



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

This standard is issued under the fixed designation E 351; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

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

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

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 below⁴:

	Sections
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 %)	4a
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	4b
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 Diantiprylmethane Spectrophotometric Method (0.006 to 0.35 %)	246
Vanadium by the Atomic Absorption Method (0.006 to 0.15 %)	227

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

¹ 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 July 15, 1993. Published September 1993. Originally published as E 351 – 68 T. Last previous edition E 351 – 89^{ε1}.

² These test methods represent revisions of methods covered by Test Methods E 30, 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.

⁴ a Discontinued.

4b Discontinued as of April 29, 1988.



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

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

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

2. Referenced Documents

2.1 ASTM Standards:

- D 1193 Specifications for Reagent Water⁵
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁶
- E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron⁷
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁸
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁸
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁹
- E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron⁸
- E 352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels⁸
- E 353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys⁸
- E 354 Test Methods for Chemical Analysis of High Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys⁸
- E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)¹⁰
- E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁸
- E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys⁸
- E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry⁸
- E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis⁸

E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition¹¹

2.2 Other Document:

ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests¹²

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 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 E 882.

4. Apparatus, Reagents, and Instrumental Practices

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

4.2 Reagents:

4.2.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the “Reagent Grade” Specifications of the American Chemical Society.¹³ Other chemicals may be used, provided it is first ascertained that they are of sufficiently high purity to permit their use without adversely affecting the expected performance of the determination, as indicated in the section on “Precision and Bias.”

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

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

5. Hazards

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

6. Sampling

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

7. Interlaboratory Studies and Rounding Calculated Values

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

¹¹ *Annual Book of ASTM Standards*, Vol 03.06.

¹² Available from American National Standards Institute, 11 West 42nd Street, 13th Floor, New York, NY 10036.

¹³ *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.

⁵ *Annual Book of ASTM Standards*, Vol 11.01.

⁶ *Annual Book of ASTM Standards*, Vol 14.02.

⁷ Discontinued 1995; see *1994 Annual Book of ASTM Standards*, Vol 03.05.

⁸ *Annual Book of ASTM Standards*, Vol 03.05.

⁹ Discontinued 1998; see *1997 Annual Book of ASTM Standards*, Vol 03.05.

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

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

MANGANESE BY THE METAPERIODATE PHOTOMETRIC METHOD

8. Scope

8.1 This method covers the determination of manganese in concentrations from 0.10 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. **Caution**—Avoid the use of this water for other purposes.

14. Preparation of Calibration Curve

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

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

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

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

14.4 *Photometry:*

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

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

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

15. Procedure

15.1 *Test Solution:*

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

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

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 E 350.

20. Concentration Range

20.1 See Section 20 of Test Methods E 350.

21. Stability of Color

21.1 See Section 21 of Test Methods E 350.

22. Interferences

22.1 See Section 22 of Test Methods E 350.

23. Apparatus

23.1 See Section 23 of Test Methods E 350.

24. Reagents

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

TABLE 1 Statistical Information—Manganese by the Metaperiodate Photometric Method

Test Specimen	Manganese Found, %	Repeatability (<i>R</i> ₁ , <i>E</i> 173)	Reproducibility (<i>R</i> ₂ , <i>E</i> 173)
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

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

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

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

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

27. Procedure

27.1 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 E 350; 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 E 350.

27.2 Proceed as directed in 27.2 through 27.5 Molybdenum Blue Photometric Method of Test Methods E 350.

28. Calculation

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

29. Precision

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

SULFUR BY THE GRAVIMETRIC METHOD

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

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

TABLE 2 Statistical Information—Phosphorus

Test Specimen	Phosphorus Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
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

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 E 350.

41. Reagents

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

42. Calibration

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

43. Procedure

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

44. Calculation

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

45. Precision

45.1 Twenty-two laboratories cooperated in testing this method; six used resistance furnaces and reported eight sets of values (Note 3) 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.

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



TABLE 3 Statistical Information—Sulfur

Test Specimen	Sulfur Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
Induction Furnace			
1. No. 1, E 352	0.006 ^A	0.002	0.003
2. No. 2, E 352	0.008 ^A	0.001	0.004
3. No. 3, E 350	0.014 ^A	0.003	0.003
4. No. 4, E 350	0.016 ^A	0.002	0.002
5. Cast iron (NBS 6f, 0.106S)	0.106 ^B	0.009	0.008
6. No. 7, E 350	0.141 ^C	0.007	0.013
7. No. 7, E 353	0.286 ^D	0.014	0.020
Resistance Furnace			
1. No. 1, E 352	0.006 ^A	0.001	0.002
2. No. 2, E 352	0.009 ^A	0.001	0.002
3. No. 3, E 350	0.014 ^A	0.001	0.003
4. No. 4, E 350	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, E 350	0.140 ^C	0.007	0.011
7. No. 7, E 353	0.288 ^D	0.012	0.021

^ACalibration standards: See Footnote^A, Table 6, Methods E 350.

^BCalibration standards: See Footnote^B, Table 6, Methods E 350.

^CCalibration standards: See Footnote^C, Table 6, Methods E 350.

^DCalibration standards: See Footnote^D, Table 6, Methods E 350.

TABLE 4 Statistical Information—Silicon

Test Specimen	Silicon Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
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

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

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

50. Procedure

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

Silicon, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dehydrating Acid, mL	
			H ₂ SO ₄ (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 E 350; 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 E 350.

50.3 Proceed as directed in 50.4 or 50.7 of Test Methods E 350.

51. Calculation

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

52. Precision

52.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 4. 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 E 350 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 C9)—Reagent No. 25B.

57.3 *Ion-Exchange Resin*.¹⁴

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) 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

¹⁴ Available from the Dow Chemical Co., Midland, MI.

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 E 350.

63. Concentration Range

63.1 See Section 55 of Test Methods E 350.

64. Stability of Color

64.1 See Section 56 of Test Methods E 350.

65. Interferences

65.1 See Section 57 of Test Methods E 350.

66. Reagents

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

67. Preparation of Calibration Curve

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

68. Procedure

68.1 *Test Solution.*

68.1.1 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, 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

TABLE 5 Statistical Information—Chromium

Test Specimen	Cobalt Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 1, E 352	1.86	0.05	0.12
2. No. 2, E 352	4.82	0.08	0.11

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 E 350.

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

69. Calculation

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

70. Precision

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. Add 20 mL of HCl (1 + 1). When dissolution is complete, cool,

TABLE 6 Statistical Information—Chromium

Test Specimen	Cobalt Found, %	Repeat-ability (<i>R</i> ₁ , E 173)	Reproducibility (<i>R</i> ₂ , E 173)
1. No. 1, E 350	0.011	0.005	0.007
2. No. 2, E 352	1.87	0.09	0.13
3. No. 3, E 352	4.94	0.08	0.17

dilute to volume, and mix. Store in a polyethylene bottle.

76.3 Magnesium, Standard Solution B ($1 \text{ mL} = (0.002 \times F) \text{ mg Mg}$)—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 ($(33 \times F) \text{ g Sr/L}$)—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 $(100 \times F) \text{ g}$ (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.¹⁵

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 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 $(1.00 \times F) \text{ g}$ (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 h before proceeding as directed in 78.3, transfer it to a

¹⁵ 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).

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:

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

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

TABLE 7 Statistical Information—Magnesium

Test Specimen	Magnesium Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
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

^ASynthetic 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.

^BSame sample; data based on calibration curves in 69.4 and 76.6, respectively.

^CNBS 4i/B.C.S. No. SS45 (0.128 Mg) = 0.781/0.219.

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 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 E 350; 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

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 E 350.

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 vigorous evolution of gas ceases. Evaporate to fumes of SO₃. Cool, add 25 mL of water, and heat to dissolve the salts. Cool, transfer to a 250-mL beaker, add 3 mL of HNO₃, and dilute to 175 mL.

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

86.2.17 Stir the solution with an automatic stirrer; start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1 A/dm². Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 to 3 A/dm² (Note 16). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 16—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm², and 2 to 3 h should be allowed for complete deposition.

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

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

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

NOTE 17—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of HNO₃ and 5 mL of H₂SO₄ in 175 mL of water contained in a 300-mL tail-form beaker. Reverse the polarity of the electrodes, and electrolyze with a current density of 3 A/dm² until the copper has been removed from the original electrode. Reverse the polarity and redeposit the copper on the original electrode as directed in 86.2.16 and 86.2.17. Proceed as directed in 86.2.18 and 86.2.19.

86.2.21 Allow the electrode to cool to room temperature undessiccated, and weigh.

NOTE 18—To prepare the electrode for reuse, immerse it in HNO₃(1+1) to dissolve the deposit of copper, rinse thoroughly with water and then with acetone or ethanol. Dry in an oven, cool to room temperature, and weigh.

87. Calculation

87.1 Calculate the percentage of copper as follows:

$$\text{Copper, \%} = [(A - B) - (C - D)]/E \times 100 \quad (8)$$

where:

- A = weight of electrode with deposit from the test solution, g,
- B = weight of electrode used in A, g,
- C = weight of electrode with deposit from the blank solution, g,
- D = weight of electrode used in C, g, and
- E = sample used, g.

88. Precision

88.1 Six laboratories cooperated in testing this method and obtained eight sets of data summarized in Table 8 for specimens 2, 3, and 4. Although samples covered by the method with copper concentrations at approximately 0.03 and 7.50 % were not available for testing, the precision data at the lower limit should be similar to those obtained for specimen 1 when using the method indicated, and at the upper limit similar to those obtained for specimen 4.

TIN BY THE SULFIDE-IODOMETRIC TITRATION METHOD

89. Scope

89.1 This method covers the determination of tin in concentrations from 0.01 to 0.35 %.

90. Summary of Method

90.1 See Section 96 of Test Methods E 350.

91. Interferences

91.1 See Section 97 of Test Methods E 350.

92. Apparatus

92.1 See Section 93 of Test Methods E 350.

93. Reagents

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

94. Procedure

94.1 For the range from 0.01 to 0.05 % tin, transfer a 10-g sample, (see 94.2.1 for white iron) weighed to the nearest 10 mg, to each of two 1-L Erlenmeyer flasks; use a single 10-g

TABLE 8 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability (R_1 , Practice E 173)	Reproducibility (R_2 , Practice E 173)
1. Low-alloy steel (NBS 152a, 0.023 Cu)	0.020	0.005	0.006
2. Cast iron (NBS 5k, 1.50 Cu)	1.49	0.02	0.03
3. Cast iron 2Ni	0.678	0.037	0.041
4. Cast iron 15Ni-2Cr-5Cu (NBS 115a, 5.52 Cu)	5.49	0.10	0.10

sample for the range from 0.05 to 0.35 %.

94.2 If the sample type is other than white iron, add 115 mL of HCl (1 + 2) plus an addition 9 mL of HCl (1 + 2) and 1 mL of HNO₃ for each gram of sample. Heat until the sample is dissolved, and then boil for 2 to 3 min. Treat samples of white iron as directed in 94.2.1 and 94.2.2.

94.2.1 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.

94.2.2 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.

94.3 Treat each sample as directed for copper by the sulfide-electrodeposition gravimetric method, described in 92.3 through 92.14 of Test Methods E 350. When two 10-g samples are used, proceed as directed in 100.3 through 100.8 of Test Methods E 350. When a single 10-g sample is used, proceed as directed in 100.5 through 100.8 of Test Methods E 350.

95. Calculation

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

96. Precision

96.1 Five to seven laboratories cooperated in testing this method, three of them submitting one additional set of data, all of which are summarized in Table 9. Although samples covered by this method were not available for testing, the precision data obtained for specimens using the method indicated in Table 9 should apply.

TOTAL CARBON BY THE COMBUSTION GRAVIMETRIC METHOD

97. Scope

97.1 This method covers the determination of tin in concentrations from 1.25 to 4.50 %.

98. Summary of Method

98.1 The sample is burned in a stream of oxygen, and the carbon dioxide in the evolved gases is collected in a suitable absorbent and weighed.

98.2 Oxygen flow rates and sweep times as well as control of plate current for induction heating depend upon the equipment

TABLE 9 Statistical Information—Tin

Test Specimen	Tin Found, %	Number of Laboratories	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 1, E 350	0.011	5	0.002	0.003
2. No. 3, E 350	0.028	5	0.002	0.001
3. No. 5, E 350	0.113	7	0.009	0.020

used, and the type of sample analyzed. The control of these parameters should be established by analysis of control samples similar in carbon content and alloy characteristics to the sample to be analyzed..

99. Interferences

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

100. Interferences

100.1 Apparatus No. 1.

NOTE 19—The induction furnace must be equipped with suitable controls to regulate the power input to the induction coil.

NOTE 20—The preferred position for a graduated flowmeter is at the exit end of the furnace. The graduated flowmeter may be positioned at the inlet, but in either case a sulfuric acid bubbler tube must be positioned at the exit end of the equipment.

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

NOTE 21—For precision-testing this balance see 7.4 of Methods E 319, or its equivalent.

101. Reagents

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

101.2 *Iron (Low-Carbon) Accelerator*—Iron chips (Note 20).

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

101.4 *Tin (Low-Carbon) Accelerator*, granular (Note 22).

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

NOTE 22—Prior to use, all accelerators should be washed three times with acetone by decantation until free of organic contaminants and then dried.

102. Preparation of Apparatus—Induction Furnace

102.1 The train of the induction furnace shall include an oxygen purifier, catalyst heater (Note 23), particle filter, and carbon dioxide purifier. The oxygen must flow from the top of the combustion tube through a small orifice so as to impinge directly on the surface of the sample.

NOTE 23—The catalyst heater contains copper oxide heater to about 300°C to ensure complete conversion of CO to CO₂.

102.2 Conditioning of Apparatus:

102.2.1 Transfer 1 g of a sample containing approximately 1.5 % carbon and 1 g of the accelerators in Section 101 to the cupelet, crucible, or boat.

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

102.2.3 Open the stopcock(s) of the absorption bulb and

connect it to the carbon train.

NOTE 24—The Fleming, Turner, and Nesbitt bulbs have all proved satisfactory. Bulbs shall not be handled with bare fingers at any time. Weighing time, that is, the interval from the completion of the burn and sweep to the completion of the weighing, must be closely controlled and kept rigidly constant. If a two-pan balance is used, a bulb may be used as a tare and may be carried alongside the sample bulb at all times in the procedure.

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

NOTE 25—During the sample burn, oxygen is consumed at a rapid rate. If necessary, manually increase the oxygen flow rate to maintain a positive pressure within the combustion tube.

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

NOTE 26—Oxygen flow rates and sweep times vary to some extent with equipment used, and the type of sample to be analyzed. Sweep times of 2 to 5 min have been found to be adequate in most cases. A control sample with carbon content and alloy characteristics similar to the sample to be analyzed should be used to control these parameters.

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

103. Preparation of Apparatus—Resistance Furnace

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

103.2 Conditioning of Apparatus:

103.2.1 Fill the boat with Alundum bedding material (Note 25). Make a furrow in the alundum large enough to contain the sample and the accelerator. Place in the furrow 1 g of a sample containing approximately 1.5% carbon so that the particles are in intimate contact. In the same manner add 1 g of one of the accelerators (see Section 101).

NOTE 27—The Alundum bedding material should be previously heated in oxygen at 1325°C for 15 min, cooled, and stored under cover.

103.2.2 Open the stopcock(s) of the absorption bulb (Note 22) and connect it to the carbon train.

103.2.3 Cover the boat with a suitable cover and introduce it into the combustion tube. Close the tube and preheat the sample for 1 to 2 min. Turn on the oxygen, adjust the oxygen flow rate to 300 to 500 mL per min, and maintain this rate for 6 to 13 min (Note 23).

NOTE 28—Oxygen flow rates and sweep times vary to some extent with equipment used and the type of sample to be analyzed. A control sample with carbon content and alloy characteristics similar to the sample to be analyzed should be used to control these parameters.

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

104. Blank Procedure

102.1 Induction Furnace:

104.1.1 Open the stopcock(s) of the absorption bulb momentarily to the atmosphere to equilibrate bulb conditions, and weigh the bulb which has been conditioned as directed in 102.2.

104.1.2 Add an amount of low-carbon iron equal to the sample weight to be used and 1 g of tin or tin-copper accelerator to a cupelet, crucible, or boat. Proceed as directed in 102.2.2–102.2.6.

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

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

104.1.5 Proceed as directed in Section 105.

104.2 Resistance Furnace:

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

104.2.2 Add an amount of low-carbon iron equal to the sample weight to be used and 1 g of tin or tin-copper accelerator to the combustion boat containing Alundum bedding material (Note 27). Proceed as directed in 103.2.2 and 103.2.4.

104.2.3 Proceed as directed in 103.2.2 and 103.2.4 of Test Methods E 350.

104.2.4 Proceed as directed in Section 105.

105. Blank Procedure

105.1 Select a control sample the carbon content and alloy characteristics of which are similar to those of the sample being analyzed, and proceed as directed in 105.2–105.5.

NOTE 29—The value obtained should not differ from the established value by more than 0.004 % carbon at levels from 0.05 to 0.2 %, nor more than 2 % of the amount present in the higher ranges of carbon.

NOTE 30—Low results may be due to (1) incomplete burning of the sample, which may be detected by examining the slag; (2) a leak in the system, which may be checked by means of a manometer; (3) improper filling of the absorption bulb, resulting in “channeling”; or (4) exhaustion of the CO₂ absorbent. High results may be due to inadequate purification of the oxygen or failure to remove oxides of sulfur.

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

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

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

Transfer it to a crucible, cupelet, or boat containing Alundum (Note 27).

105.4 Add an amount of low-carbon iron equal to the sample weight and 1 g of tin or tin-copper accelerator and proceed as directed in 102.2.2–102.2.6 and 103.2.2–103.2.4.

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

106. Calculation

106.1 Calculate the percent of carbon as follows:

$$\text{Carbon, \%} = [(A - B) \times 0.2729]/C \times 100 \quad (9)$$

where:

A = carbon dioxide found, g,

B = carbon dioxide found in the blank, g, and

C = sample used, g.

107. Precision

107.1 Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 10. Repeatability (R_1) and reproducibility (R_2) are defined in Practice E 173 and were respectively calculated from within laboratory standard deviation σ_w and the total standard deviation S . Since these last terms are related by:

$$S^2 = \sigma_w^2 + \sigma_d^2 \quad (10)$$

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

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

$$\sigma_d^2 = \sigma_{w1}^2 + \sigma_w^2 = (1.41 \sigma_w)^2. \quad (11)$$

Since

$$\sigma_w = \sigma_{w1} = \sigma_{w2}, \quad (12)$$

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

$$R_1 = 2\sigma_d = (2)(1.41)\sigma_w = 2.82 \sigma_w \quad (13)$$

TABLE 10 Statistical Information—Carbon

Test Specimen	Carbon Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. Electric furnace steel (NBS 5lb, 1.21 C)	1.22	—	0.03
2. Ductile iron (NBS 341, 1.81 C)	1.79 ^A	0.04	0.06
3. Cast iron (NBS 1182, 1.97 C)	2.00	—	0.07
4. Cast iron (B.C.S. 173 ^B , 2.42 C)	2.43	—	0.10
5. Cast iron (NBS 115a, 2.62 C)	2.60	—	0.15
6. Cast iron (NBS 1183, 3.05 C)	3.07 ^A	0.03	0.07
7. Cast iron (NBS 1181, 3.63 C)	3.65 ^C	0.12	0.12

^AThese specimens were analyzed by each laboratory in duplicate.

^BBritish Chemical Standard.

^CSix laboratories analyzed duplicate specimens, and three laboratories analyzed single portions. All other specimens were analyzed singly by each laboratory.

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

$$R_2 = 2.82 S \quad (14)$$

CARBON, GRAPHITIC, BY THE DIRECT COMBUSTION-GRAVIMETRIC AND INFRARED ABSORPTION METHODS

108. Scope

108.1 This test method covers the determination of graphitic carbon in concentrations from 1.0 to 3.0 %.

NOTE 31—The upper limit of the scope has been set at 3.0 % because sufficient numbers of test materials containing higher graphitic carbon contents were unavailable for testing in accordance with Practice E 173. Recognizing that commercial carbon determinators are capable of handling higher concentrations, this test method references a calibration procedure up to 4.5 %. Users of this standard are cautioned that the use of this test method above 3.0 % is not supported by interlaboratory testing.

109. Summary of Test Method

109.1 After decomposition of the sample in nitric acid in the presence of methanol and treatment with hydrofluoric acid, the graphitic carbon is removed by filtering through a glass-fiber filter. The glass-fiber filter containing the graphite is placed in the high-frequency induction furnace in a stream of oxygen and the graphite burned to carbon dioxide, which is collected in a suitable absorbent and weighed or measured in an infrared absorption apparatus.

110. Interferences

110.1 Elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1. However, some cast iron alloys, when extensively heat treated, yield carbides that are not soluble by this test method and may give high values for graphitic carbon.

111. Apparatus

111.1 *Combustion Apparatus:*

111.1.1 *Gravimetric Method*—Induction furnace. See the Apparatus Section of the Total Carbon by Combustion Gravimetric Method in Test Methods E 350, and Apparatus No. 1 of Practices E 50.

111.1.2 *Infrared Absorption Method*—Induction furnace. See the Infrared Absorption Method A or C of the Total Carbon by the Combustion-Instrumental Method in Test Methods E 1019.

111.2 *Filter*,¹⁶ glass-fiber, 47-mm, pore size 0.3 μm .

111.3 *Filtering Apparatus*—For use with 47-mm glass-fiber filters and suitable for use with acids.

¹⁶ Gelman Type A/E, 47-mm glass-fiber filter has been found suitable for this application.

112. Reagents

112.1 *Methanol* (CH₃OH).

112.2 *Sodium Hydroxide Wash Solution* (120 g/L)—*Cautiously dissolve 60 g of sodium hydroxide (NaOH) in about 200 mL of water. When dissolution is complete, cool, dilute to 500 mL with water, and store in a plastic bottle.*

112.3 *Tungsten Accelerator*.

112.4 *Other Reagents*—See the Reagents Section of the Total Carbon by the Combustion Gravimetric Method in the Reagents Section of Test Methods E 350.

113. Procedure

113.1 *Sample Dissolution*:

13.1.1 Select the sample weight in accordance with the following:

Graphitic Carbon, %	Sample Weight, g
1.0 to 1.5	2
1.5 to 3.0	1

Weigh the sample to the nearest 0.5 mg and transfer to a 250-mL beaker. For cast iron use drillings and for ductile iron, use solid portions approximately 10 by 10 by 0.3 mm in size.

113.1.2 For the blank determination, weigh and transfer to a 250-mL beaker the same weight of accelerator iron as the weight of sample selected in 113.1.1.

NOTE 32—Duplicate blanks are recommended. It is also recommended that the operator analyze five replicate portions of a standard sample with alloy characteristics and a known graphitic carbon content close to the samples to be analyzed. The repeatability of these analyses should be less than 0.10 % and the average value should agree with the known graphitic carbon content within 0.10 %. If it does not, the test should be repeated until these criteria are met. Calculate repeatability as follows:

$$\text{Repeatability} = 1.41 \sqrt{\frac{\sum(\bar{x} - x)^2}{n}} \quad (15)$$

where:

\bar{x} = average of the five determinations and

x = value of a single determination.

113.1.3 Add 25 mL of methanol, 50 mL of water, and 5 mL of HNO₃. Cover the beaker at once and let stand 12 to 16 h. Add 20 mL of HNO₃ and let stand until further action ceases. Place on a hot plate heated to 50 to 60°C. When vigorous action ceases, add 4 to 5 drops of HF. Continue heating until dissolution is complete. If necessary, add water to maintain the original volume.

113.2 *Filtration*:

113.2.1 Place two glass-fiber filters in a vacuum filtration apparatus and moisten with water. Filter the solution with very gentle suction. Transfer the graphite to the filter and police the beaker thoroughly. Wash the sides of the funnel to deposit all the graphite on the fiber glass filter disk.

113.2.2 Wash the filter disk once with HCl (1 + 1), twice with hot water, three times with hot NaOH wash solution, twice with hot HCl (1 + 1) and five times with hot water, in the order given.

113.2.3 Turn off the suction and remove the top part of the filter assembly. Remove the top filter disk from the filter

support, fold in half, and place in an induction furnace combustion crucible containing the same accelerators to be used in determining the blank for the sample. Remove the bottom filter disk from the filter support and use it to gently wipe any graphite off of the upper and lower parts of the filter apparatus. Fold the filter disk in half and place it in the same combustion crucible.

113.2.4 Dry the crucible containing the filters and accelerators for 2 h at 105°C, and store in a desiccator.

113.3 *Combustion With Induction Furnace, Gravimetric Determination*:

113.3.1 *Preparation of Apparatus*—Assemble the combustion train to include an oxygen purifier, catalyst heater, particle filter, and carbon dioxide purifier. The oxygen must flow from the top of the combustion tube through an orifice so as to impinge on the surface of the sample.

113.3.2 *Conditioning of Apparatus*:

113.3.2.1 Transfer 1 to 2 g of a “warm-up” sample, containing approximately 0.5 % total carbon, to a combustion crucible and add the appropriate amounts of the necessary accelerators.

113.3.2.2 Open the furnace, position the crucible with the sample in the combustion tube, close the furnace, and adjust the oxygen flow rate to 1100 to 1200 mL/min. Sweep the system with oxygen for 30 s.

113.3.2.3 Open the stopcock(s) of the absorption bulb¹⁷ and connect it to the carbon train.

NOTE 33—**Caution:** Bulbs shall not be handled with bare fingers at any time. Weighing time, that is the interval from the completion of the burn and sweep to the completion of the weighing, must be closely controlled and kept rigidly constant.

113.3.2.4 Turn on the power switch of the furnace and record the time (if an automatic timer is used, adjust it for a 5-min burning period). Burn the sample for 5 min while controlling the plate current to maintain a temperature necessary to combust the sample.

NOTE 34—During the sample burn, oxygen is consumed at a rapid rate. If necessary, manually increase the oxygen flow rate to maintain a positive pressure within the combustion tube.

113.3.2.5 Sweep the system with oxygen, maintaining the original flow rate, after the combustion is complete.

NOTE 35—Oxygen flow rates and sweep times vary to some extent with equipment used and the type of sample to be analyzed. Sweep times of 2 to 5 min have been found to be adequate in most cases. A control sample with carbon content and alloy characteristics similar to the sample to be analyzed should be used to control these parameters. (Note 16).

113.3.2.6 Detach the absorption bulb, close the stopcock(s), and allow the bulb to cool to room temperature. Remove the crucible from the furnace.

113.3.2.7 Open the stopcock(s) of the absorption bulb momentarily to the atmosphere to equilibrate bulb conditions, and weigh the bulb to the nearest 0.2 mg.

NOTE 36—To check the performance of the apparatus, use a standard sample with a total carbon content approximately that of the graphite content of the sample to be analyzed as described in the Total Carbon by the Combustion Gravimetric Method in Test Methods E 351.

¹⁷ The Fleming, Turner, and Nesbitt type absorption bulbs, available from laboratory supply houses, have been found satisfactory for this purpose.

113.3.3 *Blank*—Proceed as in 113.1.2, 113.1.3, 113.2.1 and 113.2.2. To the induction furnace combustion crucible, add 1 g of iron and tin, copper-tin or tungsten accelerator or the required combinations of these to produce the necessary combustion temperature in the induction furnace being used and proceed as in 113.2.3 and 113.2.4. Continue as in 113.3.2–113.3.2.7 and 113.3.3. Run duplicate blanks, recording the bulb weights, calculating the successive weight differences, and averaging the values for the weight of CO₂ obtained.

113.3.4 *Sample Combustion*—Proceed as in 113.3.3. Use the same accelerator selection used in determining the blank for the sample.

113.4 *Combustion with Induction Furnace, Infrared Determination:*

113.4.1 *Preparation of Apparatus*—Proceed in accordance with the Preparation of Apparatus Section of the Total Carbon by the Combustion-Instrumental Measurement Method in Test Methods E 1019.

113.4.2 Calibrate the instrument as described for Range II and Range III of the Calibration Section of the Total Carbon by the Combustion-Instrumental Measurement Method in Test Methods E 1019.

113.4.3 *Blank*—Proceed as in 113.1.2, 113.1.3, 113.2.1 and 113.2.2. To the induction furnace combustion crucible add 1 g of iron and tin, copper-tin, or tungsten accelerator, or the required combination of these, to produce the necessary combustion temperature in the induction furnace being used and proceed as in 113.2.3 and 113.2.4. Place the crucible on the furnace pedestal and raise the pedestal into position. Start the analysis cycle. Refer to the manufacturer's recommended procedure regarding entry of sample weight and blank value. Record the blank value obtained.

113.4.4 *Sample Combustion*—Proceed as in 113.4.3 for the sample. Use the same accelerator selection used in determining the blank for the sample. Record the carbon value obtained.

114. Calculation

114.1 *Combustion with Induction Furnace, Gravimetric Determination:*

114.1.1 Calculate the percent of graphitic carbon as follows:

$$\text{Graphitic Carbon, \%} = \frac{(A - B) \times 0.2729}{C} \times 100 \quad (16)$$

where:

A = weight of CO₂ found in sample, g,

B = average weight of CO₂ found in blank, g, and,

C = weight of sample used, g.

114.2 *Combustion with Induction Furnace, Infrared Determination:*

114.2.1 Calculate the percent of graphitic carbon as follows:

$$\text{Graphitic carbon, \%} = D - E \quad (17)$$

where:

D = % carbon found in sample determination, and

E = average % carbon found in blank determination.

115. Precision and Bias

115.1 *Precision*—Five laboratories cooperated in testing this test method and obtained the precision data summarized in Table 11.

115.2 *Bias*—The accuracy of this test method can be inferred from the data in Table 11 by comparing the certified values for graphitic carbon with the average values obtained.

NOTE 37—Although this test method was tested to only 2.8 %, most commercial instruments are believed to be capable of analyzing samples containing graphitic carbon up to 4.5 %.

COPPER BY THE NEOCUPROINE PHOTOMETRIC METHOD

116. Scope

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

117. Summary of Method

117.1 See Section 115 of Test Methods E 350.

118. Concentration Range

118.1 See Section 116 of Test Methods E 350.

TABLE 11 Statistical Information-Graphitic Carbon Direct Combustion-Gravimetric and Infrared Absorption Methods

Test Specimen	Statistics	<i>IR</i>	<i>Gravimetric</i>	<i>IR and Gravimetric</i>
		(5 laboratories)	(2 laboratories)	(7 laboratories)
1. Ni-Cr Ductile Iron NBS 341 (1.23 %; range: 1.21 to 1.23 %)	<i>R</i> ₁ , E 173	0.062	0.094	0.072
	<i>R</i> ₂ , E 173	0.152	0.169	0.143
	Graphitic carbon found, %	1.352	1.348	1.351
2. Cast Iron NBS 51 (1.98 %; range: 1.96 to 2.00 %)	<i>R</i> ₁ , E 173	0.073	0.086	0.077
	<i>R</i> ₂ , E 173	0.073 ^A	0.086 ^A	0.077 ^A
	Graphitic carbon found, %	1.963	1.971	1.965
3. Ni-Cr Cast Iron NBS 82b (2.37 %; range: 2.36 to 2.39 %)	<i>R</i> ₁ , E 173	0.094	0.047	0.084
	<i>R</i> ₂ , E 173	0.111	0.061	0.100
	Graphitic carbon found, %	2.318	2.337	2.324
4. Cast Iron NBS 122e (2.78 %; range: 2.77 to 2.78 %)	<i>R</i> ₁ , E 173	0.133	0.044	0.115
	<i>R</i> ₂ , E 173	0.223	0.172	0.198
	Graphitic carbon found, %	2.705	2.722	2.710

^AMSW > MSL ± C *R*₁ = *R*₂

119. Stability of Color

119.1 See Section 117 of Test Methods E 350.

120. Interferences

120.1 See Section 118 of Test Methods E 350.

121. Reagents

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

122. Preparation of Calibration Curve

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

123. Procedure

123.1 *Test Solution:*

123.1.1 Select a sample in accordance with the following:

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.03 to 0.15	1.00	1.0	100	20
0.10 to 0.25	1.00	1.0	250	30
0.20 to 0.50	1.00	0.5	250	15
0.40 to 1.00	1.00	0.5	500	15
0.80 to 1.50	1.00	0.1	500	10
1.40 to 3.00	1.00	0.1	1000	10
2.80 to 5.00	0.60	0.1	1000	10
4.80 to 7.50	0.40	0.1	1000	5

Transfer it to a 250-mL Erlenmeyer flask.

123.1.2 If the sample is other than white iron, proceed as directed in 121.1.2 of Test Methods E 350; treat samples of white iron as directed in 123.1.2.1.

123.1.2.1 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 15 mL of HClO₄ and a sufficient amount of HF to volatilize the silica.

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

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

124. Calculation

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

125. Precision

125.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 12. Although a sample covered by this method with copper concentration at approximately 7.50% was not available for testing, the precision data for specimen 6 should apply.

TABLE 12 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 3, E 350	0.021	0.004	0.010
2. Cast iron 1.07Ni-0.32Cr (NBS 82b, 0.038 Cu)	0.035	0.004	0.007
3. Cast iron high (0.79) phosphorus (NBS 7g, 0.128 Cu)	0.129	0.014	0.012
4. Cast iron (NBS 4j, 0.24 Cu)	0.239	0.017	0.016
5. Cast iron (NBS 5k, 1.50 Cu)	1.51	0.04	0.05
6. Cast iron 14Ni-5.5Cu-2Cr (NBS 115a, 5.52 Cu)	5.53	0.19	0.18

LEAD BY THE ION-EXCHANGE—ATOMIC ABSORPTION METHOD

126. Scope

126.1 This method covers the determination of lead in concentrations from 0.001 to 0.15 %.

127. Summary of Method

127.1 See Section 133 of Test Methods E 350.

128. Concentration Range

128.1 See Section 134 of Test Methods E 350.

129. Interferences

129.1 See Section 135 of Test Methods E 350.

130. Apparatus

130.1 See Section 136 of Test Methods E 350.

131. Reagents

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

132. Preparation of Calibration Curve

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

133. Procedure

133.1 *Test Solution:*

133.1.1 Proceed as directed in 139.1.1 of Test Methods E 350.

133.1.2 If the sample type is other than white iron, add 40 mL of HCl and 10 mL of HNO₃, or other ratios and concentrations of these acids as required for the decomposition of special grades of alloys. Cover the beaker and heat as required

until action ceases. Substitute a ribbed cover glass, and evaporate the solution to dryness. Add 40 mL of HCl (1 + 1) and digest until soluble salts are dissolved. Treat samples of white iron as directed in 133.1.2.1.

133.1.2.1 Crush the material in an iron mortar and use only particles passing through a No. 100 (150- μ m) sieve. Transfer the sample to a 600-mL beaker. Cover the beaker and add 40 mL of HNO₃ and 10 mL of HBr. Heat cautiously to dissolve the sample. Substitute a ribbed cover glass, evaporate the solution to a syrupy consistency, add 20 mL of HCl, and evaporate to dryness. Proceed as directed in 133.1.3.

133.1.3 Proceed as directed in 139.1.3 through 139.1.7 of Test Methods E 350.

133.2 *Reagent Blank*—Proceed as directed in 150.2 of Test Methods E 350.

133.3 *Photometry*—Proceed as directed in 139.3 of Test Methods E 350.

134. Calculation

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

135. Precision

135.1 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 13, should apply.

SULFUR BY THE CHROMATOGRAPHIC GRAVIMETRIC METHOD

(This method, which consisted of Sections 136 through 143 of this standard, was discontinued in 1980.)

CHROMIUM BY THE PEROXYDISULFATE-OXIDATION TITRIMETRIC METHOD

(This method, which consisted of Sections 144 through 151 of this standard, was discontinued in 1980.)

MANGANESE BY THE PEROXYDISULFATE-ARSENITE TITRIMETRIC METHOD

152. Scope

152.1 This method covers the determination of manganese in concentrations from 0.10 to 3.50 %

TABLE 13 Statistical Information—Lead

Test Specimen	Lead Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 1, E 353	0.0004	0.0002	0.0003
2. No. 2, E 353	0.0010	0.0001	0.0005
3. No. 3, E 353	0.0029	0.0004	0.0004
4. No. 4, E 353	0.0063	0.0009	0.0010
5. No. 5, E 353	0.0126	0.0012	0.0028
6. No. 6, E 353	0.106	0.023	0.031
7. No. 7, E 350	0.217	0.010	0.049

153. Summary of Method

153.1 Manganese ions in a sulfuric-phosphoric-nitric acid medium, or in this medium with perchloric acid present, are oxidized to permanganic acid by ammonium peroxydisulfate in the presence of silver ions. The permanganic acid is titrated with standard sodium arsenite solution.

154. Interferences

154.1 Elements ordinarily present do not interfere if their concentrations are under the maximum limits shown in 1.1. Chromium obscures the end point when more than 5 mg is present. If the sample contains between 5 and 15 mg of chromium, the color is compensated for by the addition of potassium dichromate solution to the solution used for standardization. When the sample contains more than 15 mg of chromium, it is necessary to remove it by volatilization as chromyl chloride or by precipitation with zinc oxide.

154.2 Graphitic carbon interferes in the titration; therefore it must be removed before oxidation of the manganese with ammonium peroxydisulfate.

155. Apparatus

155.1 *Platinum Cones*.

156. Reagents

156.1 *Ammonium Peroxydisulfate Solution* (250 g/L)—Dissolve 25 g of ammonium peroxydisulfate [(NH₄)₂S₂O₈] in water and dilute to 100 mL. Do not use a solution that has stood more than 1 day.

156.2 *Iron, Low in Manganese*—Use iron with maximum manganese concentration not greater than 0.002 %.

156.3 *Manganese Standard Solution A* (1 mL = 0.0008 g Mn)—Transfer an amount of high-purity manganese of known assay, equivalent to 1.6000 g of manganese, weighed to the nearest 0.1 mg, to a 250-mL beaker. Add 20 mL of HNO₃ (1 + 1) and heat gently to dissolve the metal and expel oxides of nitrogen. Cool, transfer to a 2-L volumetric flask, dilute to volume, and mix.

156.4 *Manganese, Standard Solution B* (1 mL = 0.0004 g Mn)—Using a pipet, transfer 50 mL of manganese Solution A (1 mL = 0.0008 g Mn) to a 100-mL volumetric flask, dilute to volume, and mix.

156.5 *Mixed Acids*—Slowly add 100 mL of H₂SO₄ to 525 mL of water while stirring. Cool, add 125 mL of H₃PO₄ and 250 mL of HNO₃, and mix.

156.6 *Potassium Dichromate Solution* (1 mL = 0.001 g Cr)—Dissolve 2.830 g of potassium dichromate (K₂Cr₂O₇) in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

156.7 *Silver Nitrate Solution* (8 g/L)—Reagent No. 133.

156.8 *Sodium Arsenite Solution A* (20 g/L)—Dissolve 20 g of sodium arsenite (NaAsO₂) in water, and dilute to 1 L.

156.9 *Sodium Arsenite Standard Solution B* (1 mL = 0.0005

g Mn)—Dilute 100 mL of sodium arsenite Solution A (20 g/L) to 1 L, and filter if not clear. Saturate the solution with carbon dioxide. Standardize as directed in 157.1.3–157.1.6.

156.10 *Zinc Oxide Suspension* (165 g/L)—Reagent No. 111.

157. Procedure

157.1 *For Samples Containing Less Than 5 mg of Chromium*—

157.1.1 Select a sample in accordance with the following, weigh it to the nearest 0.5 mg, and transfer to a 500-mL Erlenmeyer flask (Note 39).

Manganese, %	Sample weight, g
0.1 to 2.0	1.00
1.9 to 3.5	0.50

NOTE 38—If more than 0.020 g of manganese is present, some manganese may precipitate as manganese dioxide during oxidation with ammonium peroxydisulfate, causing low results.

157.1.2 Add 30 mL of water, 30 mL of mixed acids, and a few drops of HF, heat until the sample is decomposed, and boil to expel oxides of nitrogen. Add 50 mL of water and filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 39). Dilute to 250 mL and proceed as directed in 157.1.4 and 157.1.5.

NOTE 39—If there is reason to suspect that the sample contains acid-insoluble manganese compounds, transfer the paper and residue to a platinum crucible. Dry the paper and heat at 600°C until the carbon has been removed. Finally ignite 30 min at 1100°C, or until volatile oxides have been driven off. Cool, add 1 to 3 g of sodium hydrogen sulfate (fused), and heat until fusion of the manganese compounds occurs. Leach the melt in a 250-mL beaker containing 40 mL of water. Remove the crucible and rinse it with water. Transfer the solution to the filtrate.

157.1.3 For standardization, transfer to a 500-mL Erlenmeyer flask approximately the same weight of iron, within 50 mg, as the weight of iron in the sample solution. Add 30 mL of mixed acids. Heat until dissolution is complete, and boil to expel oxides of nitrogen. Using a pipet, transfer a portion of either (or both) manganese Solution A (1 mL = 0.008 g Mn) or B (1 mL = 0.004 g Mn) to the iron solution; use the nominal amount that will cause the volume of titrant for standardization and for the sample solution to agree within 2 mL. Dilute to 250 mL and proceed as directed in 157.1.4–157.1.6.

157.1.4 Add 10 mL of AgNO₃ solution and 15 mL of (NH₄)₂S₂O₈ solution to the sample solution and the standardization solution. Heat to boiling, and boil briskly for 60 to 90 s. Cool to 5 to 10°C in an ice bath.

157.1.5 Using a 50-mL buret, titrate each solution rapidly with the sodium arsenite solution (1 mL = 0.005 g Mn) to a clear, yellow end point that does not change with the addition of more arsenite solution. Calculate the manganese concentration of the sample as directed in 158 using the manganese equivalent found in 157.1.6.

157.1.6 Calculate the manganese equivalent of the sodium arsenite solution as follows:

$$\text{Manganese equivalent, g/mL} = A/B \quad (18)$$

where:

A = manganese present in the standardization solution, g, and

B = sodium arsenite solution required to titrate the manganese in the standardization solution, mL.

157.2 *For Samples Containing 5 to 15 mg of Chromium*:

157.2.1 Proceed as directed in 157.1.1.

157.2.2 Add 30 mL of water, 30 mL of mixed acids, and a few drops of HF, heat until the sample is decomposed, and boil to expel oxides of nitrogen. Add 50 mL of water and filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 37). Dilute to 250 mL and proceed as directed in 157.1.4 and 157.1.5.

157.2.3 For standardization, transfer to a 500-mL Erlenmeyer flask approximately the same weight of iron, within 50 mg, as the weight of iron in the sample solution. Add 30 mL of mixed acids. Heat until dissolution is complete, and boil to expel oxides of nitrogen. Using a pipet, transfer a portion of either (or both) manganese Solutions A (1 mL = 0.0008 g Mn) or B (1 mL = 0.0004 g Mn) to the iron solution; use the nominal amount that will cause the volume of titrant for standardization and for the sample solution to agree within 2 mL. Add an amount of potassium dichromate solution (1 mL = 0.001 g Cr) that will provide a chromium content within 20 % of that of the sample solution. Dilute to 250 mL and proceed as directed in 157.1.4 through 157.1.6.

157.3 *For Samples Containing More Than 15 mg of Chromium*—Proceed as directed in 157.3.1 if chromium is to be volatilized as chromyl chloride, or as directed in 157.3.2 if it is to be removed by precipitation with zinc oxide.

157.3.1 *Removal of Chromium by Volatilization as Chromyl Chloride*:

NOTE 40—The volatilization of chromium as chromyl chloride may be used for the separation of chromium when this can be accomplished without spattering and consequent loss of manganese during volatilization. (Molybdenum and tungsten in high concentrations will precipitate during fuming, causing the physical loss just mentioned.)

157.3.1.1 Proceed as directed in 157.1.1.

157.3.1.2 Add 15 mL of HCl, 5 mL of HNO₃, and a few drops of HF. Heat until the sample has decomposed, then dilute to 75 mL. Cool and filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 38). Add 20 mL of HClO₄, heat to fumes, and continue fuming until the chromium is oxidized and the white HClO₄ vapors are present only in the neck of the flask. Add, with care, 1.0 to 1.5 mL of HCl, allowing it to drain down the side of the flask. Make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming until salts begin to separate. Cool, cautiously add 30 mL of the mixed acids, dilute to 250 mL with hot water, and boil for 2 min. Proceed as directed in 157.1.4 and 157.1.5.

157.3.1.3 For standardization, transfer approximately the same weight of iron, within 50 mg, as the weight of iron in the sample to a 500-mL Erlenmeyer flask. Add 15 mL of HCl and 5 mL of HNO₃. Heat until the sample is decomposed. Using a pipet, transfer a portion of either (or both) manganese Solution A (1 mL = 0.0008 g Mn) or B (1 mL = 0.0004 g Mn) to the iron solution; use the nominal amount that will cause the volume of

titrant for standardization and for the sample solution to agree within 2 mL. Add 10 mL of HClO₄, heat to fumes, and continue fuming until salts begin to separate. Cool, cautiously add 30 mL of mixed acids, dilute to 250 mL with hot water, and boil for 2 min. Proceed as directed in 157.1.4 through 157.1.6.

157.3.2 Removal of Chromium by Precipitation with Zinc Oxide:

NOTE 41—The zinc oxide procedure is used to separate chromium, iron, titanium, zirconium, tungsten, most of the molybdenum, and other elements from manganese. Cobalt, nickel, and part of the copper accompany manganese in the filtrate. This separation may be used for all compositions covered by this method.

157.3.2.1 Proceed as directed in 157.1.1.

157.3.2.2 To decompose the sample, add 25 mL of H₂SO₄ (1 + 5) and, when the reaction ceases, 5 mL HNO₃; or, alternatively, decompose in 50 mL of HNO₃ (1 + 1). Heat gently until the sample and carbides have been decomposed (Note 42), boil to expel oxides of nitrogen, cool, and dilute to 100 mL.

NOTE 42—If the sample is not decomposed by HNO₃ or H₂SO₄, dissolve it in 15 mL of HCl plus 10 mL of HNO₃, adding a few drops of HF if necessary. Heat to decompose, then add 10 mL of HClO₄, and heat until chromium has been oxidized and carbides decomposed. Cool, dilute to 100 mL, add enough H₂O₂ to reduce chromium, boil to remove excess peroxide, cool, and proceed as directed in 157.3.2.3.

157.3.2.3 Dilute to 100 mL, filter through a medium paper into a 500-mL Erlenmeyer flask. Wash the paper and residue with hot water (Note 39).

157.3.2.4 Nearly neutralize the solution with NH₄OH, but do not precipitate hydroxides. 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 38). Allow the precipitate to settle. With the aid of suction, filter the solution through a coarse 15-cm paper supported on a cone. Transfer the filtrate from the suction flask to a 600-mL beaker. Wash the precipitate thoroughly with cold water. Add 30 mL of the mixed acids to the filtrate and reserve the filtrate.

NOTE 43—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.

157.3.2.5 Transfer the filter paper containing the ZnO precipitate to the 500-mL Erlenmeyer flask, and add 25 mL of H₂SO₄ (1 + 5). Macerate the paper and dilute the solution to about 100 mL. Repeat the ZnO separation, proceeding as directed in 157.3.2.3, and transfer the filtrate from the suction flask to the filtrate reserved in 157.3.2.4. Boil, dilute to 250 mL, and proceed as directed in 157.1.4 and 157.1.5.

157.3.2.6 For standardization, using a pipet transfer a portion of either (or both) manganese Solution A (1

mL = 0.0008 g Mn) or B (1 mL = 0.0004 g Mn) to 30 mL of mixed acids; use the nominal amount that will cause the volume of titrant for standardization and for the sample solution to agree within 2 mL. Boil to expel oxides of nitrogen, and dilute to 250 mL with water. Proceed as directed in 157.1.4–157.1.6.

158. Calculation

158.1 Calculate the percentage of manganese as follows:

$$\text{Manganese, \%} = [(A \times B)/C] \times 100 \quad (19)$$

where:

A = sodium arsenite solution required to titrate the manganese in the sample, mL,

B = manganese equivalent of the sodium arsenite solution as determined in the appropriate standardization solution, and

C = sample used, g.

159. Precision

159.1 Eight laboratories cooperated in testing this method, with one laboratory reporting a second pair of values in each instance; the data are summarized in Table 14.

159.2 Six laboratories cooperated in testing this method using a test specimen for which removal of chromium was required; the data are summarized in Table 15. Acid insoluble manganese was present and was treated in accordance with Note 39.

PHOSPHORUS BY THE ALKALIMETRIC METHOD

160. Scope

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

161. Summary of Method

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

162. Interferences

162.1 To avoid retardation of the formation of the precipitate and its contamination by vanadium, the latter is reduced to the quadrivalent state and the precipitation is performed at 10 to 20°C.

162.2 To eliminate interference of silicon, HF is added

TABLE 14 Statistical Information—Manganese

Test Specimen	Manganese Found, % ^A	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. White iron (NBS 3a, 0.048 Cr, 0.317 Mn)	0.311	0.008	0.048
2. Cast iron (NBS 4i, 0.104 Cr, 0.793 Mn)	0.799	0.021	0.061
3. Cast iron (BCS 236/2, 0.03 Cr, 1.14 Mn)	1.16	0.02	0.06
4. No. 4, E 350	1.89	0.03	0.06

^ARemoval of chromium not required.

TABLE 15 Statistical Information—Manganese (Chromium Removal Procedure)

Test Specimen	Chromium Removal Procedure	Manganese Found, %, by Laboratory No.						Average Mn, %
		1	2	3	4	5	6	
1. Cast iron 13 Ni-4Cr-5Cu (BCS 173/1, 0.82 Mn)	volatilization	0.831	...	0.815	0.820	0.810	0.850	0.826
	volatilization	0.831	...	0.819	...	0.820	0.841	0.817
	precipitation	...	0.819	0.813	0.810	0.820	...	
	precipitation	...	0.820	0.820	...	0.820	...	

during dissolution of samples containing silicon in concentrations greater than 0.5 %.

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

162.4 Graphitic carbon must be removed before precipitating the phosphorus.

163. Apparatus

163.1 *Funnel, Hirsch Porcelain*, 56-mm plate diameter and 94-mm top diameter. Place a 5.5-cm fine qualitative, smooth-surface filter paper, over the perforated filter plate. Place an 11-cm fine qualitative, rough-surface filter paper, or equivalent, on the funnel, moisten it with KNO_3 solution, and then press it gently into the funnel so that its center lies flat against the first paper. Fold the edge of the paper in a fluted manner and press it against the sides of the funnel. Add enough filter paper pulp to cover the flat center of the filter paper.

163.2 *Funnel, Glass, 60°*, fitted with a 25-mm diameter perforated porcelain filtering disk. Place a 5.5-cm fine qualitative, smooth-surface filter paper, over the perforated plate. Place an 11-cm fine qualitative, rough-surface filter paper, on the funnel, moisten it with KNO_3 solution, and then press it gently into the funnel so that its center lies flat against the first paper. Fold the edge of the paper in a fluted manner and press it against the sides of the funnel. Add enough filter paper pulp to cover the flat center of the filter paper.

164. Reagents

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

164.2 *Ferrous Sulfate Solution (100 g/L)*—Dissolve 100 g of ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in 1 L of H_2SO_4 (5 + 95).

164.3 *Nitric Acid, Standard* (1 mL = approximately 0.00013 g P)—Transfer 6.3 mL of HNO_3 to a 1-L volumetric flask containing 500 mL of water. Dilute to volume, and mix. Standardize the solution as follows: Using a pipet, transfer 20 mL of NaOH standard solution (1 mL = approximately 0.00013 g P), described in 164.7, to a 125-mL Erlenmeyer flask. Add 3 drops of phenolphthalein indicator solution and titrate with the HNO_3 until 1 drop causes the pink color to disappear. Calculate the phosphorus equivalent as follows:

$$P \text{ phosphorus equivalent, g P/mL} = (A \times B)/C \quad (20)$$

where:

A = NaOH solution, mL,

B = phosphorus equivalent of the NaOH solution, and

C = HNO_3 solution, mL.

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

164.5 *Potassium Nitrate Solution (10 g/L)*— Dissolve 10 g of potassium nitrate (KNO_3) in water, dilute to 1 L, and mix.

164.6 *Potassium Permanganate Solution (25 g/L)*— Dissolve 26 g of potassium permanganate (KMnO_4) in water, dilute to 1 L, and mix.

164.7 *Sodium Hydroxide, Standard Solution* (1 mL = approximately 0.00013 g P)—Transfer 4.0 g of sodium hydroxide (NaOH) to a 1-L volumetric flask, and dissolve in freshly boiled water that has been cooled to room temperature. Dilute to volume with the boiled water and mix. Standardize the solution as follows: Transfer to a 300-mL Erlenmeyer flask 0.5000 g of the National Bureau of Standards standard sample of potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) previously dried for 2 h at 105°C. Add 100 mL of freshly boiled water that has been cooled to room temperature and 3 drops of phenolphthalein indicator solution. Swirl to dissolve the salt. Titrate with the NaOH solution until 1 drop produces a pink color. Calculate the phosphorus equivalent as follows:

$$\begin{aligned} \text{Phosphorus equivalent, g P/mL} & \quad (21) \\ & = A \times (0.001347/B) \times 0.2042 \end{aligned}$$

where:

A = potassium acid phthalate, g, and

B = NaOH solution, mL.

165. Procedure

165.1 Select and weigh a sample to the nearest 5 mg in accordance with the following:

Phosphorus, %	Sample Weight, g
0.01 to 0.10	2.0
0.10 to 0.25	1.0
0.25 to 0.90	0.5

Transfer the sample to a 300-mL Erlenmeyer flask.

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

165.3 If the sample is other than a white iron, add 100 mL of HNO_3 (1 + 3) and, if the silicon concentration is greater than 0.5 %, 3 to 5 drops of HF. Treat samples insoluble in HNO_3 (1 + 3) as directed in 165.4; treat samples of white iron as directed in 165.5. When the sample is decomposed, add KMnO_4 solution dropwise, while heating the solution, until a

permanent, brown precipitate forms. Boil the solution 3 min. Add H₂SO₃ dropwise until the precipitate dissolves, and boil 3 min to expel oxides of nitrogen. If graphitic carbon or other insoluble material is present, filter through an 11-cm coarse paper into a 300-mL Erlenmeyer flask. Wash the flask and paper several times with hot water, discard the precipitate. Adjust the volume to 100 mL, and cool to room temperature.

165.4 If the sample is not soluble in HNO₃ (1 + 3), dissolve it with HNO₃ and HCl; if the silicon concentration is greater than 0.5 %, add 3 to 5 drops of HF. Heat, as required, to hasten dissolution. When the sample is decomposed, add 15 mL of HClO₄, heat to fumes, and evaporate nearly to dryness. Cool, add 75 mL of HNO₃ (1 + 3), and heat at 90°C until the salts are dissolved. Add KMnO₄ solution dropwise, while heating the solution, until a permanent, brown precipitate forms, and boil 3 min. Add H₂SO₃ dropwise until the precipitate dissolves, and boil 3 min to expel oxides of nitrogen. If graphitic carbon or other insoluble matter is present, filter through an 11-cm coarse paper into a 300-mL Erlenmeyer flask. Wash the flask and paper several times with hot water. Discard the precipitate, adjust the volume to 100 mL, and cool to room temperature.

165.5 If the sample is a white iron, crush it in an iron mortar and use only particles passing through a No. 50 (297-μm) sieve. Proceed as directed in 165.1 and 165.2, and then add 30 mL of HNO₃ and 10 mL of HBr. Heat cautiously to dissolve the sample. Add 3 to 5 mL of HF and 15 mL of HClO₄, heat to fumes, and evaporate nearly to dryness. Cool, add 75 mL of HNO₃ (1 + 3), and heat at 90°C until the salts are dissolved. Add KMnO₄ solution dropwise, while heating the solution, until a permanent, brown precipitate forms, and boil 3 min. Add H₂SO₃ dropwise until the precipitate dissolves, and boil 3 min to expel the oxides of nitrogen. If insoluble matter is present, filter through a coarse paper into a 300-mL Erlenmeyer flask. Wash the flask and the paper several times with hot water. Discard the precipitate, adjust the volume to 100 mL, and cool to room temperature.

165.6 While swirling the flask, slowly add 20 mL of NH₄OH for a 0.5 or 1-g sample, or 17 mL of NH₄OH for a 2-g sample, so that no precipitate forms (Note 44). Adjust the temperature to 45°C.

NOTE 44—The quantity of NH₄OH specified should result in a pH of 0.1 to 0.6 after the addition of the NH₄OH and a pH of 0.2 after the addition of ammonium molybdate solution to the flask. Care must be exercised in the dissolution step to prevent excessive loss of acid. An excessive amount of NH₄OH will precipitate iron as ferric hydroxide. Failure to carefully control the acidity will retard the precipitation of the ammonium phosphomolybdate.

165.7 Add 40 mL of ammonium molybdate solution, stopper the flask, and shake 10 min on a mechanical shaker. If the vanadium concentration is less than 0.1 %, allow the precipitate to settle at least 20 min at room temperature: for samples containing higher concentrations of vanadium, cool the solution to 10 to 20°C, add 5 mL of ferrous sulfate solution and 2 to 3 drops of H₂SO₃, and allow the precipitate to settle at least 20 min at 10 to 20°C.

165.8 Filter the solution with the aid of suction using a Hirsch porcelain crucible (163.1) or a glass funnel fitted with a perforated porcelain filtering disk (163.2). Rinse the flask 3 to 5 times with a total volume of approximately 40 mL of KNO₃

solution, transferring all the precipitate to the filter. Wash the filter paper 12 to 15 times with a total volume of approximately 100 mL of KNO₃ solution (Note 45). Discard the filtrate.

NOTE 45—Analysts not having experience with this method should familiarize themselves with the proper washing technique. Blanks obtained by the method as written should not be measurable provided the reagents are of the quality specified in Practices E 50.

165.9 Return the precipitate and the filter papers to the flask, and add 50 to 75 mL of freshly boiled water that has been cooled to room temperature. Shake the flask to break up the filter paper. Using a 25-mL buret, or a 50-mL buret for samples containing more than 0.5 % phosphorus, add enough NaOH standard solution to dissolve the precipitate. Stopper the flask and let stand, shaking or swirling the flask occasionally, until a change in color from yellow to white or almost white is noted; then add 2 mL in excess. Add 3 drops of phenolphthalein indicator solution, and shake. Record the buret reading.

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

166. Calculation

166.1 Calculate the percentage of phosphorus as follows:

$$P \text{ phosphorus, \%} = \frac{(AB - CD) - (EB - FD)}{G} \times 100 \quad (22)$$

where:

- A = NaOH solution used for the sample (165.9), mL,
- B = phosphorus equivalent of the NaOH solution,
- C = HNO₃ solution required by the sample (165.10), mL,
- D = phosphorus equivalent of the HNO₃ solution,
- E = NaOH solution used for the blank, mL,
- F = HNO₃ solution required by the blank, mL, and
- G = sample used, g.

167. Precision¹⁸

167.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 16. Although

¹⁸ Supporting data are available from ASTM Headquarters. Request RR:E03-1002.

TABLE 16 Statistical Information—Phosphorus

Total Specimen	Phosphorus Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 1, E 353	0.017	0.001	0.006
2. No. 2, E 353	0.017	0.004	0.007
3. No. 3, E 353	0.024	0.003	0.011
4. No. 4, E 353	0.024	0.003	0.009
5. No. 5, E 350	0.045	0.003	0.009
6. Cast iron (NBS 4j, 0.17 P)	0.166	0.007	0.012
7. No. 6, E 350	0.274	0.017	0.017
8. Cast iron (NBS 7g, 0.794 P)	0.783	0.031	0.048

samples at the lower end of the scope were not tested, the precision data obtained for other types of alloys using the methods indicated in Table 16 should apply.

NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD

168. Scope

168.1 This method covers the determination of nickel in concentrations from 0.1 to 36.00 %.

169. Summary of Method

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

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

170. Interferences

170.1 Cobalt, copper, and manganese are present in the divalent state and consume dimethylglyoxime, making it necessary to add an excess of the precipitant over that required to precipitate nickel. When the anion-exchange separation is used, manganese is present in the solution from which nickel is precipitated, and an excess of the precipitant is required.

171. Apparatus

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

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

171.3 *pH Meter*—Apparatus No. 3A.

172. Reagents

172.1 *Ammonium Citrate Solution* (200 g/L)—*Dissolve 200 g of diammonium hydrogen citrate [(NH₄)₂HC₆H₅O₇] in 600 mL of water. Filter and dilute to 1 L.*

172.2 *Anion Exchange Resin*:

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

having a crosslinkage of 8 % and a 200 to 400 nominal mesh size.¹⁹ To remove those beads greater than 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.

172.2.2 Prepare the column as follows: Place a 10- to 20-mm layer of glass wool or poly(vinyl chloride) plastic fiber in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 140 mm. Place a 20-mm layer of glass wool or poly(vinyl chloride) plastic fiber at the top of the resin bed to protect it from being carried into suspension when the solutions are added. While passing a minimum of 100 mL of HCl (3 + 1) through the column, with the hydrostatic head 100 mm above the top of the resin bed, adjust the flow rate, by means of the upper stopcock, to not more than 3.0 mL/min. Drain to 5 to 10 mm above the top of the resin bed and then close the lower stopcock.

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

173. Procedure

173.1 *Double Precipitation*:

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

Nickel, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.1 to 1.0	3.0	1.0
1.0 to 5.0	1.0	0.5
5.0 to 10.0	0.5	0.2
10.0 to 20.0	0.25	0.1
20.0 to 36.0	1.0	0.5

Transfer it to a 600-mL beaker.

173.1.2 If the sample is other than white iron, add 60 mL of HCl (1 + 1) and 10 mL of HNO₃. Heat to dissolve the sample and boil to expel oxides of nitrogen. Cool the solution and add 30 mL of HClO₄. Heat to strong fumes of HClO₄ and continue fuming for 5 min. Cool, and dilute to 100 mL with water. Treat samples of white iron as directed in 173.1.3.

173.1.3 If the sample is a white iron, crush it in an iron mortar and weigh only particles passing through a No. 100 (150- μ m) sieve. Transfer the sample to a 250-mL beaker, and add 20 mL of HNO₃ and 20 mL of HBr. Cover the beaker and

¹⁹ Dowex 1, manufactured by the Dow Chemical Co., Midland, MI, has been found satisfactory.

heat cautiously to dissolve the sample. Cool, rinse the cover glass, add 30 mL of HClO_4 , and heat to strong fumes of HClO_4 . Continue fuming for 5 min. Cool, and dilute to 100 mL with water.

173.1.4 Filter the solution obtained in 173.1.2 or 173.1.3 through an 11-cm coarse paper into a 600-mL beaker. Transfer any insoluble matter to the paper with hot HCl (5 + 95). Wash the beaker and paper alternately with hot HCl (5 + 95) and hot water until iron salts are removed. Finally, wash the paper 3 times with 5-mL portions of hot water. Discard the residue. If the nickel concentration is greater than 20 %, transfer the filtrate from the beaker to a 200-mL volumetric flask, dilute to volume, and mix. Using a pipet, transfer a 20-mL aliquot to a 600-mL beaker and add 10 mL of HCl .

173.1.5 Add 200 mL of water and 20 mL of ammonium citrate solution. Using a pH meter, adjust the pH to at least 7.5 with NH_4OH . Acidify the solution with HCl to $\text{pH } 6.3 \pm 0.1$.

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

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

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

173.1.9 Add 30 mL of HNO_3 and 15 mL of HClO_4 . Evaporate to strong fumes and continue fuming for 5 min. Cool and add 50 mL of water.

173.1.10 Filter through an 11-cm coarse paper into a 600-mL beaker. Wash the paper 5 times with HCl (5 + 95) and 3 times with water. Dilute the filtrate to 200 mL with water and proceed as directed in 173.3–173.7.

173.2 Anion-Exchange Separation:

173.2.1 Proceed as directed in 173.1.1.

173.2.2 If the sample is other than white iron, proceed as directed in 173.1.2.

173.2.3 If the sample is a white iron, proceed as directed in 173.1.2, but dilute with only 50 mL of water.

173.2.4 Filter the solution obtained in 173.2.2 or 173.2.3 through an 11-cm coarse paper, collecting the filtrate in a 250-mL beaker. Transfer any insoluble matter to the paper with hot HCl (5 + 95). Wash the paper alternately with hot water and hot HCl (5 + 95) until iron salts are removed. Finally, wash the paper 3 times with 5-mL portions of hot water. Discard the residue.

173.2.5 Carefully evaporate to dryness at moderate heat to avoid spattering. Cool, add 10 mL of HCl , and evaporate to dryness. Cool, add 20 mL of HCl (3 + 1) and heat, if necessary, to dissolve salts, but avoid loss of HCl by overheating or prolonged heating.

173.2.6 Precondition the ion-exchange column with 50 mL of HCl (3 + 1), and adjust the flow rate by means of the upper stopcock to not more than 3.0 mL/min. Allow the acid to drain to 5 to 10 mm from the top of the resin bed.

173.2.7 Place a clean 600-mL beaker under the ion-exchange

column and open the bottom stopcock. Transfer the solution from 173.2.5 to the column. Allow the sample solution to drain to 5 to 10 mm from the top of the resin bed. Rinse the 250-mL beaker with a 5-mL portion of HCl (3 + 1) and transfer the rinsing to the column. When it has drained to 5 to 10 mm above the resin bed, add a second 5-mL rinse portion from the 250-mL beaker. Repeat this operation 3 more times, and allow the level to drop to 5 to 10 mm above the resin bed before adding the next. Add sufficient HCl (3 + 1) at the top of the column to collect a total of 200 mL in the 600-mL beaker. Close the lower stopcock and reserve the solution.

173.2.8 Precondition the column for the next sample as follows: Open the lower stopcock. Drain any remaining solution in the column to 5 to 10 mm from the top of the resin bed. Add HCl (1 + 19) in 50-mL increments until iron has been eluted and the eluate is visibly free of color (approximately 300 mL). Drain the solution to 5 to 10 mm from the top of the resin bed and close the lower stopcock. If the column is not to be used immediately, cover, and store. If another sample solution is to be put through the column, proceed as directed in 173.2.6.

173.2.9 Heat the solution reserved in 173.2.7 to boiling and evaporate to 60 mL to remove excess HCl . If the sample contains less than 20 % nickel, cool and dilute to 200 mL. If the sample contains more than 20 % nickel, cool, transfer the solution to a 200-mL volumetric flask, add 20 mL of HCl , dilute to volume, and mix. Using a pipet, transfer a 20 mL aliquot to a 600-mL beaker, and dilute to 200 mL with water.

173.3 Add 10 mL of ammonium citrate solution and 10 mL of HCl . Using a pH meter, adjust the pH to at least 7.5 with NH_4OH . Remove and rinse the electrodes with water, collecting the rinsings in the original beaker.

173.4 Add 2 mL of HCl and, while stirring the solution, add 10 mL of dimethylglyoxime solution plus an additional 0.4 mL for each milligram of nickel present. If the separation was made by anion-exchange, add an additional 0.4 mL for each milligram of manganese present.

173.5 Using a pH meter, adjust the pH to $7.4 + 0.1$ with NH_4OH . Remove and rinse the electrodes with water. Heat at 50 to 70°C for 30 min and allow to stand for at least 4 h at 20 to 25°C.

173.6 With the aid of suction, filter using a weighed (Note 46) fritted glass crucible. Wash the beaker and precipitate 6 times with cold water.

NOTE 46—Heat the crucible at 150°C, and cool in a desiccator before weighing.

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

174. Calculation

174.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = \frac{(A - B) \times 0.2032}{C} \times 100 \quad (23)$$

where:

A = weight of crucible and precipitate, g,

B = weight of crucible, g, and

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

175. Precision

175.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 17. Although a sample covered by this method with a nickel concentration at approximately 36 % was not available for testing, the precision data for specimen 3 should apply.

NICKEL BY THE ION EXCHANGE-ATOMIC ABSORPTION METHOD

176. Scope

176.1 This method covers the determination of nickel in concentrations from 0.005 to 1.00 %.

177. Summary of Method

177.1 Nickel is separated from interfering elements by elution from an anion exchange column using a hydrochloric acid solution. The eluate is aspirated into the air-acetylene flame. Spectral energy at 2320 Å from a nickel hollow-cathode tube is passed through the flame and the absorbance is measured. The spectrophotometer is calibrated with known concentrations of nickel.

178. Concentration Range

178.1 The recommended concentration range is from 0.001 to 0.010 mg of nickel per mL of solution.

179. Interferences

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

180. Apparatus

180.1 *Atomic Absorption Spectrophotometer*, capable of resolving the 2320 Å line, equipped with a nickel hollow-cathode tube whose radiation is modulated with a detector system tuned to the same frequency and with a premix air-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (0.015 mg/mL) produces an absorbance of 0.350 or higher, and a calibration curve whose deviation from linearity is within the limits defined in 182.3.

TABLE 17 Statistical Information—Chromium

Test Specimen	Nickel Found, %	Repeat-ability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. Cast iron (NBS 7g, 0.121 Ni)	0.115	0.006	0.006
2. Ni-Cr cast iron 1 Ni - .3 Cr (NBS 82b, 1.22 Ni)	1.22	0.05	0.06
3. Ductile iron (NBS 341, 20.32 Ni)	20.31	0.20	0.20

180.2 *Anion-Exchange Column*, approximately 25 mm in diameter and 300 mm long, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. Apparatus No. 8 may be adapted to this method. A reservoir for the eluants may be added at the top of the column. However, the eluants must be added as described in 183.1.4.

181. Reagents

181.1 Anion Exchange Resin:

181.1.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and 200 to 400 nominal mesh size.⁸ 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 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 to avoid undue clogging of the openings. When the bulk of the resin has settled in the 2-L beaker, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19) and stir vigorously, allow the resin to settle for 4 to 6 min, decant 150 to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more and reserve the coarser resin for the column preparation.

181.1.2 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 top of resin bed to protect it from being carried into suspension when the solutions are added. Add 100 to 125 mL of HCl (3 + 1) to the column and, when the solution level is 10 to 20-mm above the top of the resin bed, close the lower stopcock.

181.2 *Nickel, Standard Solution* (1 mL = 0.1 mg Ni)—Transfer 1.000 g of nickel (purity: 99.9 % minimum) to a 400-mL beaker. Add 50 mL of HNO₃ (1 + 1), cover and heat gently until dissolution is complete. Remove cover and evaporate to dryness slowly to prevent loss of spattering. Cool, rinse sides of beaker with water, add 10 mL HCl, and evaporate to dryness. Perform the rinse and evaporation procedure twice. Cool, add 50 mL of HCl (1 + 1). Warm gently to dissolve salts and dilute to 300 mL with water. Transfer solution to a 1-L volumetric flask, dilute to volume with water, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask. Dilute to volume with water, and mix.

NOTE 47—Prepare the dilute nickel standard solution immediately before preparation of the calibration solution described in 182.1 to maintain proper concentration.

182. Preparation of Calibration Curve

182.1 *Calibration Solutions*—Using pipets, transfer 0, 1, 3, 5, 7, 10, and 15 mL of nickel solution (1 mL = 0.1 mg Ni) to 100-mL volumetric flasks. Add 20 mL of HCl (1 + 1), dilute to volume with water, and mix. Do not use solutions that have stood more than 2 h.

182.2 *Photometry*:

182.2.1 With the nickel hollow-cathode tube in position, energized and stabilized, locate the wavelength setting in the vicinity of 2320 Å that gives the maximum response of the detector system.

182.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the nickel solution with the highest concentration from the series prepared as directed in 182.1 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 48—Recalibration is required whenever these parameters are changed.

182.2.3 Aspirate the nickel solution used in 182.2.2 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 reading as follows:

$$s = (A - B) \times 0.40 \quad (24)$$

where:

A = the highest of the six values found, and

B = the lowest of the six values found.⁷

182.2.4 Beginning with the solution to which no nickel was added in 182.1, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values recorded in 182.2.3 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, deposit in the burner or clogged capillary), correct it, and repeat the steps as directed in 182.2.1–182.2.4.

182.3 *Calibration Curve*—Plot the net absorbance values against milligrams of nickel per mL on rectangular coordinate paper. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \quad (25)$$

where:

C = absorbance value for 0.015 mg Ni/mL,

D = absorbance value for 0.010 mg Ni/mL, and

E = absorbance value for 0.005 mg Ni/mL.

If the calculated value is less than 0.60, correct the indicated malfunction or maladjustment of instrument or hollow-cathode tube and repeat the calibration.

183. Procedure

183.1 *Test Solution*:

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

Nickel, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution After Separation, mL	Aliquot Required, mL	HCl (1 + 1) in Final Dilution, mL	Final Dilution, mL
0.005 to 0.025	1.0	0.1	25	0	5	25
0.020 to 0.10	1.0	0.1	100	0	20	100
0.10 to 0.50	1.0	0.1	100	20	15	100
0.40 to 1.00	1.0	0.1	100	10	20	100

Transfer it to a 400-mL beaker.

183.1.2 If the sample is other than white iron, add 25 mL of HNO₃ (1 + 4). Cover the beaker and warm gently to dissolve. Rinse the sides of the beaker with water. Add 10 drops of HF, 5 mL of HCl, and 15 mL of HClO₄. Evaporate to dryness, carefully and with moderate heat to avoid spattering. Cool, rinse sides of beaker with water, add 10 mL of HCl, and evaporate to dryness carefully and with moderate heat. Cool, add 20 mL of HCl (3 + 1), warm gently to dissolve salts, and cool to room temperature.

NOTE 49—If precipitation remains after recommended procedures, filter the solution through glass wool placed in a funnel of the ion exchange column. Add all the rinsings and the eluant through this funnel to the column.

183.1.3 If the sample is a white iron, crush it in an iron mortar and weigh only particles passing through a No. 100 (150-μm) sieve. Transfer the sample to a 400-mL beaker, and add 20 mL of HNO₃ and 20 mL of HBr. Cover the beaker and heat cautiously to dissolve the sample. Cool, rinse the cover glass, add 30 mL of HClO₄, and heat to strong fumes of HClO₄. Evaporate to dryness, carefully and with moderate heat. Cool, rinse sides of beaker with water, add 10 mL of HCl, and evaporate to dryness, carefully and with moderate heat. Cool, add 20 mL of HCl (3 + 1), warm gently to dissolve salts, and cool to room temperature (Note 40).

183.1.4 Place a clean 400-mL beaker under the ion-exchange column. Transfer the solution obtained in 183.1.2 or 183.1.3 to the column and open the lower stopcock. When the solution reaches a level of 10 to 20 mm above the resin bed, rinse the original beaker with 5 to 6 mL of HCl (3 + 1) 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 (3 + 1) 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 (3 + 1) to the column until a total of 200 mL has been collected. Reserve the solution.

183.1.5 Precondition the column for the next test solution as follows: Open the stopcock. Drain the remaining solution in the column 10 to 20 mm above the top of the resin. Add in 50-mL increments, HCl (1 + 9) until the iron has been eluted, and the eluate is visibly free of color (Note 31). When the column is free of iron, drain the solution to 10 to 20 mm above the top of the resin and close the stopcock. If the column is not to be used immediately, cover and store. If it is to be used

immediately, pass 100 mL of HCl (3 + 1) through the column, and proceed as directed in 181.1.2.

NOTE 50—Approximately 300 mL of HCl (1 + 9) are required.

183.1.6 To the eluate obtained in 183.1.4, add 30 mL of HNO₃ and evaporate to approximately 100 mL. Add 20 mL of HNO₃ and 15 mL of HClO₄. Evaporate to dryness and cool. If the nickel content is greater than 0.10 % (183.1.1) add 20 mL HCl (1 + 1) and warm to dissolve salts. Cool to room temperature, and transfer to a 100-mL volumetric flask. Dilute to volume with water, and mix. If no dilution is necessary, add the amount of HCl (1 + 1) listed in 183.1.1, and warm gently to dissolve salts. Cool to room temperature, and transfer to appropriate volumetric flask (183.1.1). Dilute to volume with water, and mix.

183.2 Prepare a reagent blank by treating the same amounts of all reagents as directed in 183.1.1–183.1.6, but omitting the sample. Use reagents from the same lots for blank and test solutions.

183.3 *Photometry*—Aspirate and record the absorbance of the reference, calibration, test, and reagent blank solutions.

NOTE 51—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 182.2.4 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 182.2.2, or by more than 0.01 multiplied by the average of the six values used to calculate *s*, whichever is greater, determine the cause. Correct the deficiency (deposits in burner, clogged capillary, etc.), repeat the calibration procedure and recheck the readings of the test solutions and reagent blank solution.

184. Calculation

184.1 Convert the absorbance of the test solution and the reagent blank to mg of nickel per mL of the final test solution by means of the calibration curve. Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = \frac{(A - B) \times C}{W \times 10} \quad (26)$$

where:

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

185. Precision²⁰

185.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 18. Although samples covered by this method at the lower end of the scope were not tested, the data obtained for other types of alloys using the methods indicated in Table 18 apply.

TABLE 18 Statistical Information—Chromium

Test Specimen	Nickel Found, %	Repeat-ability (<i>R</i> ₁ , E 173)	Reproducibility (<i>R</i> ₂ , E 173)
1. No 1, E 350	0.0058	0.002	0.002
2. No 2, E 350	0.055	0.002	0.007
3. Cast Iron (NBS 7g, 120 Ni)	0.122	0.009	0.015
4. No 4, E 350	0.217	0.012	0.020
5. Cast Iron (NBS 82 ^a , 1.07 Ni)	1.07	0.052	0.069

TIN BY THE SOLVENT EXTRACTION—ATOMIC ABSORPTION METHOD

186. Scope

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

187. Summary of Method

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

188. Concentration Range

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

189. Interferences

189.1 Copper, when present above 0.1 g, interferes by precipitating as cuprous iodide (CuI). This interference may be eliminated by incorporating a suitable copper separation scheme into the procedure prior to the solvent extraction step.

190. Apparatus

190.1 *Atomic Absorption Spectrophotometer*, capable of resolving the 2863 Å line, equipped with a tin hollow-cathode lamp or tin electrodeless discharge lamp whose radiant energy is modulated, with a detector system tuned to the same frequency and a premix nitrous oxide – acetylene burner. The performance of the instrument must be such that, the upper limit of the concentration range (40 µg/mL) produces an absorbance of 0.15 or higher, and a calibration curve whose deviation from linearity is within the limits specified in 192.4.

191. Reagents

191.1 *Ascorbic Acid*.

191.2 *Iodide-Ascorbic Acid Solution*— Dissolve 30 g of potassium iodide and 10 g of ascorbic acid in 60 mL of HCl (1 + 5). Dilute to 100 mL with water and mix. Do not use a solution that has stood more than one day.

²⁰ Supporting data are available from ASTM Headquarters. Request RR:E03-1009.



191.3 Methyl Isobutyl Ketone (MIBK).

191.4 Tin, Standard Solution A (1 mL = 1.0 mg Sn)—Dissolve 1.000 g of tin (purity: 99.9 % minimum) in 100 mL of HCl. Cool, transfer to a 1-L volumetric flask, dilute to volume with HCl (1 + 2), and mix.

191.5 Tin, Standard Solution B (1 mL = 50.0 µg Sn)—Using a pipet, transfer a 10-mL aliquot of Solution A to a 200-mL volumetric flask. Dilute to volume with HCl (1 + 2) and mix.

191.6 Trioctylphosphine Oxide (TOPO-MIBK) Solution (50 g/L)—Transfer 12.5 g of TOPO to a 250-mL volumetric flask. Dilute to volume with MIBK and mix until dissolution is complete.

192. Procedure

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

NOTE 52—Volumetric flasks with ground-glass stoppers must be used.

192.2 Extraction:

192.2.1 Add 15 mL of HCl (1 + 1), 3 g of ascorbic acid, and mix. Add 15 mL of iodide – ascorbic acid solution, adjust the volume to approximately 50 mL, and mix.

192.2.2 Using a pipet, add 10.0 mL of TOPO-MIBK solution, stopper the flask, invert, and shake vigorously several times for a period of 1 min. Allow the phases to separate. Add water to bring the entire organic layer up into the neck portion of the flask. Stopper, invert several times, and allow the phases to separate.

NOTE 53—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

192.3 Photometry:

192.3.1 With a tin hollow-cathode lamp or electrodeless discharge lamp in position, energized and stabilized, adjust the wavelength setting to the location that gives the maximum detector response in the immediate vicinity of 2863 Å.

192.3.2 Following the instrument manufacturer's specific directions, ignite the burner using the air – acetylene mode of operation. Immediately after ignition, switch over to the nitrous oxide – acetylene mode of operation and allow the burner to reach thermal equilibrium while aspirating water. Cautiously adjust the height of the red cone of the flame to approximately 12 mm by means of the fuel flow needle valve. Adjust the detector response to zero while aspirating water. Aspirate Solution B (1 mL = 50 µg Sn) and adjust the height of the burner to obtain maximum response from the detector system. Remove the capillary from the solution and allow air to aspirate for 15 to 30 s. Aspirate MIBK for 30 s, then readjust the detector response to zero, if necessary.

NOTE 54—From this point on, only MIBK solutions should be aspirated until all test and calibration solution measurements have been completed. If the burner slot shows any sign of blockage, shut off the flame according to the instrument manufacturer's approved procedures, clean the slot, and relight as in 192.3.1.

192.3.3 Aspirate the solution with the highest concentration (40 µg Sn/mL) from the series prepared in 192.1 a sufficient number of times to establish that the absorbance is not drifting.

NOTE 55—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 56—Due to the small amount of extract available for making this test, the number of readings and the time between readings must be kept to a minimum.

192.3.4 Beginning with the calibration solution to which no tin was added, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration (40 µg Sn/mL) differs from the average values obtained in 192.3.3 by more than 0.03 multiplied by the average of the values, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposit in the burner or clogged capillary), correct it, and repeat the procedure in 192.3.1–192.3.4.

192.3.5 Proceed immediately as directed in 193.3.

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

$$\text{Deviation from linearity} = (A - B)/C \quad (27)$$

where:

A = absorbance value for 40 µg Sn/mL,

B = absorbance value for 30 µg Sn/mL, and

C = absorbance value for 10 µg Sn/mL.

If the calculated value is less than 0.60, correct the indicated malfunction or maladjustment of the instrument or lamp and repeat the calibration.

193. Procedure

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

193.2 Test Solution:

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

Tin, %	Sample weight, g	Dilution, mL	Aliquot, mL	Aliquot factor
0.002 to 0.005	3.00	—	—	1
0.004 to 0.010	2.00	—	—	1
0.009 to 0.050	1.00	—	—	1
0.050 to 0.080	1.00	100	50	2
0.080 to 0.100	1.00	100	20	5

Transfer it to a 250-mL poly(tetrafluoroethylene) beaker.

193.2.3 Add 30 mL of HCl (1 + 1) and ten drops of HF. Cover the beaker with a poly(tetrafluoroethylene) cover and heat at a low temperature (approximately 90°C) until dissolution is complete.

193.2.3 Remove the cover with platinum-tipped tongs and cautiously rinse into the beaker with water. Cautiously evaporate the solution at a low temperature (approximately 90°C) to 15 mL. Rinse the sides of the beaker with water and dilute to approximately 50 mL with water. Filter through medium porosity, hard-surface filter paper. Wash the paper several times with water. Collect the filtrate and washings in a 250 mL beaker. Discard the filter paper. Add 20 mL of HCl (1 + 1) to the solution and again evaporate to 15 mL.

193.2.4 Rinse the sides of the beaker with about 5 mL of water and cool. If an aliquot is to be taken (refer to table in

193.2.1), transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix. Using a pipet, transfer the aliquot to a 150-mL beaker and evaporate at a low temperature to 15 mL. Rinse the sides of the beaker with about 5 mL of water and cool.

193.2.5 Add 3 g of ascorbic acid for a 1-g sample, plus 2 g of ascorbic acid for each additional 1 g of sample. Swirl to dissolve. Add 15 mL of the iodide-ascorbic acid solution.

193.2.6 Transfer the sample to a 100-mL volumetric flask and adjust the volume to approximately 50 mL with water. Using a pipet, transfer 10 mL of the TOPO-MIBK solution to the flask, stopper, invert, and shake vigorously several times for 1 min.

193.2.7 Allow the phases to separate. Add water to bring the entire organic layer into the neck of the flask. Stopper, invert several times, and allow the phases to separate.

193.3 *Photometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 53) and record the absorbance values. Take three readings on each solution (Note 55). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drifts as in 192.3.4 and 192.3.5.

194. Calculation

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

$$\text{Tin, \%} = [(D - E) \times F] / (G \times 1000) \quad (28)$$

where:

- D = tin, μg , per mL of the final test solution,
- E = tin, μg , per mL of the final reagent blank solution,
- F = aliquot factor (refer to table in 193.2.1), and
- G = sample used, g.

195. Precision and Accuracy²¹

195.1 *Precision*—Eleven laboratories cooperated in the testing of this method and obtained the precision data listed as No. 2 in Table 19. This method differs only slightly from the method for tin, Method E 350, in that a filtration step was added to remove acid insoluble material (graphite). The fact that the precision obtained for No. 2 by this method is the same as the precision obtained for No. 3, Method E 350, suggests that the precision of the two methods is the same.

²¹ Supporting data are available from ASTM Headquarters. Request RR:E03-1022.

TABLE 19 Statistical Information—Tin

Test Specimen	Tin Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 1, E 350	0.0034	0.0006	0.0007
2. Cast iron (NBS 5k), 0.009 Sn (not certified)	0.009	0.001	0.002
3. No. 3, E 350	0.011	0.001	0.002
4. No. 6, E 350	0.097	0.011	0.011

195.2 *Accuracy*—No information on the accuracy of this method is available.

MOLYBDENUM BY THE PHOTOMETRIC METHOD

196. Scope

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

197. Summary of Method

197.1 The test solution is treated with thiocyanate to develop the molybdenum and iron thiocyanate complexes. Molybdenum and iron are reduced with stannous chloride, and the molybdenum complex is extracted with butyl acetate. Photometric measurement is made at approximately 475 nm.

198. Concentration Range

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

NOTE 57—This method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

199. Stability of Color

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

200. Interferences

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

201. Reagents

201.1 *Butyl Acetate*:

NOTE 58—Operations with this chemical should be carried out away from heat and open flame and are best done in a well ventilated hood. Avoid prolonged breathing of vapor.

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

201.3 *Iron*²²—(Purity: 99.8 % minimum, molybdenum 0.001 % maximum.)

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

201.5 *Iron Solution B* (1 mL = 0.84 mg Fe)—Add 12 mL of iron solution A to 175 mL of $\text{H}_2\text{SO}_4(1 + 1)$, and dilute to 1 L.

²² Johnson-Mathey JMC 847 sponge iron has been found suitable for this purpose.



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

201.7 *Molybdenum, Standard Solution B* (1 mL = 0.1 mg Mo)—Using a pipet, transfer 50 mL of molybdenum solution A to a 100-mL volumetric flask, dilute to volume, and mix.

201.8 *Molybdenum, Standard Solution C* (1 mL = 0.01 mg Mo)—Using a pipet, transfer 10 mL of molybdenum solution A to a 200-mL volumetric flask, dilute to volume, and mix.

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

201.10 *Stannous Chloride Solution* (350 g/L)—Transfer 350 g of stannous chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and 200 g of tartaric acid to a 1-L beaker, add 400 mL of HCl (1 + 1), and heat at 60 to 70°C until dissolution is complete. Cool, and dilute to 1 L. Add several pieces of tin, and store in an air-tight bottle.

NOTE 59—This solution is used for color development in 202.3, 203.3, 204.3, and 205.3. When an absorption cell is used sequentially for a number of photometric measurements, a white film of an insoluble tin compound may adhere to the inside of the cell and must be removed before further measurements are made.

202. Preparation of Calibration Curve for Concentration from 0.01 to 0.05 %

202.1 Calibration Solutions:

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

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

202.1.3 Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 202.3.

202.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 202.1.2, 202.1.3, and 202.3.

202.3 *Color Development*—Using a pipet, transfer 100 mL to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of SnCl_2 solution, and 25 mL of butyl acetate, measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl_2 solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel, containing a dry filter paper, to fill an absorption cell.

NOTE 60—This funnel should be cleaned thoroughly after each filtration to avoid development of a pink color that would contaminate the filtrate.

202.4 *Reference Solution*—Butyl acetate.

202.5 *Photometry:*

202.5.1 *Multiple Cell Photometer*—Measure the reagent

blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at approximately 475 nm. Using the test cell, take the photometric readings of the calibration solutions.

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

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

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

203.1 Calibration Solutions:

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

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

203.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 203.3.

203.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 203.1.2, 203.1.3, and 203.3.

203.3 *Color Development*—Using a pipet, transfer 50 mL to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of SnCl_2 solution, and 50 mL of butyl acetate, measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H_2SO_4 (1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl_2 solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 60.)

203.4 *Reference Solution*—Butyl acetate.

203.5 *Photometry:*

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

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

203.6 *Calibration Curve*—Plot the net photometric readings

of the calibration solutions against milligrams of molybdenum per 50 mL of butyl acetate.

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

204.1 Calibration Solutions:

204.1.1 Transfer 0.3 g of iron to each of five 250-mL Erlenmeyer flasks. Using pipets, transfer 5, 10, 15, 20, and 25 mL of molybdenum solution A (1 mL = 0.2 mg Mo) to the flasks. Add 30 mL of dissolving solution and heat until dissolution is complete.

204.1.2 Increase the temperature and evaporate to HClO₄ fumes. Cool, add 50 mL of water, and 70 mL of H₂SO₄ (1 + 1). Heat to boiling and cool in a water bath.

204.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 203.3.

204.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 204.1.2, 204.1.3, and 204.3.

204.3 *Color Development*—Using a pipet, transfer 25 mL of iron solution B and 25 mL of the calibration solution, to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of SnCl₂ solution and 100 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H₂SO₄ (1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl₂ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, and drain off and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 60.)

204.4 *Reference Solution*—Butyl acetate.

204.5 Photometry:

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

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

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

205. Procedure

205.1 Test Solution:

205.1.1 Transfer a 0.3-g sample, weighed to the nearest milligram to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution, and heat until dissolution is complete. One to two drops of HF may be added for the decomposition of

some alloy types containing high percentages of silicon.

205.1.2 Increase the temperature and heat to HClO₄ fumes. Continue fuming until chromium, if present, is oxidized, and the white fumes are present only in the neck of the flask. Add, with care, 1.0 to 1.5 mL of HCl, allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been volatilized. Continue fuming the solution until the volume has been reduced to about 15 mL. Cool, add 50 mL of water and 70 mL of H₂SO₄ (1 + 1), heat to boiling, and cool in a water bath.

205.1.3 Transfer to a volumetric flask that provides for dilution, in accordance with the following aliquot guide, dilute to volume, and mix:

Molybdenum, %	Dilution, mL	Aliquot volume, mL	Iron Solution B, mL	Butyl acetate, mL	Weight of sample in final butyl acetate solution, g
0.01 to 0.05	200	100	None	25	0.15
0.05 to 0.55	500	50	None	50	0.03
0.40 to 1.50	500	25	25	100	0.015

205.1.4 Proceed as directed in 205.3.

205.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 205.1.2, 205.1.3, and 205.3, using the same dilution and aliquots used for the test solution.

205.3 *Color Development*—Using a pipet, transfer the appropriate aliquot to a 250-mL separatory funnel containing the appropriate amount of iron solution for the specified aliquot. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of SnCl₂ solution, and, measured with a pipet, the amount of butyl acetate specified in the aliquot guide. Stopper the separatory funnel and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H₂SO₄ (1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl₂ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, and drain off and discard the aqueous phase. Drain enough of the solvent layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 44.)

205.4 *Reference Solution*—Butyl acetate.

205.5 *Photometry*—Take the photometric reading of the test solution and of the reagent blank solution as directed in 204.5.

206. Calculation

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

$$\text{Molybdenum, \%} = \frac{A}{B \times 10} \quad (29)$$

where:

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

B = sample, g, represented in 25, 50, or 100 mL, as appropriate, of butyl acetate (see 205.1.3).

207. Precision and Bias²³

207.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 20. This method is identical with the methods for molybdenum Methods E 350, E 352, and E 353. The fact that the data from the two cast iron samples (Table 20, No. 2 and 3) had similar precision to the specimens used to test the other methods suggests that the precision for these methods is the same.

207.2 *Bias*—The accuracy can be inferred by comparing the certified values for molybdenum with the values found for molybdenum for those specimens listed in Table 20.

CHROMIUM BY THE ATOMIC ABSORPTION METHOD

208. Scope

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

209. Summary of Method

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

210. Concentration Range

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

211. Interferences

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

212. Apparatus

212.1 *Atomic Absorption Spectrophotometer*; capable of resolving the 3579Å line, equipped with a chromium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it meets the limits defined in 214.4. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this method.

213. Reagents

213.1 *Chromium, Standard Solution* (1 mL = 0.1 mg Cr)—Transfer 2.8290 g of potassium dichromate ($K_2Cr_2O_7$) (NBS 136 or equivalent) to an 800-mL borosilicate beaker, add 500 mL of water, and mix. When dissolution is complete, add 5 mL of H_2SO_4 and, while stirring, add 10 mL of H_2O_2 (30 %). Heat at near boiling for 5 min to remove excess H_2O_2 . Cool, transfer the solution to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask, dilute to volume, and mix.

213.2 *Iron,²⁴ Low Chromium—Cr 0.0001%*.

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

214. Preparation of Calibration Curves

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

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

²³ Supporting data are available from ASTM Headquarters. Request RR:E03-1023.

TABLE 20 Statistical Information—Molybdenum

Test Specimen	Molybdenum Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 1, E 352	0.037	0.002	0.006
2. Cast iron, Leco 501 to 741	0.195	0.018	0.03
3. Cast iron (NBS 107, 0.69 Mo)	0.699	0.03	0.04
4. No. 5, E 350	1.03	0.04	0.07
5. No. 4, E 353	1.34	0.03	0.09

²⁴ Johnson-Mathey sponge iron or Spex iron has been found suitable for this purpose.

214.3 Photometry:

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

214.3.2 Light the burner, allow it to thermally equilibrate, and adjust the instrument to zero while aspirating water. Aspirate the chromium solution with the highest concentration from the series prepared as directed in 214.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is required.

214.3.3 Aspirate the chromium solutions used in 214.3.2 to assure that the absorbance reading is repeatable. Record 6 readings, and calculate the standard deviation, s , of the readings as follows:

$$s = (A - B) \times 0.40 \quad (30)$$

where:

- A = the highest of 6 values found, and
- B = the lowest of the 6 values found.¹¹

214.3.4 Using water as a reference solution, and beginning with the solution to which no addition of chromium was made in 214.1 and 214.2, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of 6 values calculated in 214.3.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the 6 values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, correct it, and repeat the steps in 214.3.1–214.3.4.

214.3.5 Proceed immediately as directed in Section 238.

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

$$\text{Deviation from linearity} = (C - D)/E \quad (31)$$

where:

- C = absorbance value for 0.015 mg Cr/mL,
- D = absorbance value for 0.010 mg Cr/mL, and
- E = absorbance value for 0.005 mg Cr/mL.

If the calculated value is less than 0.60, make the proper adjustment of instrument or hollow cathode lamp, and repeat the calibration. The absorbance value for C must be 0.200 or higher.

214.5 *Calibration for Concentrations from 0.10 to 1.00 %*—Proceed as directed in 214.4.

215. Procedure

215.1 Test Solution:

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution after dissolution, mL	Aliquot Required, mL	HCl to be added to Aliquot, mL	Final Dilution, mL
0.005–0.10	1	0.10	100	0	0	100
0.10–1.00	1	0.10	100	10	9	100

Transfer it to a 250-mL borosilicate beaker.

215.1.2 Add 20 mL HCl, 10 mL HNO₃, and 5 drops of HF. Heat to dissolve. Remove from the hot plate and dilute to approximately 50 mL. Add a small amount of filter pulp and filter the solution through 11-cm fine filter paper into a 250-mL borosilicate beaker. Wash the paper 5 times with HCl (1 + 99), and reserve the filtrate.

215.1.3 Transfer the paper and contents to a platinum crucible. Dry on a hot plate, and transfer to a muffle furnace that is less than 400°C. Gradually heat to 600°C and hold at this temperature for 1 hr. Cool, add 0.5 g of K₂CO₃, and carefully fuse over a free flame until a clear melt is obtained (see Note 1). Cool and add 15 mL of water. Add HCl dropwise until reaction ceases. Add 5 drops of HCl in excess and warm on a hot plate, if necessary to obtain a clear solution.

NOTE 61—Fusion of the residue is made in order to include in the sample solution any chromium that might exist in the sample in an acid insoluble form.

215.1.4 Transfer this solution to the filtrate from 215.1.2 and evaporate just to dryness. Add 10 mL HCl and warm to dissolve salts. Transfer quantitatively to a 100-mL volumetric flask, dilute to volume, and mix. For samples with expected chromium concentrations less than 0.10 % proceed as directed in 215.3. For samples with expected chromium concentration greater than 0.10 %, transfer by pipet 10 mL to a 100-mL volumetric flask, add 9 mL of HCl, dilute to volume, and mix.

215.2 Prepare for each concentration range a reagent blank by treating the same amount of all reagents as directed in 215.1.1–215.1.4 including the low chromium iron. Use reagents from the same lots for blank and test solutions.

215.3 *Photometry*—Using water as a reference solution, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of 4 or fewer test solutions and reagent blank solutions has been aspirated, apply the test using the standard solution as directed in 214.3.4, depending on the concentration range. If the value differs from the average of the 6 values by more than twice the standard deviation, s , found in 214.3.3, or more than 0.01 multiplied by the average of 6 values used to calculate s , whichever is greater, determine the cause and repeat the calibration and aspiration of test solutions.

216. Calculation

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

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (32)$$

where:

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

217. Precision and Bias²⁵

217.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 21.

217.2 *Bias*—The accuracy can be inferred from the data in Table 21 by comparing the certified values for chromium with the average value obtained by using this method.

CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

218. Scope

218.1 This method covers the determination of chromium in concentrations from 0.05 to 30.0 %.

219. Summary of Method

219.1 Chromium in an acid solution of the sample is oxidized to the hexavalent state with ammonium peroxydisulfate in the presence of silver nitrate catalyst. The sample is then titrated with excess ferrous ammonium sulfate to reduce chromium and the excess back-titrated with either potassium permanganate or potassium dichromate depending upon the presence or absence of vanadium.

NOTE 62—In the dichromate titration, the vanadium is not oxidized along with the excess ferrous ions and, therefore, the volume of dichromate added reflects the total of vanadium and chromium and the calculated value for % Cr is high. In the permanganate titration, the V^{IV} is oxidized to V^V , thereby compensating for the reduction of vanadium by ferrous sulfate in a previous step.

220. Interferences

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

1.1. This method may not dissolve all of the chromium carbides in Class II, Type B and C alloy iron castings.

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

$$(2.6A + 0.05B + 0.01C)D \quad (33)$$

where:

- A = tungsten, %, in the sample,
- B = copper, %, in the sample,
- C = nickel, %, in the sample, and
- D = sample weight, g.

When the value exceeds 1.300, the end point must be determined potentiometrically if $K_2Cr_2O_7$ is the back-titrant.

221. Apparatus

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

222. Reagents

222.1 *Ammonium Peroxydisulfate Solution*—Dissolve 15 g of ammonium peroxydisulfate $[(NH_4)_2S_2O_8]$ in water and dilute to 100 mL. Do not use solutions that have stood for more than 24 h.

222.2 *Ferrous Ammonium Sulfate, Standard Solution* (0.05 N and 0.01 N)—Reagent No. 5 (Practices E 50) but use 20 and 40 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, respectively, instead of the specified weight. Standardize the solution as directed in 223.1, 223.2, or 223.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

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

222.4 *Potassium Permanganate Solution* (25 g/L)—Dissolve 25 g of reagent grade $KMnO_4$ in 200 mL of water, dilute to 1 L, and mix.

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

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

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

222.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 M)—Reagent No. 122 (Practices E 50).

223. Preparation of Calibration Curves

²⁵ Supporting data are available from ASTM Headquarters. Request RR:E03-1030.

TABLE 21 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 1, E 350	0.0063	0.0014	0.003
2. NBS 3C 0.047 Cr	0.045	0.003	0.004
3. NBS 107b 0.56 Cr	0.559	0.026	0.052
4. No. 5, E 350	0.961	0.036	0.093

223.1 Against Potassium Permanganate Solution:

223.1.1 Transfer 180 mL of water, 12 mL of H₂SO₄(1 + 1), and 5 mL of H₃PO₄ into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 or 0.10 N Fe(NH₄)₂(SO₄)₂ with either 0.05 or 0.10 N KMnO₄ solution (222.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 1 to 2 drops of 1,10 phenanthroline indicator solution. Using a 25-mL buret, titrate the ferrous ions with 0.05 N KMnO₄ standard solution (222.5) while swirling the flask. As the end point is approached, add KMnO₄ dropwise. Continue until the pink color changes to clear green and persists for at least 60 s.

223.1.2 Calculate the normality of the Fe(NH₄)₂(SO₄)₂ solutions as follows:

$$\text{Normality} = AB/C \quad (34)$$

where:

A = normality of KMnO₄ solution (222.5),

B = KMnO₄ solution, mL, and

C = Fe(NH₄)₂(SO₄)₂ solution, mL.

223.2 Against Potassium Dichromate Solution Using Diphenylamine Sulfonate End Point:

223.2.1 Transfer 180 mL of water, 12 mL of H₂SO₄(1 + 1), and 5 mL of H₃PO₄ into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 or 0.10 N Fe(NH₄)₂(SO₄)₂ (222.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using a 25-mL buret, titrate the ferrous ions with either 0.05 or 0.10 N K₂Cr₂O₇ solution, while swirling the flask. As the end point is approached, add the K₂Cr₂O₇ titrant dropwise. Continue until a blue color appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL. Refill the burets, add the same volume of Fe(NH₄)₂(SO₄)₂ solution as before and again titrate with either 0.05 or 0.10 N K₂Cr₂O₇ solution to the blue end point. Record the buret reading. Subtract this volume of K₂Cr₂O₇ solution from the volume recorded for the first titration. Record the difference as the indicator blank.

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

$$\text{Normality} = (0.05 \text{ or } 0.10 (A - B))/C \quad (35)$$

where:

A = 0.05 or 0.10 N K₂Cr₂O₇ solution, mL, used in the first titration,

B = equivalent to the indicator blank, mL, and

C = Fe(NH₄)₂(SO₄)₂ solution, mL, used in the first titration.

223.3 Against Potassium Dichromate Using Potentiometric End Point:

223.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 or 0.10 N K₂Cr₂O₇ solution into a 600-mL beaker. Reserve the remaining 0.05 or 0.10 N K₂Cr₂O₇ solution in the buret for the back-titration. Add 150 mL of water, 10 mL of H₂SO₄(1 + 1), and 5 mL of H₃PO₄. Insert the saturated calomel reference electrode and the platinum indicator electrode into the beaker and connect them to the potentiometer apparatus. While stirring the solution, add Fe(NH₄)₂(SO₄)₂ until the dichromate ion yellow color disappears and then add a slight excess. Record the volume of the Fe(NH₄)₂(SO₄)₂ solution to the nearest 0.01 mL. Back-titrate with the remaining 0.05 or 0.10

N K₂Cr₂O₇ solution by adding the solution in 0.1-mL increments as the end point is approached. Record the voltage when equilibrium is reached after each 0.1-mL increment. Inspect the data for the maximum voltage change per 0.1-mL increment. Determine the voltage change for the 0.1-mL increments before and after this maximum change. Determine the two differences between the three voltage readings corresponding to the volume (0.1-mL) increment before the maximum, the maximum, and after the maximum. This is a very close approximation of the second derivative of the volume versus change in voltage curve corresponding to the maximum inflection, if this curve were plotted. Sum the two voltage differences. Determine the ratio of the first of these two differences to the sum and multiply 0.1 mL by this ratio to obtain the volume to be added to the smaller volume between the two incremental additions that the maximum change in voltage occurred. See the following example:

Volume of 0.05 N K ₂ Cr ₂ O ₇ Back Titrant (mL)	Voltage (mV)	ΔVoltage (mV)	Difference Be- fore and After Maximum
20.80	555		
20.90	570		
21.00	620	50	50
21.10	720	80	20
21.20	800		
21.30	835		
21.40	854		

Maximum voltage change occurred between 21.00 and 21.10 mL of K₂Cr₂O₇ solution. The changes in voltage were 50 mV before the maximum, 100 mV at the maximum, and 80 mV after the maximum. The two differences between the maximum, corresponding to before and after the maximum, were 50 and 20 mV, respectively. Their sum equals 70 and the ratio of the first to the sum equals 50/70. Thus 50/70 multiplied by 0.1 mL must be added to the smaller volume between the two increments where the maximum change in voltage occurred. The end point is 21.07 mL.

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

$$\text{Normality} = 0.05 \text{ or } 0.10 A/B \quad (36)$$

where:

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

B = Fe(NH₄)₂(SO₄)₂ solution, mL.

224. Procedure

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Normal- ity of Titrants
0.05 to 0.50	3.50	2.0	0.05
0.40 to 1.00	2.00	1.0	0.05
0.80 to 1.60	1.25	0.5	0.05
1.50 to 3.50	0.50	0.3	0.05
3.30 to 8.00	0.25	0.1	0.05
8.00 to 14.00 ^A	0.50	0.1	0.10
14.00 to 20.00 ^A	0.40	0.1	0.10
20.00 to 30.00 ^A	0.20	0.1	0.10



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

Transfer it to a 600-mL beaker.

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

224.3 If the alloy is insoluble in the acids specified in 224.2, add amounts of HCl or HNO₃, or mixtures and dilutions of these acids, or bromine and HCl in a ratio of 1 to 3 (plus a few drops of HF), which are sufficient to dissolve the sample. When decomposition is complete, add 80 mL of H₂SO₄(1 + 5) and 5 mL of H₃PO₄, and evaporate to light fumes. Rinse the cover and walls of the beaker, again evaporate to fumes, and fume strongly for 1 min. Cool, add 100 mL of water, and heat at 85 to 100°C until the salts are dissolved.

224.4 Dilute the solution to 150 mL, add paper pulp and filter through an 11-cm fine paper into a 500-mL Erlenmeyer flask or a 600-mL beaker if the potentiometric titration procedure is to be used. Wash the residue 10 to 12 times with warm water, and reserve the filtrate.

224.5 Transfer the paper and residue to a platinum crucible, char the paper, and ignite at 850 to 900°C for 15 min. Cool, add sufficient H₂SO₄ (1 + 1) to moisten the residue, and then add 3 to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until H₂SO₄ is removed. Fuse the residue with a minimum amount of either fused sodium hydrogen sulfate (sodium pyrosulfate—Na₂S₂O₇) or potassium pyrosulfate (K₂S₂O₇). Cool the crucible, place in a 250-mL beaker, and dissolve the melt in 20 mL of H₂SO₄ (1 + 10). Remove the crucible, rinse with water, and transfer the solution to the reserved filtrate (224.4) and dilute to 200 mL.

224.6 Add 5 mL of AgNO₃ solution and 20 mL of (NH₄)₂S₂O₈ solution. If a beaker is used, cover it with a ribbed cover glass. Boil the solution 8 to 10 min, maintaining the volume at 200 mL by additions of hot water. If the color due to permanganate ions does not develop, or develops but does not persist, add 2 drops of KMnO₄ solution (222.4), 5 mL more of AgNO₃ solution, and 20 mL more of (NH₄)₂S₂O₈ solution, and boil for an additional 8 to 10 min. Add hot water to maintain the volume at 200 mL during this operation and the operations that follow in 224.7.

224.7 Reduce the permanganate ions as follows: Add 5 mL of HCl (1 + 3) and continue boiling for 10 min after the disappearance of permanganate color. If the permanganate ions have not been completely reduced or if MnO₂ is present, add 2 mL of HCl (1 + 3) and boil again for 10 min. Repeat the addition of HCl and boiling until all manganese is present as colorless manganous ions. Cool to room temperature and dilute to 200 mL. If vanadium is present or its absence has not been confirmed, proceed as directed in 224.8. If vanadium is absent and the criteria of 220.2 are met, proceed as directed in 224.9. If vanadium is absent and the criteria of 220.2 are not met, or if the potentiometric titration is preferred and vanadium is absent, proceed as directed in 224.10.

224.8 *Titration With Potassium Permanganate*—While swirling the flask, add 1 to 2 drops of 1,10 phenanthroline indicator solution and then add sufficient Fe(NH₄)₂(SO₄)₂

solution to effect a change in color from clear green to pink. Add 1 to 2 mL more and record the buret reading to the nearest 0.01 mL. Using a 25-mL buret, back-titrate the excess ferrous ions with 0.05 N KMnO₄ standard solution. Add KMnO₄ dropwise as the end point is approached. Continue the titration until the pink color has changed to clear green which persists for 60 s. Record the buret reading to the nearest 0.01 mL.

224.9 *Titration with Potassium Dichromate to the Diphenylamine Sulfonate End Point*—While swirling the flask, add Fe(NH₄)₂(SO₄)₂ solution from a 25-mL buret until the disappearance of the yellow color. Then add 1 to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using another 25-mL buret, back-titrate the excess ferrous ions with 0.05 N K₂Cr₂O₇ standard solution. Add the K₂Cr₂O₇ solution dropwise as the end point is approached. Continue the titration until a blue color appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL.

224.10 *Titration with Potassium Dichromate and Potentiometric End Point Detection*—Stir the sample solution in the 600-mL beaker with a magnetic stirrer and insert the saturated calomel reference and platinum indicator electrodes. With the electrodes connected to the potentiometer apparatus, add from a 25-mL buret, the Fe(NH₄)₂(SO₄)₂ solution with the stirrer running until the yellow color disappears. Then add 1 to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Using another 25-mL buret, add 0.05 N K₂Cr₂O₇ standard solution in 0.1-mL increments recording the voltage after equilibrium for each increment. Inspect the data for the maximum voltage change between increments of standard dichromate solution (see 223.3). Determine the voltage change for the increments before and after the maximum change and interpolate the end point to the nearest 0.01 mL as described in 223.3.

225. Calculation

225.1 If KMnO₄ was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (37)$$

where:

- A = Fe(NH₄)₂(SO₄)₂ solution, mL,
- B = normality of Fe(NH₄)₂(SO₄)₂ solution,
- C = KMnO₄ solution used, mL
- D = normality of the KMnO₄ solution, and
- E = sample taken, g.

225.2 If K₂Cr₂O₇ was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (38)$$

where:

- A = Fe(NH₄)₂(SO₄)₂ solution, mL,
- B = normality of Fe(NH₄)₂(SO₄)₂ solution,
- C = K₂Cr₂O₇ solution, mL,
- D = normality of K₂Cr₂O₇ solution, and
- E = sample taken, g.

226. Precision and Bias²⁶

226.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data shown in Tables 22 and 23. Although a sample at the high end of the scope was not evaluated by Practice E 173, the precision data for other types of alloys using the methods indicated in Table 22 should apply.

226.2 *Bias*—No information on the accuracy of this method is known. The accuracy of this method may be judged, however, by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing (see Table 22).

VANADIUM BY THE ATOMIC ABSORPTION METHOD

227. Scope

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

228. Summary of Method

228.1 The sample is dissolved in hydrochloric, nitric, and perchloric acids. An aluminum solution is added as a spectrochemical buffer. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrophotometer. Spectral energy at approximately 318.4 nm from a vanadium hollow cathode lamp is passed through the flame, and the absorbance is measured. This absorbance is compared with the absorbance of a series of standard calibration solutions.

229. Concentration Range

229.1 The recommended concentration range is 0.002 to 0.016 mg vanadium/mL of solution.

230. Interferences

230.1 Iron interferes by acting as a depressant. This interference is overcome by the addition of aluminum chloride, which acts as a spectrochemical buffer. Titanium and tungsten interfere when present in concentrations greater than 0.5 and 1.0 %, respectively.

231. Apparatus

²⁶ Supporting data are available from ASTM Headquarters. Request RR:E03-1036.

TABLE 22 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. Cast Iron (NBS 3b, 0.052 Cr)	0.044	0.008	0.024
2. Cast Iron (NBS 115a, 1.98 Cr)	1.96	0.10	0.16
3. No. 5, E 353	21.62	0.18	0.58

231.1 *Atomic Absorption Spectrophotometer*, capable of resolving the 318.4-nm line, equipped with a vanadium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it is suitable for use as described in Guide E 1024.

232. Reagents

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

232.2 *Vanadium, Standard Solution* (1 mL = 0.2 mg V)—Dissolve 0.200 g of vanadium (purity, 99.9 % min) in 20 mL of aqua regia (three volumes of HCl to one volume of HNO_3). Evaporate to near dryness and add 10 mL of HCl. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

NOTE 63—As an alternative to vanadium metal, ammonium metavanadate may be used to prepare the standard vanadium solution. It is prepared as follows: Dry several grams of ammonium metavanadate (NH_4VO_3), minimum purity 99.9 %, in an air oven at 105 to 110°C for at least 1 h and cool to room temperature in a desiccator. Weigh 0.4592 g of the dried product into a 600-mL beaker, add 400 mL of hot water, and gently simmer to dissolve. Cool, transfer to a 1000-mL volumetric flask, dilute to volume, and mix (1 mL = 0.20 mg V).

233. Preparation of Calibration Curve

233.1 *Calibration Solutions*—To each of five, 250-mL borosilicate beakers, add 10 mL of $HClO_4$. Using a microburet, transfer 0.0, 1.0, 2.0, 4.5, and 8.0 mL of vanadium standard solution to each beaker, respectively. Cover with a watch glass, heat, and evaporate to fumes. Continue heating until solutions are near dryness (Note 46). Cool, dissolve the salts with 10 mL of HCl and 20 mL of water. Filter through a medium-porosity filter paper into a 100-mL volumetric flask, wash well with warm HCl (2 + 100). Cool, add 10 mL of $AlCl_3$ solution (232.1), dilute to volume, and mix.

NOTE 64—The remaining amount of $HClO_4$ must be at a minimum.

233.2 Photometry:

233.2.1 With the vanadium hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 318.4 nm line.

233.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the vanadium solution with the highest concentration from the series prepared as directed in 233.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more these parameters are changed, recalibration is necessary.

233.2.3 Aspirate the vanadium solution used in 233.2.2 to assure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, s , of the readings as follows:

$$s = (A - B) \times 0.40 \quad (39)$$

where:

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

TABLE 23 Statistical Information—Chromium

Test Specimen	Chromium Found, %								
	Laboratory Number								
	1	2	3	4	5	6	7	8	9
1. HC 250 + V		25.48	23.15	24.51	25.34	25.41			25.50
2. ACIPCO High Cr Cast Iron		25.44	23.76	24.54	25.32	25.42			25.06

233.2.4 Using water as a reference, and beginning with the solution to which no addition of vanadium was made in 233.1, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values calculated in 233.2.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 233.2.1 through 233.2.4.

233.2.5 *Calibration Curve*—Plot the average net absorbance values against milligrams of vanadium per mL on rectangular coordinate paper. Test for linearity as given in Guide E 1024.

234. Procedure

234.1 Test Solution:

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

234.1.2 Add 20 mL of HCl, 4 mL of HNO₃, and cover with a cover glass. Heat until dissolution is complete. Add 10 mL of HClO₄ and evaporate to fumes. Continue heating until solutions are near dryness (Note 43). Cool, dissolve the salts with 10 mL of HCl and 20 mL of water. Filter through a medium-porosity filter paper into a 100-mL volumetric flask, and wash well with warm HCl (2 + 100). Cool, add 10 mL of AlCl₃ solution (232.1), dilute to volume, and mix.

234.1.3 Prepare a reagent blank by using a 250-mL borosilicate beaker and proceeding as directed in 234.1.2. Use reagents from the same lots as those used for the sample solution.

234.2 *Photometry*—Using water as a reference, aspirate and record the absorbance of the calibration, sample, and reagent blank solutions. After each group of four or fewer sample and reagent blank solutions has been aspirated, apply the test using the standard solution as directed in 233.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 233.2.3, or more than 0.01 multiplied by the average of six values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration, sample, and reagent blank measurements.

235. Calculation

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

$$\text{Vanadium, \%} = ((A - B) \times 10) / C \quad (40)$$

where:

A = vanadium, mg, per mL of the final sample solution,

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

C = weight of sample, g.

236. Precision and Bias²⁷

236.1 *Precision*—Twenty-three laboratories participated in testing this method under the auspices of WG-9 of ISO Committee TC 17/SC 1 and obtained the data summarized in Table 24. All testing meets the requirements of Practice E 173.

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

CERIUM AND LANTHANUM BY THE D-C PLASMA OPTICAL EMISSION METHOD

237. Scope

237.1 This method covers the determination of cerium in concentrations from 0.003 to 0.50 % and lanthanum in concentrations from 0.001 to 0.30 %.

238. Summary of Method

238.1 The sample is dissolved in mineral acids and evaporated to perchloric acid fumes. The diluted sample solution is measured using a d-c plasma optical emission spectrometer. Wavelengths of 456.24 nm for cerium and 408.67 nm for lanthanum are selected. The spectrometer is calibrated with known concentrations of cerium and lanthanum in the presence of iron and programmed to read out in milligrams per litre of cerium and lanthanum.

239. Concentration Range

²⁷ Supporting data are available from ASTM Headquarters. Request RR:E03-1040.

TABLE 24 Statistical Information—Vanadium

Test Specimen	Vanadium Found, %	Repeatability (<i>R</i> ₁ , E 173)	Reproducibility (<i>R</i> ₂ , E 173)
Pig iron (0.008 V)	0.008	0.002	0.003
No. 1, E 352	0.032	0.002	0.004
No. 1, E 353	0.038	0.003	0.005
No. 1, E 350	0.107	0.008	0.014
No. 2, E 352	0.161	0.007	0.011

239.1 The recommended concentration range is 0.3 to 50 mg/L of cerium and 0.1 to 30 mg/L of lanthanum.

240. Interference

240.1 Spectral interference is minimized by matching matrices of calibration and sample solutions and by carefully peaking the wavelength.

240.2 It is very important that the 456.24 nm wavelength be used for Ce determinations. There are several other Ce wavelengths of comparable intensity, but these are all subject to spectral interferences. For example:

Wavelength (nm)	Interference
393.109	Fe
394.215	Mo, Fe
394.275	Mo, Co, Mn (Ca and Al cause a baseline shift)
394.314	Fe
394.350	(not intense enough to use)
394.389	Al
399.924	Nb, Ti, V, Zr
401.239	Cr
413.380	Fe
418.660	Fe
418.732	Zr
429.667	Zr, Cr, Ni, Mo
446.021	Nb, Zr, V
456.236	Ti (only if 100 times greater than Ce)

241. Apparatus

241.1 An optical emission instrument equipped with a direct current argon plasma excitation source, photomultiplier assembly, nebulizer system, and dedicated microprocessor (Note 65) and capable of emitting spectral energy at 456.24 nm and 408.67 nm. The instrument is calibrated and programmed according to the manufacturer's instructions. The recording system is calibrated in milligrams per litre of solution.

NOTE 65—Instruments without a microprocessor can be programmed manually in accordance with their capabilities.

242. Reagents

242.1 *Cerium Standard Solution* (1 mL = 1.0 mg Ce)—Dry the cerium ammonium nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (purity: 99.9 % minimum) (Note 61) at 82 to 85°C for 4 to 6 h and store in a desiccator over anhydrous magnesium perchlorate desiccant. Dissolve 3.9121 g of the dried $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in 300 mL of HNO_3 (1 + 10). Transfer to a 1-L volumetric flask, dilute to volume with HNO_3 (1 + 50), and mix.

NOTE 66—Also listed as ammonium hexanitrate cerate.

242.2 *Iron, cerium and lanthanum free.*

NOTE 67—NBS SRM 365 or equivalent material may be used.

242.3 *Lanthanum, Standard Solution* (1 mL = 1.0 mg La)—Ignite the lanthanum oxide (La_2O_3) (purity: 99.9 % minimum) at 1000°C for 1 h and store in a desiccator over anhydrous magnesium perchlorate desiccant. Dissolve 1.1782 g of the ignited La_2O_3 in 500 mL of HNO_3 (1 + 10). Transfer to a 1-L volumetric flask, dilute to volume with HNO_3 (1 + 50), and mix.

242.4 *Cerium and Lanthanum, Composite Standard Solution*

(1 mL = 0.1 mg Ce and 0.1 mg La)—Using a pipet, transfer 10.0 mL of cerium standard solution (1 mL = 1.0 mg Ce) and 10.0 mL of lanthanum standard solution (1 mL = 1.0 mg La) to a 100-mL volumetric flask. Dilute to volume with HNO_3 (1 + 50) and mix.

242.5 *Cerium Solution for Wavelength Optimization*—Transfer approximately 10 mL of cerium standard solution (1 mL = 1.0 mg Ce) as prepared in 242.1 to a 100-mL beaker. Dilute to approximately 75 mL with water and mix. This solution does not need to be accurately prepared since it is used only to select the optimum wavelength for cerium spectral energy near 456.24 nm.

242.6 *Lanthanum Solution for Wavelength Optimization*—Transfer approximately 10 mL of lanthanum standard solution (1 mL = 1.0 mg La) as prepared in 242.3 to a 100-mL beaker. Dilute to approximately 75 mL and mix. This solution does not need to be accurately prepared since it is used only to select the optimum wavelength for lanthanum spectral energy at 408.67 nm.

243. Procedure

243.1 *Calibration Solutions:*

243.1.1 *Calibration Solution A*—(0.10 % upper limit; 10 mg Ce/L and 10 mg La/L)—To a 250-mL beaker (Note 49), add 1.0 g of iron (242.2), and 10.0 mL of cerium and lanthanum composite standard solution (1 mL = 0.1 mg Ce and 0.1 mg La) as prepared in 242.4. Add 15 mL of HNO_3 (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until dissolution is complete. Add 15 mL of HClO_4 , cover, and heat to perchloric acid fumes. Cool, rinse cover and sides of beaker with water, add 10 mL of HNO_3 (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. Cool, transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix.

NOTE 68—The use of poly(tetrafluoroethylene) beakers and covers are required. If borosilicate glass is used, varying amounts of Ca may be dissolved out of the glass, shifting the background and causing erratic readings.

243.1.2 *Calibration Solution B* (0.50 % upper limit for Ce and 0.30 % upper limit for La; 50 mg Ce/L and 30 mg La/L)—To a 250-mL beaker (Note 52), add 1.0 g of iron (242.2) and 5.0 mL of Ce standard solution (1 mL = 1.0 mg Ce) as prepared in 242.1 and 3.0 mL of La standard solution (1 mL = 1.0 mg La) as prepared in 242.3. Add 15 mL of HNO_3 (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until dissolution is complete. Add 15 mL of HClO_4 , cover, and heat to perchloric acid fumes. Cool, rinse cover and sides of beaker with water, add 10 mL of HNO_3 (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. Cool, transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix.

243.1.3 *Matrix Blank Solution—Both Concentration Ranges*—To a 250-mL beaker (Note 52), add 1.0 g of iron (242.2). Add 15 mL of HNO_3 (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until

dissolution is complete. Add 15 mL of HClO₄, cover, and heat to perchloric acid fumes. Cool, rinse cover and sides of beaker with water, add 10 mL of HNO₃ (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. Cool, transfer the solution to a 100-mL volumetric flask, dilute to volume with water, and mix.

243.2 Test Solution—Transfer a 1.0 g sample, weighed to the nearest 1.0 mg, to a 250-mL poly(tetrafluoroethylene) beaker (Note 52). Add 15 mL of HNO₃ (1 + 1). After the reaction subsides, add 20 mL of HCl and 1 mL of HF. Cover with a poly(tetrafluoroethylene) cover and heat using low heat until dissolution is complete. Add 15 mL of HClO₄, cover, and heat to perchloric acid fumes. Cool, rinse cover and sides of beaker with water. Add 10 mL of HNO₃ (1 + 1), dilute to approximately 50 mL with water, and warm to dissolve all salts. If necessary, filter the solution through high porosity filter paper into a 100-mL volumetric flask. Cool, dilute to volume with water, and mix.

243.3 Preparation of Instrument—Follow the instrument manufacturer's instructions for startup and wavelength selection.

243.3.1 Cerium—Using the wavelength optimization solution described in 242.5, select the cerium 456.24 nm wavelength. Further optimize the instrument with the high calibration solution according to manufacturer's instructions.

243.3.2 Lanthanum—Using the wavelength optimization solution described in 242.6, select the lanthanum 408.67 nm wavelength. Further optimize the instrument with the high calibration solution according to manufacturer's instructions.

243.4 Measurement:

243.4.1 Calibration Solutions—Enter the value for the appropriate calibration solution (mg/L) and also the value for the matrix blank into the computer. Auto range (A/R) while introducing the appropriate calibration solution into the plasma with the instrument set to average 3 readings at 10 s each. Introduce the matrix blank into the plasma and complete the auto range sequence.

NOTE 69—Caution: Observe instrument during calibration cycle when instrument is calibrated for a maximum of 50 mg Ce/L (or 30 mg La/L). If a maximum count is reached and then falls off before calibration cycle is completed, this indicates a possible saturation of the detector. The results will be in error. This situation may be remedied by reducing the photomultiplier tube voltage, decreasing the slit width, or in extreme cases locating an alternate emission line or diluting sample and standards. This note may not apply to all instruments.

243.4.2 Test Solution—To ensure that the instrument is in calibration, measure the calibration solution as a test solution. If the reading differs by more than 2 % from the established value, recalibrate and repeat. Introduce a series of five (or fewer) test solutions into the plasma with the instrument set to average three readings at 10 s each. Check the calibration by measuring the calibration solution as a test solution. If the reading differs by less than 2 % from the established value, continue with another series of five (or fewer) test solutions. After each series of test solutions, check the calibration by measuring the calibration solution as a test solution. If the reading for the calibration solution differs by more than 2 % from the established value, recalibrate the instrument and remeasure the test solutions.

NOTE 70—To ensure close calibration tolerances, a series of test solutions can be measured by recalibrating before each test sample.

244. Calculation

244.1 Convert the instrument readings (in mg/L) to % analyte in the sample as follows:

$$\text{Cerium, \%} = \frac{A \times B}{C \times 10} \quad (41)$$

where:

- A = cerium mg/L, in test solution,
- B = volume of final test solution (244.2), L, and
- C = weight of sample, g.

$$\text{Lanthanum, \%} = \frac{D \times B}{C \times 10} \quad (42)$$

where:

- D = lanthanum in test solution, mg/L.

245. Precision and Bias²⁸

245.1 Precision—Eight laboratories cooperated in testing this method and obtained the data summarized in Tables 25 and 26.

245.2 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.

**TOTAL TITANIUM BY THE
DIANTIPYRYLMETHANE
SPECTROPHOTOMETRIC METHOD**

246. Scope

²⁸ Supporting data are available from ASTM Headquarters. Request RR:E03-1042.

TABLE 25 Statistical Information—Cerium

Test Specimen	Cerium Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. Low Alloy (NBS 362, 0.0019 Ce)	0.0027	0.0002	0.0005
2. Low Alloy (NBS 361, 0.0040 Ce)	0.0041	0.0003	0.0006
3. Cast Iron	0.0059	0.0002	0.0004
4. R. E. Cast Iron (Leco 206, 0.011 Ce)	0.011	0.0005	0.0008
5. R. E. Cast Iron (Leco 207, 0.016 Ce)	0.016	0.0005	0.0013
6. Low Alloy (NBS 1286)	0.018	0.0004	0.0008
7. R. E. Cast Iron (Leco 208, 0.018 Ce)	0.018	0.0004	0.0010
8. R. E. Cast Iron (Leco 209, 0.026 Ce)	0.025	0.0009	0.0027
9. Ductile Iron (NBS 1140)	0.086	0.0015	0.0033
10. Low Alloy	0.16	0.0049	0.0066
11. Cast Iron	0.28	0.0067	0.0154
12. Cast Iron	0.38	0.0079	0.0183

TABLE 26 Statistical Information—Lanthanum

Test Specimen	Lanthanum Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. Low Alloy (NBS 362, 0.001 La)	0.0008	0.0001	0.0004
2. Low Alloy (NBS 361, 0.001 La)	0.0012	0.0001	0.0004
3. Cast Iron	0.0028	0.0002	0.0006
4. R. E. Cast Iron (Leco 206)	0.0037	0.0002	0.0005
5. R. E. Cast Iron (Leco 207)	0.0032	0.0002	0.0006
6. Low Alloy (NBS 1286)	0.0083	0.0003	0.0008
7. R. E. Cast Iron (Leco 208)	0.0057	0.0002	0.0007
8. R. E. Cast Iron (Leco 209)	0.0075	0.0004	0.0012
9. Ductile Iron (NBS 1140)	0.024	0.0007	0.0027
10. Low Alloy	0.098	0.0033	0.0108
11. Cast Iron	0.16	0.0038	0.0142
12. Cast Iron	0.20	0.0055	0.0152

246.1 This method covers the determination of titanium in concentrations from 0.006 to 0.35 %.

247. Summary of Method

247.1 Dissolution of the sample is followed by reduction and complexation of interfering elements. The titanium 4,4' dianthipyrylmethane complex is formed and determined spectrophotometrically. The spectrophotometric measurement is made at approximately 390 nm.

248. Concentration Range

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

249. Stability of Color

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

250. Interferences

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

251. Apparatus

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

252. Reagents

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

252.2 *Diantipyrylmethane (DAPM)* (20 g/L)—Dissolve 5 g of 4,4'-diantipyrylmethane monohydrate ($C_{23}H_{24}N_4O_2 \cdot H_2O$) in HCl (1 + 9) and dilute to 250 mL with the dilute hydrochloric acid. Prepare as needed.

252.3 *Potassium Hydrogen Sulfate, Fused* (a mixture of $K_2S_2O_7$ and $KHSO_4$).

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

252.5 *Titanium Sulfate Standard Solution* (1 mL = 0.010 mg Ti)—Transfer 0.1000 g of titanium metal (purity: 99.9 % minimum) weighed to within ± 0.2 mg to a 1-L volumetric flask. Add 50 mL of H_2SO_4 (1 + 3) and dissolve at less than

150°C. Oxidize the titanium by adding HNO_3 dropwise (Note 70). Cool, dilute to volume with H_2SO_4 (1 + 9), and mix. Using a pipet, transfer 10 mL to a 100-mL volumetric flask, add 10 mL of tartaric acid solution, dilute to volume, and mix. Do not use a solution that has stood more than one day.

NOTE 71—An excess of HNO_3 should be avoided. Two to three drops of HNO_3 should be sufficient to oxidize the titanium sulfate solution and discharge the blue color.

253. Preparation of Calibration Curve

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

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

NOTE 72—Take spectrophotometric readings of the calibration solutions containing 0.5, 1, 2, 4, and 6 mL of titanium solution using a 2-cm light path. Use a 1-cm light path for the remaining solutions.

253.3 *Reference Solution*—Water.

253.4 *Reagent Blank*—Transfer 10 mL of water to a 50-mL volumetric flask and proceed as directed in 253.5.

253.5 *Color Development*:

253.5.1 Add 3.0 mL of (HCl 1 + 1) and 5 mL of ascorbic acid solution and allow to stand for 10 min. Add 10 mL of DAPM solution, dilute to volume with water, mix, and allow the solution to stand for at least 90 min.

253.6 *Spectrophotometry*:

253.6.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction using absorption cells with either a 1-cm light path or a 2-cm light path and a light band centered at approximately 390 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions and the reagent blank solutions versus the reference solution.

253.6.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1 or 2-cm light path and adjust the spectrophotometer using a light band centered at approximately 390 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank solutions.

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

254. Procedure

254.1 *Test Solution*:

254.1.1 Select a sample, weighed to the nearest 1 mg, in accordance with the following:

Titanium, %	Sample Weight, g	Tolerance in		Aliquot Volume, mL	Cell Size, cm
		Sample Weight, mg	Final Volume, mL		
0.006 to 0.07	1.00	1	100	10.00	2
0.07 to 0.14	1.00	1	100	10.00	1

0.14 to 0.35 0.40 0.5 100 10.00 1

Transfer it to a 250-mL beaker.

254.1.2 Add 20 mL of HCl and digest at a low temperature until dissolution is complete. Add 5 mL of HNO₃ and evaporate the solution to dryness.

NOTE 73—The use of a coarse screen of 3-mm (1/8-in.) wire, or triangles on the hot plate, permits more rapid evaporation without the danger of spattering.

Cool, add 5 mL of HCl to the glass-covered beaker and dissolve the iron salts at 90 to 100°C and then add 15 mL of water.

254.1.3 Filter through an 11-cm medium-porosity filter paper containing paper pulp into a 100-mL volumetric flask as directed in 254.1.1 and rinse the beaker and filter paper three times each with hot water. Remove the iron salts by washing the paper with 10 mL of HCl (1 + 1) and hot water. Volume in the flask at this point should not exceed 70 mL.

254.1.4 Transfer the paper to a platinum crucible, dry the paper and residue, and then heat in a muffle furnace at about 700°C until the carbon is removed. Cool, and add a few drops of H₂SO₄ (1 + 1) followed by 2 mL of HF. Evaporate to dryness, and then heat at a gradually increasing rate until the H₂SO₄ is removed. Cool, add 2 g of fused potassium pyrosulfate, fuse over a gas burner and heat until a clear melt is obtained. Add 10 mL of tartaric acid solution to the cooled melt, heat at 90 to 100°C, and when the melt is dissolved, add this solution to the reserved filtrate in the volumetric flask (254.1.3). Dilute to volume, and mix.

254.1.5 Using a pipet, transfer a 10-mL portion to a 50-mL volumetric flask and treat as directed in 253.5.1 using 1 mL of HCl (1 + 1).

254.2 *Sample Blank Solution*—Using a pipet, transfer a second 10-mL portion of the test solution to a 50-mL volumetric flask and treat as directed in 254.1.1 and 253.5.1, omitting the addition of DAPM.

254.3 *Reagent Blank Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents with the sample omitted (254.1.1–254.1.5).

254.4 *Reference Solutions*—Water and the sample blank solution, as described in 254.5.

254.5 *Spectrophotometry*—Take the spectrophotometric reading of the reagent blank solution versus water and of the test solution versus the sample blank solution, as directed in 253.6.

255. Calculation

255.1 Convert the spectrophotometric reading of the test solution to milligrams of titanium by means of the appropriate calibration curve. Calculate the percentage of titanium as follows:

$$\text{Titanium, \%} = (A - B)/(C \times 100) \times 100 \quad (43)$$

where:

A = titanium, mg, found in the final color development solution,

B = titanium found, mg, in the reagent blank, and

C = original sample weight (g) as determined in 254.1.1.

256. Precision and Bias

256.1 *Precision*—Eight laboratories cooperated in testing this method and obtained the data summarized in Table 27.

256.2 *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.

MOLYBDENUM BY THE ION EXCHANGE—8-HYDROXYQUINOLINE GRAVIMETRIC METHOD

257. Scope

257.1 This method covers the determination of molybdenum in concentrations from 1.5 to 5.0 %.

258. Summary of Method

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

259. Interferences

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

260. Apparatus

260.1 *Ion Exchange Column, Polystyrene*,²⁹ approximately 400 mm long and 25 mm in inside diameter, the bottom tapered to a 2-mm bore outlet, fitted with a hosecock or stopcock to control the liquid flow. All parts of the apparatus must be constructed of HF-resistant plastic, such as polytetrafluoroethylene, polyethylene, or poly(vinyl chloride) (Note 74).

NOTE 74—The ion exchange column system must be carefully assembled and checked to avoid possible leakage of solutions containing HF.

261. Reagents

261.1 *Ammonium Chloride Solution* (240 g/L)—Dissolve 240 g of ammonium chloride (NH₄Cl) in 800 mL of water. Warm to room temperature, dilute to 1 L and mix.

²⁹ Columns available from Ledoux & Co., Inc., Teaneck, NJ have been found satisfactory.

TABLE 27 Statistical Information—Titanium

Test Specimen	Titanium Found, %	Repeatability, % (R ₁ , E 173)	Reproducibility, % (R ₂ , E 173)
1. Low Alloy (NBS 19 g, 0.027 Ti)	0.028	0.0013	0.0043
2. Low Alloy (NBS 170a, 0.281 Ti)	0.282	0.0097	0.0228
3. Cast Iron (NBS 122d, 0.007 Ti)	0.006	0.0019	0.0037
4. Blast Furnace Iron (NBS 1144a, 0.32 Ti)	0.33	0.0118	0.0168

261.2 *Ammonium Fluoride* (NH_4F).

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

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

261.5 *Eluent Solutions* (**Warning**—See Note 75.)

NOTE 75—(**Warning**: HF causes serious burns which may not be immediately painful; read the paragraph about HF in the Safety Precautions section of Practices E 50.)

261.5.1 *Hydrofluoric Acid/Hydrochloric Acid/Water* (4 + 1 + 95)—To 800 mL of water in a 1-L polyethylene graduated cylinder, add 40 mL of HF and 10 mL of HCl; dilute to 1 L and mix. Store in an HF-resistant plastic bottle.

261.5.2 *Hydrofluoric Acid/Hydrochloric Acid/Water* (1 + 5 + 4)—To 300 mL of water in a 1-L polyethylene graduated cylinder, add 100 mL of HF and 500 mL of HCl; dilute to 1 L and mix. Store in an HF-resistant plastic bottle.

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

261.5.4 *Hydrofluoric Acid/Ammonium Chloride/Water* (4 + 60 + 36)—To 600 mL of ammonium chloride solution (240 g/L) in a 1-L polyethylene graduated cylinder, add 40 mL HF; dilute to 1 L and mix. Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH_4Cl on a weight/volume basis.)

261.5.5 *Ammonium Fluoride/Ammonium Chloride Solution*—To 600 mL of ammonium chloride solution (240 g/L) in a 1-L polyethylene graduated cylinder, add 41 g of NH_4F . Add water to the 900 mL mark and stir to dissolve. Dilute to 1 L and mix. With narrow-range pH paper, verify that the pH is between 5.6 and 5.8. If it is above this range, adjust the solution with dropwise additions of HF; if it is below this range, adjust the solution with dropwise additions of NH_4OH . Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH_4Cl and 4.1 % in NH_4F on a weight/volume basis.)

261.6 *8-Hydroxyquinoline Solution* (30 g/L)—Dissolve 30 g of 8-hydroxyquinoline in 120 mL of glacial acetic acid (CH_3COOH). Cautiously add water, with stirring to a total solution volume of 600 mL. Warm to 40°C. Add NH_4OH (1 + 1) dropwise with stirring until a slight permanent precipitate is formed. Carefully add glacial CH_3COOH with stirring until the precipitate first dissolves. Dilute to 1 L.

261.7 *Ion-Exchange Resin*:

261.7.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and of 200 to 400 nominal U.S. mesh size.³⁰ To remove those beads greater than about 180 μm in diameter, as well as the very small diameter beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow at least 30 min for the beads to undergo maximum swelling. Place a No. 80 (180 μm) screen, 150 mm in diameter, over a 2-L beaker. Prepare a thin slurry of the resin and pour it into the screen. Wash the fine beads through the screen using a small stream of water. Discard the

beads retained on the screen periodically to avoid undue clogging of the openings. When the bulk of the resin has settled in the 2-L beaker, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19) and stir vigorously. Allow the resin to settle for 4 to 6 min, decant 150 to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

261.7.2 Prepare the column as follows: Place a 10- to 20-mm layer of poly(vinyl chloride) plastic fiber³¹ in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 150 to 175 mm. Place a 20-mm layer of poly(vinyl chloride) plastic fiber on the top of the resin surface to protect it from being carried into suspension when the solutions are added. Add 100 to 125 mL of HCl (3 + 1) to the column. When the solution level is 5 to 10 mm above the top of the resin bed add 100 mL of HCl (1 + 9) to the column. Repeat this cycle twice more and finally wash the resin bed with 200 mL HCl (1 + 3) turning off the stopcock when the solution level is 10 to 20 mm above the top of the resin bed.

261.8 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in about 100 mL of water. When dissolution is complete, cool, and dilute to 1 L. Store in a plastic bottle.

261.9 *Sodium Hydroxide Solution* (10 g/L)—Dissolve 10 g of NaOH in about 100 mL of water. Cool and dilute to 1 L. Store in a plastic bottle.

262. Procedure

262.1 Transfer 1 g of sample weighed to the nearest 0.1 mg to a 200-mL polytetrafluoroethylene beaker marked at the 100 mL level on the outside. Add 10 mL of HF and cover with a polytetrafluoroethylene watchglass. Warm the solution with low heat and cautiously add HNO_3 in 1-mL increments allowing the reaction to subside between additions. High chromium samples may also require cautious dropwise additions of HCl. When dissolution is complete, cool the beaker, remove the cover with platinum-tipped tongs and cautiously rinse it into the solution with water.

262.2 Over a steambath of other low temperature arrangement evaporate the solution to dryness. Cool, wash down the sides of the beaker with HCl (1 + 1) and again evaporate to dryness over low heat. Cool, add 5 mL of HF and 25 mL water. Warm over low heat until all salts are dissolved (Note 76). Cool to room temperature and dilute to 100 mL with water.

NOTE 76—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

262.3 Drain the solution in the ion exchange column by passing 100 mL of HF/HCl/water (4 + 1 + 95) through it at a ratio of approximately 2 mL/min. Allow the solution to drain to the top of the resin bed. Collect the effluent in a plastic beaker and discard it.

262.4 Place an 800 mL plastic beaker under the column.

³⁰ AGI-X8, 200 to 400 mesh, chloride form, which is available from Bio-Rad Laboratories, Richmond, CA, has been found satisfactory.

³¹ Dynel plastic wool available from Union Carbide Corp., Chemical Division, Textile Fibers Department, Needham Heights, MA, has been found satisfactory.

Place a small plastic funnel holding a high-porosity hard-surface filter paper in the top of the column. Ensure that an air seal does not form between the funnel and the column. Cautiously filter the sample solution onto the column. Adjust the effluent flow to about 2 mL/min. Rinse the beaker with HF/HCl/water (4 + 1 + 95) transferring the washings to the paper. Cautiously police the beaker with a polytetrafluoroethylene policeman, if necessary, and rinse onto the paper with HF/HCl/water (4 + 1 + 95). Wash the paper well with HF/HCl/water (4 + 1 + 95). Cautiously, remove and discard paper (Note 77).

NOTE 77—If insoluble molybdenum compounds are suspected or known to be present, halt the flow from the column when the washing of the paper is complete. Cautiously transfer the paper to a platinum crucible and ignite at 500°C (no higher) in a muffle furnace. Cool in a desiccator, add 1 g anhydrous sodium carbonate powder (Na₂CO₃) and fuse over a burner. Cool, add 20 mL water and heat to dissolve the melt. Carefully acidify with dropwise additions of HCl (1 + 4) until effervescence ceases plus 10 drops excess. Evaporate to dryness, cool, add 20 mL HF/HCl/water (4 + 1 + 95), heat to dissolve, cool, and transfer this solution to the column. Resume the 2 mL/min flow from the column.

262.5 Continue to add HF/HCl/water (4 + 1 + 95) until 650 mL have been collected in the 800 mL plastic beaker (Note 78). Drain solution to the top of the resin bed. Cautiously discard this solution.

NOTE 78—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper and manganese.

262.6 Place an 800-mL plastic beaker under the column and elute 500 mL of HF/HCl/water (1 + 5 + 4) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 79).

NOTE 79—This solution contains all the tungsten, titanium, zirconium, and hafnium.

262.7 Place an 800-mL polytetrafluoroethylene beaker under the column and elute the molybdenum with 500 mL of HF/HCl/water (20 + 25 + 55) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Proceed with this eluent solution as described in paragraph 262.11.

262.8 Place an 800-mL plastic beaker under the column and elute 300 mL of HF/NH₄Cl/water (4 + 60 + 36) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 80).

NOTE 80—This solution contains all the niobium.

262.9 Place an 800-mL plastic beaker under the column and elute 350 mL of NH₄F/NH₄Cl solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 81).

NOTE 81—This solution contains all the tantalum.

262.10 Place an 800-mL plastic beaker under the column and elute 100 mL of water, then 100 mL of HCl (1 + 3), stopping the flow when the liquid level is 10 to 20 mm above the resin bed. Cautiously discard the solution. The column is now ready to be stored for future use or to be preconditioned for another sample (262.3).

262.11 To the eluent containing the molybdenum (from 262.7) cautiously add 15 mL of H₂SO₄ (1 + 1) and evaporate

to light fumes on a sanbath or other carefully controlled heat source (see Note 82).

NOTE 82—Warning: Ensure that the applied temperature does not exceed the softening point of polytetrafluoroethylene. Cool and cautiously rinse into 1 400-mL borosilicate glass beaker. Heat to low volume (about 10 mL), cool, add 2 mL of HNO₃, and evaporate to strong fumes of SO₃.

262.12 Cool to room temperature, dilute to about 30 mL with water, add 5 mL of HNO₃ and 5 mL of HCl. Cover and heat for 10 min.

262.13 Dilute to 100 mL. Heat to boiling and while hot, cautiously add NaOH solution (100 g/L) until litmus paper moistened with the solution just turns blue, then add 10 mL excess. Boil for 1 min. If a precipitate is present, filter through high porosity, surface hardened filter paper and wash paper thoroughly with warm NaOH solution (10 g/L). Discard paper. If no precipitate is present proceed directly to 262.14.

262.14 Adjust the volume of the solution or filtrate obtained in 262.13 to about 200 mL. Add 10 mL of EDTA solution (10 g/L) and 3 g of ammonium oxalate. Warm gently to obtain a clear solution and cool to room temperature. Adjust the pH to 4.0 using a pH meter and dropwise additions of HCl (1 + 1) and NaOH solution (10 g/L).

262.15 Heat the solution to boiling, remove from heat and slowly add 20 mL of 8-hydroxyquinoline solution (30 g/L) while stirring. Heat at just below the boiling point for 10 min, stirring occasionally.

262.16 Filter through a tared medium-positivity fritted glass filtering crucible using gentle suction. Wash the contents of the beaker into the filtering crucible with hot water and wash the precipitate with additional hot water for a total of about 100 mL.

262.17 Dry the precipitate in a drying oven set at 125°C for at least 4 h. Cool the filtering crucible for at least 2 h in a desiccator and weigh.

263. Calculation

263.1 Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, \%} = [(A - B) \times 23.05]/C \quad (44)$$

where:

A = weight of crucible plus precipitate, in g,

B = weight of crucible, in g, and

C = sample weight, in g

264. Precision and Bias

264.1 *Precision*—Seven laboratories cooperated in testing this method and obtained the data summarized in Table 28.

TABLE 28 Statistical Information—Molybdenum Ion Exchange—8-Hydroxyquinoline Gravimetric Method

Test	Molybdenum Found, %	Repeatability, (<i>R</i> ₁ , E 173 ^A)	Reproducibility, (<i>R</i> ₂ , E 173 ^A)
1. White cast iron (NBS 1146, 1.51 Mo)	1.48	0.070	0.086
2. No. 1, E 354	3.92	0.219	0.250
3. No. 3, E 352	8.85	0.180	0.188

^AThe test was conducted in accordance with the 1980 version of Practice E 173.

While the testing range exceeds the upper limit of the Scope, the data for Test Material 3 were included to illustrate the ruggedness of the method's precision at levels near the upper limit of the Scope.

264.2 *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.

265. Keywords

265.1 carbon content; cast iron; cerium; chromium; cobalt; combustion analysis; copper; graphitic carbon; infrared absorption; lanthanum; lead; magnesium; manganese; molybdenum; nickel; phosphorus; silicon; sulfur; tin; titanium; vanadium

APPENDIX

(Nonmandatory Information)

X1. TEST OF SUITABILITY OF IRON AND STRONTIUM CHLORIDE

X1.1 Iron

X1.1.1 Transfer $(5 \times F)$ g of iron (76.1) weighed to the nearest 10 mg, to a 400-mL beaker; dissolve it, evaporate the solution to dryness and bake as directed in 76.1. Add 15 mL of HCl and heat gently until salts are dissolved. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Transfer 20.0 mL of each of three 25-mL volumetric flasks, dilute one of them to volume, and mix. To the other two add 2.0 and 4.0 mL, respectively, of magnesium solution B (76.3), dilute to volume, and mix.

X1.1.2 Prepare a reagent blank by evaporating to dryness the volumes of HCl (1 + 1) and HNO₃ used in 1.1 to dissolve the iron. Add 15 mL of HCl and heat gently to dissolve any salts. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Transfer 20.0 mL to each of three 25-mL volumetric flasks, dilute one of them to volume, and mix. To the other two add 2.0 and 4.0 mL, respectively, of magnesium solution B (76.3), dilute to volume, and mix.

X1.1.3 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.

X1.1.4 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the solution to which 4 mL of magnesium standard solution was added in 1.1 a sufficient number of times to establish that the reading is not drifting. Record the absorbance. Aspirate the other two solutions and the three solutions prepared as directed in 1.2.

X1.1.5 Plot two curves on rectangular coordinate paper, one based on the absorbance values recorded for the three solutions from 1.1 and the other based on the three values found for the solutions from 1.2 against milligrams of magnesium added, namely 0, $0.004 \times F$, and $0.008 \times F$ (75.1.4). Extrapolate each curve to zero absorbance and record the corresponding values for milligrams of magnesium in 25 mL of the final solution.

X1.1.6 Calculate the percentage of magnesium in the iron as follows:

$$\text{Magnesium, \%} = (A - B)/(10 \times F) \quad (\text{X1.1})$$

where:

- A = magnesium, mg, in 25 mL of the final solution of iron,
- B = magnesium, mg, in 25 mL of the final blank solution, and
- F = sensitivity factor (75.1.4).

X1.2 Strontium Chloride

X1.2.1 Transfer 10.0 mL of the solution prepared as directed in 76.4 to each of three 25-mL volumetric flasks, dilute one of them to volume, and mix. To the other two add 2.0 and 4.0 mL, respectively, of magnesium solution B (76.3), dilute to volume, and mix.

X1.2.2 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.

X1.2.3 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the solution to which 4 mL of magnesium standard solution was added in X1.2.1 a sufficient number of times to establish that the reading is not drifting. Record the absorbance. Aspirate the other two solutions and record the absorbance values.

X1.2.4 Plot a curve on rectangular coordinate paper based on the absorbance values of the three solutions (A1.2.3) against milligrams of magnesium added, namely 0, $0.004 \times F$, and $0.008 \times F$ (75.1.4). Extrapolate the curve to zero absorbance and record the corresponding value for milligrams of magnesium in 25 mL of the final solution.

X1.2.5 Calculate the percentage of magnesium in the strontium chloride as follows:

$$\text{Magnesium, \%} = A/(10 \times F) \quad (\text{X1.2})$$

where:

- A = magnesium, mg, in 25 mL of the final strontium chloride solution, and
- F = sensitivity factor (75.1.4).



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