

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

PHOSPHORUS BY THE MOLYBDENUM BLUE PHOTOMETRIC METHOD

18. Scope

18.1 This method covers the determination of phosphorus in concentrations from 0.02 to 0.90 %.

19. Summary of Method

19.1 See Section 19 of Test Methods E350.

20. Concentration Range

20.1 See Section 20 of Test Methods E350.

21. Stability of Color

21.1 See Section 21 of Test Methods E350.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Photometric 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 |

22. Interferences

22.1 See Section 22 of Test Methods E350.

23. Apparatus

23.1 See Section 23 of Test Methods E350.

24. Reagents

24.1 Proceed as directed in 24.1 through 24.7 of Test Methods E350.

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

25.1 Proceed as directed in 25.1 through 25.6 of Test Methods E350.

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

26.1 Proceed as directed in 26.1 through 26.6 of Test Methods E350.

27. Procedure

27.1 Test Solution:

27.1.1 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.

27.1.2 If the sample is other than white iron, proceed as directed in 27.1.2 and 27.1.3 of Test Methods E350; treat samples of white iron as directed in 27.1.2.1 and 27.1.2.2.

27.1.2.1 Crush the material in an iron mortar and weigh only particles passing through a No. 50 (300- μ m) sieve. Transfer the weighed sample to a 250-mL Erlenmeyer flask. Add 15 mL of HNO₃ and 5 mL of HBr. Heat until dissolution is complete. Add 10 mL of HClO₄, 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.

27.1.2.2 Proceed as directed in 27.1.3 of Test Methods E350.

27.2 Proceed as directed in 27.2 through 27.5 Molybdenum Blue Photometric Method of Test Methods E350.

28. Calculation

28.1 Proceed as directed in Section 28 of Test Methods E350.

29. Precision and Bias

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

TABLE 2 Statistical Information—Phosphorus

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

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

37. Scope

37.1 This method covers the determination of sulfur in concentrations from 0.005 to 0.25 %.

38. Summary of Test Method

38.1 See Section 38 of Test Methods E350.

39. Interferences

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

40. Apparatus

40.1 See Section 40 of Test Methods E350.

41. Reagents

41.1 Proceed as directed in 41.1 through 41.6 of Test Methods E350.

42. Calibration

42.1 Proceed as directed in 42.1 through 42.6 of Test Methods E350.

43. Procedure

43.1 Proceed as directed in 43.1 through 43.2 of Test Methods E350.

44. Calculation

44.1 Proceed as directed in Section 44 of Test Methods E350.

45. Precision

45.1 Twenty-two laboratories cooperated in testing this method; six used resistance furnaces and reported eight sets of values (Note 3) and sixteen used induction furnaces (Note 4). They obtained the data summarized in Table 3 for specimen 5. Although samples covered by this method with sulfur concentrations near the lower limit of the scope were not available for testing, the precision data obtained using the methods indicated in Table 4 should apply. None was available to permit a test near the upper limit of the scope.

TABLE 3 Statistical Information—Sulfur

| Test Specimen | Sulfur Found, % | Repeatability (R_1 , E173) | Reproducibility (R_2 , E 173) |
|--------------------------------|--------------------|-------------------------------|----------------------------------|
| Induction Furnace | | | |
| 1. No. 1, E352 | 0.006 ^A | 0.002 | 0.003 |
| 2. No. 2, E352 | 0.008 ^A | 0.001 | 0.004 |
| 3. No. 3, E350 | 0.014 ^A | 0.003 | 0.003 |
| 4. No. 4, E350 | 0.016 ^A | 0.002 | 0.002 |
| 5. Cast iron (NBS 6f, 0.106S) | 0.106 ^B | 0.009 | 0.008 |
| 6. No. 7, E350 | 0.141 ^C | 0.007 | 0.013 |
| 7. No. 7, E353 | 0.286 ^D | 0.014 | 0.020 |
| Resistance Furnace | | | |
| 1. No. 1, E352 | 0.006 ^A | 0.001 | 0.002 |
| 2. No. 2, E352 | 0.009 ^A | 0.001 | 0.002 |
| 3. No. 3, E350 | 0.014 ^A | 0.001 | 0.003 |
| 4. No. 4, E350 | 0.015 ^A | 0.002 | 0.003 |
| 5. Cast iron (NBS 6f, 0.106 S) | 0.105 ^B | 0.007 | 0.008 |
| 6. No. 7, E350 | 0.140 ^C | 0.007 | 0.011 |
| 7. No. 7, E353 | 0.288 ^D | 0.012 | 0.021 |

^ACalibration standards: See Footnote^A, Table 6, Methods **E350**.

^BCalibration standards: See Footnote^B, Table 6, Methods **E350**.

^CCalibration standards: See Footnote^C, Table 6, Methods **E350**.

^DCalibration standards: See Footnote^D, Table 6, Methods **E350**.

TABLE 4 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 (NBS 107b, 1.35 Si) | 1.36 | 0.02 | 0.02 |
| 2. Cast iron (NBS 4i, 1.45 Si) | 1.45 | 0.04 | 0.05 |
| 3. Cast iron 1.07Ni-0.32Cr (NBS 82a, 2.07 Si) | 2.08 | 0.04 | 0.05 |
| 4. Cast iron (NBS 5k, 2.08 Si) | 2.08 | 0.03 | 0.05 |
| 5. Cast iron, high (0.79) phosphorus (NBS 7g, 2.41 Si) | 2.40 | 0.04 | 0.07 |
| 6. White cast iron (NBS 1176, 3.19 Si) | 3.20 | 0.03 | 0.10 |
| H ₂ SO ₄ Dehydration | | | |
| 1. Cast iron 1.2Ni-0.3Cr-0.8Mo (NBS 107b, 1.35 Si) | 1.36 | 0.02 | 0.03 |
| 2. Cast iron (NBS 4i, 1.45 Si) | 1.45 | 0.04 | 0.06 |
| 3. Cast iron 1.07Ni-0.32Cr (NBS 82a, 2.07 Si) | 2.08 | 0.04 | 0.04 |
| 4. Cast iron (NBS 5k, 2.08 Si) | 2.08 | 0.04 | 0.05 |
| 5. Cast iron, high (0.79) phosphorus (NBS 7g, 2.41 Si) | 2.41 | 0.03 | 0.05 |

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

NOTE 4—The recovery of sulfur as SO₂ ranged from 80 to 96 %, an average value of 88 % based on calibration standards designated *b*, *c*, and *d* in **Table 3**.

SILICON BY THE GRAVIMETRIC METHOD

46. Scope

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

47. Summary of Test Method

47.1 See Section 47 of Test Methods **E350**.

48. Interferences

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

49. Reagents and Materials

49.1 Proceed as directed in 49.1 through 49.4 of Test Methods **E350**.

50. Procedure

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

| Silicon, % | Sample Weight, g | Tolerance in Sample Weight, mg | Dehydrating Acid, mL H ₂ SO ₄ (1 + 4) | 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 50.2 or 50.3 of Test Methods **E350**; 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- μ m) sieve. Add 30 mL of HNO₃ 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 HNO₃ and 10 mL of HBr, and heat gently until dissolution is complete. Combine the two portions of the solution and add the amount of H₂SO₄ or HClO₄ specified in 50.1.

50.2.2 Proceed as directed in 50.2.2 or 50.3.2 of Test Methods **E350**.

50.3 Proceed as directed in 50.4 or 50.7 of Test Methods **E350**.

51. Calculation

51.1 Proceed as directed in Section 51 of Test Methods **E350**.

52. Precision

52.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in **Table 4**. Although samples covered by this method with silicon concentrations 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 concentrations 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 hydrochloric acid. 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 concentrations are under the maximum limits shown in 1.1.

56. Apparatus

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

56.2 *Apparatus No. 3B*, 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* (1 mL = 1.5 mg of Co)—Reagent No. 25B.

57.3 *Ion-Exchange Resin*.⁹

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 to 400 nominal mesh size. To remove those beads greater than about 180- μ m 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- μ m) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 to 6 min, decant 150 to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

57.3.2 Prepare the column as follows: Place a 10 to 20-mm layer of glass wool or poly(vinyl chloride) plastic fiber in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 140 mm. Place a 20-mm layer of glass wool or poly(vinyl chloride) plastic fiber at the top of the resin bed to protect it

from being carried into suspension when the solutions are added. While passing a minimum of 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 to 20 mm above the top of the resin bed and then close the lower stopcock.

NOTE 5—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 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 6):

$$C \text{ cobalt equivalent, mg/mL} = (A \times B)/C \quad (2)$$

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 6—Duplicate or triplicate values should be obtained for the cobalt equivalent. The values obtained should check within 1 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 5). Cover the beaker and digest at 60 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 to 70 C until salts are dissolved (approximately 10 min).

NOTE 7—Other ratios and concentrations of acids, with or without the addition of 1 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 to 20 mm above the resin bed, rinse the original beaker with 5 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)

⁹ Available from the Dow Chemical Co., Midland, MI. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

2 or 3 times and allow the level to drop to 10 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 to 185 mL of solution (sample solution and washings) containing mainly chromium, manganese, and nickel is collected (Note 8). When the solution in the column reaches a level 10 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 8—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 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 to 20 mm above the resin bed, pass 35 to 50 mL of HCl (7 + 5) through the column until 10 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 HNO₃ and 15 mL of HClO₄ to the solution from 58.3 and evaporate to fumes of HClO₄. Cool, add 25 to 35 mL of water, boil for 1 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 K₃Fe(CN)₆ solution to oxidize the cobalt and to provide an excess of about 5 to 8 mL. Record the buret reading to the nearest 0.01 mL. Add 50 mL of NH₄OH and cool to 5 to 10 C. Transfer the beaker to the potentiometric titration apparatus and maintain the 5 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 9). Using a 50-mL buret, titrate the excess K₃Fe(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 9—For a successful titration, the sample solution must be added to the excess K₃Fe(CN)₆ solution.

59. Calculation

59.1 Calculate the percentage of cobalt as follows:

$$\text{Cobalt, \%} = [(AB - CD)/E] \times 100 \quad (3)$$

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 5, should apply.

COBALT BY THE NITROSO-R-SALT PHOTOMETRIC METHOD

61. Scope

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

62. Summary of Method

62.1 See Section 54 of Test Methods E350.

63. Concentration range

63.1 See Section 55 of Test Methods E350.

64. Stability of Color

64.1 See Section 56 of Test Methods E350.

65. Interferences

65.1 See Section 57 of Test Methods E350.

66. Reagents

66.1 Proceed as directed in 58.1 through 58.4 of Test Methods E350.

67. Preparation of Calibration Curve

67.1 Proceed as directed in 59.1 through 59.5 of Test Methods E350.

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 |

TABLE 5 Statistical Information—Chromium

| 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 |

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

68.1.2 Add 5 mL of a mixture of 1 volume of HNO₃ and 3 volumes of HCl. Heat gently until the sample is dissolved. Boil the solution until brown fumes have been expelled. Add 50 to 55 mL of water and cool.

68.1.3 Proceed as directed in 60.1.2 of Test Methods E350.

68.2 Proceed as directed in 60.2 through 60.4 of Test Methods E350.

69. Calculation

69.1 Proceed as directed in Section 61 of Test Methods E350.

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 6, should apply.

MAGNESIUM BY THE ATOMIC ABSORPTION METHOD

71. Scope

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

72. Summary of Method

72.1 A hydrochloric acid solution of the sample is aspirated into the air-acetylene flame. The radiation from a magnesium hollow cathode tube at 2852 Å is passed through the flame, and the attenuation is measured. The spectrophotometer is calibrated with 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 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 Interferences 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 spectrophotometer capable of resolving the 2852-Å 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 ± 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 2852 Å 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:

$$S \text{ sensitivity factor, } F = (0.400 \times A)/(15 \times B) \quad (4)$$

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 8). 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 HNO₃. 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 10—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.

TABLE 6 Statistical Information—Chromium

| Test Specimen | Cobalt Found, % | Repeatability (R_1 , E173) | Reproducibility (R_2 , E 173) |
|----------------|-----------------|-------------------------------|----------------------------------|
| 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 |

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 = $(0.002 \times F)$ 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 ($(33 \times F)$ g Sr/L)—Select a lot of strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) containing not more than 0.0002 % magnesium (approximately 0.0005 % with respect to Sr) (Note 8). Transfer $(100 \times F)$ g (81.14) 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 Concentrations from 0.002 to 0.03 %—Using pipets, transfer 0, 5, 10, 15, 20, 25, 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 11—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 Concentrations from 0.025 to 0.10 %—Proceed as directed in 77.1 adding 6 mL of iron solution instead of 20 mL (see Note 9)

77.3 Photometry for Concentrations 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 2852 Å 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 12). 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 12—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:

$$s = (A - B) \times 0.40 \quad (5)$$

where:

A = the highest of the six values found, and

B = the lowest of the six values found.¹⁰

77.3.4 Begining 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 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 Concentrations from 0.002 to 0.03 %—Subtract the absorbance value found for the solution to which no magnesium was added (Note 10) from the value recorded for each of the other solutions. Plot the net absorbance values against milligrams of magnesium per 100 mL on rectangular coordinate paper.

77.5 Photometry for Concentrations 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 Concentrations 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 to 15 mL. Collect approximately 100 mL in a dry beaker. Using a pipet, transfer 50 mL if the expected magnesium concentration is 0.002 to 0.030 %, or 15 mL if the magnesium concentration 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

¹⁰ 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).

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.

78.3 *Photometry*—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 13—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).

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

$$\text{Milligrams of magnesium in 100 mL of the final reagent blank solution} = [(0.004 A)/B] \times F \quad (6)$$

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:

$$\text{Magnesium, \%} = (A - B)/(C \times 100) \quad (7)$$

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 7. 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

TABLE 7 Statistical Information—Magnesium

| Test Specimen | Magnesium Found, % | Repeatability (R_1 , E173) | Reproducibility (R_2 , E173) |
|---|---------------------|-------------------------------|---------------------------------|
| 1. Cast iron (NBS 4i, 0.002 Mg, min) ^A | 0.0022 | 0.0003 | 0.0006 |
| 2. Cast iron (NBS 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 (NBS 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 (NBS 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 (75.3) to NBS 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 NBS 4i/B.C.S. No. SS45 (0.128 Mg) = 0.781/0.219.

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 concentrations 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 14). Chloride ions are removed from the filtrate, and copper, as the metal, is deposited on a platinum cathode.

NOTE 14—This method describes the preliminary separations for the determination of tin by the sulfide-iodatimetric titration method.

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

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 15).

84. Apparatus

84.1 Apparatus No. 9.

85. Reagents

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

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

85.3 *Sulfamic Acid* (H(NH₂)SO₃).

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 99.2 through 99.21 of Test Methods E350; 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- μ m) sieve. Add 30 mL of HNO₃ 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 to 3 min.

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

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

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

86.2.4.2 Transfer the paper and precipitate to a platinum crucible. Dry the paper and heat at 600°C until the carbon is removed. Finally ignite for 30 min at 1100°C. Cool, add 3 drops of HNO₃ and 1 to 2 mL of HF, and evaporate to dryness. Add 10 mL of HNO₃ (1 + 1) and digest at 90 to 100°C for 5 min. Transfer the contents of the crucible to the original flask, add 10 mL of HClO₄, and heat to mild fumes of HClO₄.

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

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

86.2.7 Add 5 mL of H₂SO₄ and heat at 85 to 95°C for 30 min. If insoluble matter persists, repeat the steps as directed in 86.2.4.1 through 86.2.7. When dissolution is complete, combine the solution with the filtrate reserved in 86.2.4.

86.2.8 If the volume is less than 600 mL, dilute the solution approximately to that volume and treat with H₂S; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 to 15 h.

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

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

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

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

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

86.2.14 Add 10 mL of FeCl₃ solution to the filtrate. Add just enough NH₄OH (1 + 1) to precipitate the iron, tin, and chromium and to complex the copper (indicated by the formation of a blue color), and then add 1 to 2 mL in excess. Add paper pulp, and heat the solution to boiling to coagulate the precipitate. Filter the hot solution through a coarse filter paper, and wash alternately five times each with hot NH₄OH (1 + 99) and water into an 800-mL beaker. Reserve the filter and filtrate. Dissolve the precipitate by washing the filter alternately with hot HCl (1 + 1) and hot water, and reserve the filter paper. Precipitate the iron, tin, and chromium as before. Wash the reserved filter paper three times with hot NH₄OH (1 + 99) and then filter the hot solution into the 800-mL beaker reserved from the first filtration; wash alternately five times each with hot NH₄OH (1 + 99) and water.

NOTE 15—If tin is to be determined by using the same sample, reserve the precipitate and proceed as directed in 100.5 through 100.8 of Test Methods E350.

86.2.15 Acidify the combined filtrates with HNO₃, and evaporate at low heat until salts begin to appear. Remove the beaker from the hot plate and while the solution is still hot add 5 mL of HNO₃. When the reaction has subsided, add another 5 mL of HNO₃ and again wait until the reaction subsides. Continue adding 5-mL increments of HNO₃ in this manner until there is no further reaction with the chloride ions. Cover the beaker with a ribbed cover glass and warm gently until the