



Standard Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels¹

This standard is issued under the fixed designation E 352; 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.

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

1. Scope

1.1 These test methods² cover the chemical analysis of tool steels and other similar medium- and high-alloy steels having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	0.005 to 1.5
Boron	0.001 to 0.10
Carbon	0.03 to 2.50
Chromium	0.10 to 14.0
Cobalt	0.10 to 14.0
Copper	0.01 to 2.0
Lead	0.001 to 0.01
Manganese	0.10 to 15.00
Molybdenum	0.01 to 10.00
Nickel	0.02 to 4.00
Nitrogen	0.001 to 0.20
Phosphorus	0.002 to 0.05
Silicon	0.10 to 2.50
Sulfur	0.002 to 0.40
Tungsten	0.01 to 21.00
Vanadium	0.02 to 5.50

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

	Sections
Carbon, Total, by the Combustion—Thermal Conductivity Method	2 ^a
Carbon, Total, by the Combustion Gravimetric Method	(0.05 to 2.50 %) 78
Chromium by the Atomic Absorption Method	(0.006 to 1.00 %) 174
Chromium by the Peroxydisulfate Oxidation—Titration Method	(0.10 to 14.00 %) 184
Chromium by the Peroxydisulfate-Oxidation Titrimetric Method	2 ^b
Cobalt by the Ion-Exchange—Potentiometric Titration Method	(2 to 14 %) 52

¹ These test methods are under the jurisdiction of the 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 352 – 68 T. Last previous edition E 352 – 89^{ε1}.

² These test methods represent revisions of methods covered by ASTM E 30, which appear in this publication. Typical alloy specification numbers for this category are listed in the Appendix.

^{2a} Discontinued April 25, 1986. Its replacement appears as part of ASTM Methods E 1019, found in *Annual Book of ASTM Standards*, Vol 03.05.

^{2b} Discontinued May 30, 1980.

^{2c} Discontinued April 29, 1988.

		Sections
Cobalt by the Nitroso-R-Salt Photometric Method	(0.10 to 5.0 %)	60
Copper by the Neocuproine Photometric Method	(0.01 to 2.00 %)	89
Copper by the Sulfide Precipitation-Electrodeposition Gravimetric Method	(0.01 to 2.0 %)	70
Lead by the Ion-Exchange—Atomic Absorption Method	(0.001 to 0.001 %)	99
Nickel by the Dimethylglyoxime Gravimetric Method	(0.1 to 4.0 %)	144
Manganese by the Periodate Photometric Method	(0.10 to 5.00 %)	8
Molybdenum by the Ion Exchange—8-Hydroxyquinoline Gravimetric Method		203
Molybdenum by the Photometric Method	(0.01 to 1.50 %)	162
Phosphorus by the Alkalimetric Method	(0.01 to 0.05 %)	136
Phosphorus by the Molybdenum Blue Photometric Method	(0.002 to 0.05 %)	18
Silicon by the Gravimetric Method	(0.10 to 2.50 %)	45
Sulfur by the Gravimetric Method		2 ^c
Sulfur by the Combustion-Iodate Titration Method	(0.005 to 0.4 %)	36
Sulfur by the Chromatographic Gravimetric Method		2 ^b
Tin by the Solvent Extraction—Atomic Absorption Method	(0.002 to 0.10 %)	152
Vanadium by the Atomic Absorption Method	(0.006 to 0.15 %)	193

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

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

2. Referenced Documents

2.1 ASTM Standards:

- D 1193 Specification for Reagent Water³
 E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications⁴
 E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron⁵
 E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals⁶
 E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals⁶
 E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁷
 E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron⁶
 E 351 Test Methods for Chemical Analysis of Cast Iron—All Types⁶
 E 353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys⁶
 E 354 Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic and Other Similar Iron, Nickel, and Cobalt Alloys⁶
 E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)⁸
 E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁶
 E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys⁶
 E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry⁶
 E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis⁶
 E 1806 Practice for Sampling Steel and Iron for Determination of Chemical Composition⁹
- ### 2.2 Other Document:
- ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests¹⁰

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 A1 on Steel, Stainless Steel, and Related Alloys. It is

assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide E 882.

4. Apparatus, Reagents, and Instrumental 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.¹¹ Other chemicals may be used, provided it is first ascertained that they are of sufficiently high purity to permit their use without adversely affecting the expected performance of the determination, as indicated in the section on “Precision and Bias.”

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

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

5. Hazards

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

6. Sampling

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

7. Interlaboratory Studies and Rounding Calculated Values

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

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

MANGANESE BY THE METAPERIODATE PHOTOMETRIC METHOD

8. Scope

8.1 This method covers the determination of manganese in concentrations from 0.10 to 5.00 %.

9. Summary of Method

9.1 Manganous ions are oxidized to permanganate ions by treatment with periodate. Tungsten when present at concentrations greater than 0.5 % is kept in solution with phosphoric acid. Solutions of the samples are fumed with perchloric acid

³ *Annual Book of ASTM Standards*, Vol 11.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.02.

⁵ Discontinued 1995; see *1994 Annual Book of ASTM Standards*, Vol 03.05.

⁶ *Annual Book of ASTM Standards*, Vol 03.05.

⁷ Discontinued 1998; see *1997 Annual Book of ASTM Standards*, Vol 03.05.

⁸ Discontinued 1997; see IEEE/ASTM SI 10—Standard, Vol 14.04.

⁹ *Annual Book of ASTM Standards*, Vol 03.06.

¹⁰ Available from American National Standards Institute, 11 West 42nd Street, 13th Floor, New York, NY 10036.

¹¹ “Reagent Chemicals, American Chemical Society Specifications,” Am. Chemical Soc., Washington, DC. For suggestions on the testing of Reagents not listed by the American Chemical Society, see “Reagent Chemicals and Standards,” by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the “United States Pharmacopeia.” United States Pharmacopeial Convention, Rockville, MD 20852.

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

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

12.3 Tungsten, when present in amounts of more than 0.5 % interferes by producing a turbidity in the final solution. A special procedure is provided for use with samples containing more than 0.5 % tungsten which eliminates the problem by preventing the precipitation of the tungsten.

13. Reagents

13.1 *Manganese, Standard Solution* (1 mL = 0.032 mg Mn)—Transfer the equivalent of 0.4000 g of assayed, high-purity manganese (purity: 99.99 % minimum), to a 500-mL volumetric flask and dissolve in 20 mL of 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 Solutions*—Select and weigh a sample in accordance with the following:

Manganese, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.10 to 0.5	0.80	0.5	100	20
0.45 to 1.0	0.35	0.3	100	20
0.85 to 2.0	0.80	0.5	500	20
0.95 to 5.0	0.80	0.5	500	10

Transfer it to a 300-mL Erlenmeyer flask.

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

15.1.1.1 To dissolve samples that do not require HF, add 8 to 10 mL of HCl (1+1), and heat. Add 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. Proceed to 15.1.3.

15.1.1.2 For samples whose dissolution is hastened by HF, add 8 to 10 mL of HCl (1+1), and heat. 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. Proceed to 15.1.3.

15.1.2 For Samples Containing More Than 0.5 % Tungsten:

15.1.2.1 To dissolve samples that do not require HF, add 8 to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 to 6 mL of H₂SO₄, and 3 to 4 mL of HNO₃. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO₃. Cool, add 50 mL of water, and digest, if necessary, to dissolve the salts. Transfer the solution to either a 100- or 500-mL volumetric flask as directed in 15.1. Proceed to 15.1.3

15.1.2.2 For samples whose dissolution is hastened by HF, add 8 to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 to 6 mL of H₂SO₄, 3 to 4 mL of HNO₃, and a few drops of HF. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO₃. 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 directed in 15.1. Proceed to 15.1.3.

15.1.3 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.

15.1.4 Using a pipet, transfer 10 to 20 mL aliquots, as specified in 15.1 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 10 mL of nitric-phosphoric acid mixture, and heat the solution at not less than 90°C for 20 to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

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

15.5 Photometry—Establish the cell corrections with the Reagent Blank Reference solution to be used as a reference

solution for Background Color solutions. Take the photometric readings of the Background Color Solutions and the test solutions versus the respective Reagent Blank Reference 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.

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 test method covers the determination of phosphorus in concentrations from 0.002 to 0.05 %.

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.

TABLE 1 Statistical Information—Manganese by the Metaperiodate Photometric Method

Test Specimen	Manganese Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. Special W high-speed tool steel (NIST 440, 0.15 Mn)	0.160	0.012	0.035
2. Tool steel (NIST 153a, 0.192 Mn)	0.183	0.005	0.010
3. W high-speed tool steel (NIST 441, 0.27 Mn)	0.268	0.010	0.034
4. Alloy Steel (NIST, 159, a807 Mn)	0.819	0.010	0.034
5. Low Alloy Steel (NIST 100b, 1.89 Mn)	1.91	0.02	0.04
6. Stainless Steel (NIST 444, 4.62 Mn)	4.60	0.04	0.13

22. Interferences

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

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.

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. Procedure

26.1 *For Samples Containing Less Than 0.5 % Tungsten:*

26.1.1 *Test Solution:*

26.1.1.1 Proceed as directed in 27.1.1 through 27.1.3 of Test Methods E 350.

26.1.2 Proceed as directed in 27.2 through 27.5 of Test Methods E 350.

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

26.2.1 *Test Solution:*

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

26.2.1.2 Add 5 mL of a mixture of 1 volume of HNO₃ and 3 volumes of HCl. When the reaction has ceased, add 2.5 mL of HClO₄ and 5 mL of HBr (1 + 4). Evaporate the solutions to copious white fumes; then, without delay, fume strongly enough to cause the white fumes to clear the neck of the flasks, and continue at this rate for 1 min.

26.2.1.3 Cool the solutions, and add 10 mL of water. Filter through a 9-cm fine paper collecting the filtrate in a 100-mL borosilicate glass volumetric flask. Wash the paper and insoluble matter 5 times with 3-mL portions of water. Treat one solution as directed in 26.2.3 and the other as directed in 26.2.4.

26.2.2 *Reagent Blank Solution*—Proceed as directed in 26.2.1.2 and 26.2.1.3.

26.2.3 *Color Development*—Proceed as directed in 25.3 of Test Methods E 350.

26.2.4 *Reference Solutions*—Proceed as directed in 27.4 of Test Methods E 350.

26.2.5 *Photometry*—Proceed as directed in 27.5 of Test Methods E 350.

27. Calculation

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

28. Precision

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

SULFUR BY THE GRAVIMETRIC METHOD

(This method, which consisted of Sections 29 through 35 of

TABLE 2 Statistical Information—Phosphorus

Test Specimen	Phosphorus Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. Tool steel 5Mo-6W-4Cr-2V (NBS 132a, 0.029 P)	0.029	0.011	0.008
2. Tool steel 8Co-9Mo-2W-4Cr-2V (NBS 153a, 0.023 P)	0.023	0.008	0.007
3. Tool steel 18W-4Cr-1V (NBS 50c, 0.022 P)	0.022	0.005	0.007

this standard, was discontinued in 1988.)

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

36. Scope

36.1 This method covers the determination of sulfur in concentrations from 0.005 to 0.4 %.

37. Summary of Method

37.1 See Section 38 of Test Methods E 350.

38. Interferences

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

39. Apparatus

39.1 See Section 40 of Test Methods E 350.

40. Reagents

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

41. Calibration

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

42. Procedure

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

43. Calculation

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

44. Precision

44.1 Twenty-two laboratories cooperated in testing this method; six used resistance furnaces and reported eight sets of values (Note 3); sixteen used induction furnaces (Note 4). They obtained the data summarized in Table 3 for specimens 1 and 2. Although samples covered by this method with sulfur concentration near the upper limit of the scope were not available for testing, the precision data obtained using the methods indicated in Table 3 should apply.

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

TABLE 3 Statistical Information—Sulfur

Test Specimen	Sulfur Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
Induction Furnace			
1. High-alloy steel 8Co-9Mo-2W-4Cr-2V (NBS 153a, 0.007S)	0.006 ^A	0.002	0.003
2. Tool steel 18W-4Cr-1V (NBS 50c, 0.010S)	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. No. 7, E 350	0.141 ^B	0.007	0.013
6. No. 7, E 353	0.286 ^C	0.014	0.020
Resistance Furnace			
1. High-alloy steel 8Co-9Mo-2W-4Cr-2V (NBS 153a, 0.007S)	0.006 ^A	0.001	0.002
2. Tool steel 18W-4Cr-1V (NBS 50c, 0.010S)	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. No. 7, E 350	0.140 ^B	0.007	0.011
6. No. 7, E 353	0.288 ^C	0.012	0.021

^ACalibration standards: See Footnote ^A, Table 5, Methods E 350.

^BCalibration standards: See Footnote ^C, Table 5, Methods E 350.

^CCalibration standards: See Footnote ^D, Table 5, Methods E 350.

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

SILICON BY THE GRAVIMETRIC METHOD

45. Scope

45.1 This method covers the determination of silicon in concentrations from 0.10 to 2.50 %.

46. Summary of Method

46.1 See Section 47 of Test Methods E 350.

47. Interferences

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

48. Reagents

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

49. Procedure

49.1 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
0.1 to 0.1	4.0	4	150	60
1.0 to 1.75	3.0	3	100	50
1.75 to 2.50	2.0	2	100	40

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

49.2 Proceed as directed in 50.2 of Test Methods E 350 if tungsten is greater than 0.5 %.

49.3 Proceed as directed in 50.2 or 50.3 of Test Methods E 350 if tungsten is less than 0.5 %.

49.4 Proceed as directed in 50.4 through 50.6 of Test Methods E 350.

49.5 Proceed as directed in 50.7, Test Methods E 350, but if the sample contains more than 0.5 percent tungsten, ignite at 750 C instead of 1100 to 1150 C after volatilization of SiO₂.

50. Calculation

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

51. Precision

51.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 4. Samples with tungsten below 0.5 % were not available for testing the HClO₄ dehydration procedure; neither were samples available with tungsten greater than 0.5 % for testing the H₂SO₄ dehydration procedure near the upper limit of the scope.

COBALT BY THE ION-EXCHANGE—POTENTIOMETRIC TITRATION METHOD

52. Scope

52.1 This method covers the determination of cobalt in concentrations from 2 to 14 %.

53. Summary of Method

53.1 See Section 54 of Test Methods E 351.

54. Interferences

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

55. Apparatus

55.1 See Section 56 of Test Methods E 351.

56. Reagents

56.1 Proceed as directed in 57.1 through 57.4 of Test Methods E 351.

57. Procedure

57.1 Proceed as directed in 58.1 of Test Methods E 351.

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

57.2 Proceed as directed in 58.2 through 58.6 of Test Methods E 351.

58. Calculation

TABLE 4 Statistical Information—Silicon

Test Specimen	Silicon Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
H ₂ SO ₄ Dehydration			
1. Tool steel 5Mo-6W-4Cr-2V (NBS 132a, 0.19 Si)	0.193	0.019	0.031

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

59. Precision

59.1 Ten laboratories cooperated in testing the method and obtained the data summarized in Table 5 for specimens 1, 2, and 3. Although samples covered by this method with cobalt concentrations near the upper limit of the scope were not available for testing, the precision data obtained for specimens 4 and 5 using the method indicated should apply.

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

60. Scope

60.1 This method covers the determination of cobalt in concentrations from 0.10 to 5.0 %.

61. Summary of Method

61.1 See Section 54 of Test Methods E 350.

62. Concentration Range

62.1 See Section 55 of Test Methods E 350.

63. Stability of Color

63.1 See Section 56 of Test Methods E 350.

64. Interferences

64.1 See Section 57 of Test Methods E 350.

65. Reagents

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

66. Preparation of Calibration Curve

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

67. Procedure

67.1 *Test Solution:*

67.1.1 Proceed as directed in 68.1.1 through 68.1.3 of Test Methods E 351.

NOTE 6—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. If HF is used, the sample should be dissolved in a 150-mL beaker and the solution transferred to the specified volumetric flask.

TABLE 5 Statistical Information—Cobalt

Test Specimen	Cobalt Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. High alloy steel 4Mo-6W-4Cr-2V	1.86	0.05	0.12
2. Tool steel 18W-4Cr-1V	4.82	0.08	0.11
3. High-alloy steel 8Co-9Mo-2W-4Cr-2V (NBS 153a, 8.47 Co)	8.46	0.03	0.07
4. No. 4, E 354	11.27	0.06	0.16
5. No. 5, E 354	13.88	0.09	0.18

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

68. Calculation

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

69. Precision ⁶

69.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 6 for specimens 2 and 3. Although a sample covered by this method with cobalt concentration of approximately 0.1 % was not available for testing, the precision data obtained for specimen 1 by Test Methods E 353 should apply.

**COPPER BY SULFIDE PRECIPITATION-
ELECTRODEPOSITION GRAVIMETRIC METHOD**

70. Scope

70.1 This method covers the determination of copper in concentrations from 0.01 to 2.0 %.

71. Summary of Method

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

NOTE 7—This method describes the preliminary separations for the determinations of tin by the sulfide-iodatimetric titration method.

72. Interferences

72.1 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 10).

73. Apparatus

73.1 Apparatus No. 9.

74. Reagents

74.1 *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).

74.2 *Ferric Chloride Solution* (2 g Fe/L)—Dissolve 10 g of ferric chloride hexahydrate (FeCl₃·6H₂O) in about 800 mL of

TABLE 6 Statistical Information—Cobalt

Test Specimen	Cobalt Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 2, E 353	0.094	0.006	0.013
2. High-alloy steel 4Mo-6W-4Cr-2V	1.87	0.09	0.13
3. High-speed tool steel 8Mo-2W-5Cr-1V (NBS 438, 4.9 Co)	4.94	0.08	0.17

HCl (1+99) and dilute to 1 L with HCl (1+99).

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

75. Procedure

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

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.01 to 1.0	10	10
1.0 to 2.0	5	5

Transfer it to a 1-L Erlenmeyer flask.

75.2 Add 115 mL of HCl (1+2) plus an additional 9 mL of HCl (1+2) and 1 mL of HNO_3 for each gram of sample. Heat until dissolution is complete, and then boil the solution for 2 to 3 min. If the solution is clear, proceed as directed in 92.3 and 92.8 through 92.21.

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

75.4 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 75.4.1 or 75.4.2 according to preference, bearing in mind that the latter procedure may be the easier to apply when copious amounts of insoluble matter are encountered.

75.4.1 Transfer the paper and precipitate to the original flask, add 20 mL of HNO_3 and 10 mL of HClO_4 , heat moderately to oxidize organic matter, and finally heat to mild fumes of HClO_4 . Cool the solution, add 1 to 2 mL of HF, and repeat the fuming.

75.4.2 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 HNO_3 and 1 to 2 mL of HF, and evaporate to dryness. Add 10 mL of $\text{HNO}_3(1+1)$ and digest at 90 to 100°C for 5 min. Transfer the contents of the crucible to the original flask, add 10 mL of HClO_4 , and heat to mild fumes of HClO_4 .

75.4.3 Cool the solution from 75.4.1 or 75.4.2, add 100 mL of water and digest at or near boiling for about 45 min.

75.5 If tungsten is present, as indicated by the presence of a bright yellow precipitate of tungstic acid, add a slight excess of NH_4OH and 20 g of tartaric acid. When the tartaric acid has dissolved, again add a slight excess of NH_4OH and digest near the boiling point until dissolution is complete, or nearly so.

75.6 Add 5 mL of H_2SO_4 and heat at 85 to 95°C for 30 min. If insoluble matter persists, repeat the steps as directed in 75.4 through 75.6. When dissolution is complete, combine the solution with the filtrate reserved in 75.2.

75.7 If the volume is less than 600 mL, dilute the solution approximately to that volume and treat with H_2S ; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 to 15 h.

75.8 Add paper pulp and filter using a fine filter paper. Wash the filter thoroughly with ammonium sulfate-hydrogen sulfide

wash solution. Discard the filtrate.

75.9 Transfer the filter paper and precipitate to the original flask, add 12 mL of H_2SO_4 , and heat to char the paper. Add 20 mL of HNO_3 , and evaporate to fumes to destroy organic matter. Add HNO_3 in 1-mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

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

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

75.12 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.

75.13 Add 10 mL of FeCl_3 solution to the filtrate. Add just enough NH_4OH (1+1) to precipitate the iron, tin, and chromium and to complex the copper (indicated by the formation of a blue color), and then add 1 to 2 mL in excess. Add paper pulp, and heat the solution to boiling to coagulate the precipitate. Filter the hot solution through a coarse filter paper, and wash alternately five times each with hot NH_4OH (1+99) and water into an 800-mL beaker. Reserve the filter and the filtrate. Dissolve the precipitate by washing the filter alternately with hot HCl (1+1) and hot water, and reserve the filter paper. Precipitate the iron, tin, and chromium as before. Wash the reserved filter paper three times with hot NH_4OH (1+99) and then filter the hot solution into the 800-mL beaker reserved from the first filtration; wash alternately five times each with hot NH_4OH (1+99) and water.

NOTE 8—If tin is to be determined by using the same sample, reserve the precipitate and proceed as directed in 100.5 through 100.8 in Test Methods E 350.

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

75.15 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.

75.16 Stir the solution with an automatic stirrer, start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1 A/dm^2 . Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 to 3 A/dm^2 (Note 9). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 9—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm^2 , and 2 to 3 h should be allowed for complete deposition.

75.17 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.

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

75.19 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 10—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 tall-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 75.15 and 75.16. Proceed as directed in 75.17 and 75.18.

76. Calculation

76.1 Proceed as directed in 87.1 of Test Methods E 351.

77. Precision

77.1 Six laboratories cooperated in testing this method and obtained eight sets of data summarized in Table 7 for specimen 2. Although samples covered by this method with copper concentration at the lower and upper limits of the scope were not available for testing, the precision data obtained using the methods indicated should apply.

TOTAL CARBON BY THE COMBUSTION GRAVIMETRIC METHOD

78. Scope

78.1 This test method covers the determination of carbon in concentrations from 0.05 to 2.50 %.

79. Summary of Method

79.1 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.

79.2 Oxygen flow rates and sweep times as well as control of plate current for induction heating depend upon the equipment used, and the type of sample analyzed. The control of these parameters should be established by analysis of control samples similar in carbon content and alloy characteristics to the sample to be analyzed.

80. Interferences

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

81. Apparatus

81.1 Apparatus No. 1.

NOTE 11—The induction furnace must be equipped with suitable controls to regulate the power input to the induction coil.

NOTE 12—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.

81.2 *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 13—For precision-testing this balance see 7.4 of Methods E 319, or its equivalent.

82. Reagents

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

82.2 *Iron (Low-Carbon) Accelerator*—Iron chips (Note 14).

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

82.4 *Tin (Low-Carbon) Accelerator*, granular (Note 14).

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

NOTE 14—Prior to use, all accelerators should be washed three times with acetone by decantation until free of organic contaminants and then dried.

83. Preparation of Apparatus—Induction Furnace

83.1 The train of the induction furnace shall include an oxygen purifier, catalyst heater (Note 15), 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 15—The catalyst heater contains copper oxide heater to about 300°C to ensure complete conversion of CO to CO₂.

83.2 Conditioning of Apparatus:

83.2.1 Transfer 1 g of a sample containing approximately 1.5 % carbon and 1 g of one of the accelerators in Section 82 to the cupelet, crucible, or boat.

83.2.2 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.

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

NOTE 16—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.

TABLE 7 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 1, E 350	0.020	0.005	0.006
2. Tool steel 18W-4Cr-1V (NBS 50c, 0.079 Cu)	0.079	0.003	0.006
3. No. 2, E 351	1.49	0.02	0.03

83.2.4 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 17—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.

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

NOTE 18—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.

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

84. Preparation of Apparatus—Resistance Furnace

84.1 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.

84.2 Conditioning of Apparatus:

84.2.1 Fill the boat with Alundum bedding material (Note 19). 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 82).

NOTE 19—The Alundum bedding material should be previously heated in oxygen at 1325°C for 15 min, cooled, and stored under cover.

84.2.2 Open the stopcock(s) of the absorption bulb (Note 16) and connect it to the carbon train.

84.2.3 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 17).

NOTE 20—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.

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

85. Blank Procedure

85.1 Induction Furnace:

85.1.1 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 83.2.

85.1.2 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 83.2.2–83.2.6.

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

85.1.4 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.

85.2 Resistance Furnace:

85.2.1 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 84.2.

85.2.2 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 19). Proceed as directed in 84.2.2.

85.2.3 Proceed as directed in 85.1.3 and 85.1.4.

85.2.4 Proceed as directed in Section 86.

86. Procedure

86.1 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 86.2 through 86.5.

NOTE 21—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 22—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.

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

86.3 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 19).

86.4 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 83.2.2–83.2.6 and 84.2.2–84.2.4.

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

87. Calculation

87.1 Calculate the percent of carbon as follows:

$$\text{Carbon, \%} = [(A - B) \times 0.2729 / C] \times 100 \quad (2)$$

where:

A = carbon dioxide found, g,

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

C = sample used, g.

88. Precision

88.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 8. 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:

$$S^2 = \sigma_w^2 + \sigma_a^2 \quad (3)$$

where σ_a 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.

88.1.1 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:

$$\sigma_d^2 = \sigma_{w1}^2 + \sigma_w^2 = (1.41 \sigma_w)^2 \quad (4)$$

Since

$$\sigma_w = \sigma_{w1} = \sigma_{w2} \quad (5)$$

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

$$R_1 = 2\sigma_d = (2)(1.41) \sigma_w = 2.82 \sigma_w \quad (6)$$

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

$$R_2 = 2.82 S \quad (7)$$

**COPPER BY THE NEOCUPROINE
PHOTOMETRIC METHOD**

89. Scope

89.1 This method covers the determination of copper in concentrations from 0.01 to 2.00 %.

90. Summary of Method

90.1 See Section 115 of Test Methods E 350.

91. Concentration Range

91.1 See Section 116 of Test Methods E 350.

92. Stability of Color

TABLE 8 Statistical Information—Carbon

Test Specimen	Carbon Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. Stainless steel (NBS 101e, 0.054 C)	0.052	0.006	0.006
2. Stainless steel (NBS 160a, 0.062 C)	0.061 ^A	—	0.007
3. Tool steel (NBS 153a, 0.902 C)	0.90	0.02	0.04
4. Tool steel 5Cr-1W-4.5V-1Mo	2.24	0.04	0.05

^A Based on single determinations by each laboratory; all other values based on duplicate determinations by each laboratory.

92.1 See Section 117 of Test Methods E 350.

93. Interferences

93.1 See Section 118 of Test Methods E 350.

94. Reagents

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

95. Preparation of Calibration Curve

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

96. Procedure

96.1 *Test Solution:*

96.1.1 Select a sample in accordance with the following:

Copper, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution, mL	Aliquot Volume, mL
0.01 to 0.15	1.00	1.0	100	20
0.10 to 0.25	1.00	1.0	250	30
0.20 to 0.50	1.00	0.5	250	15
0.40 to 1.00	0.50	0.5	250	15
0.90 to 2.00	0.50	0.5	500	15

Transfer it to a 250-mL Erlenmeyer flask.

96.1.2 Add amounts of HCl or HNO₃, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample (Note 7). Heat as required to hasten dissolution. Add HNO₃ to provide an excess of 3 to 4 mL, a sufficient amount of HF to volatilize the silica, and 15 mL of HClO₄.

NOTE 23—Some alloys are more readily decomposed by a mixture of 5 mL of bromine, 15 mL of HCl, and 1 to 2 drops of HF.

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

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

97. Calculation

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

98. Precision

98.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 9. Although samples covered by this method with copper concentrations near the

TABLE 9 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 1, E 354	0.006	0.001	0.004
2. No. 2, E 354	0.014	0.002	0.006
3. No. 3, E 350	0.021	0.004	0.010
4. No. 3, E 354	0.033	0.005	0.004
5. Tool steel 18W-4Cr-1V (NBS 50c, 0.079 Cu)	0.078	0.005	0.010
6. Tool steel 5Mo-6W-4Cr-2V (NBS 132a, 0.120 Cu)	0.118	0.007	0.016
7. No. 8, E 353	0.221	0.013	0.022
8. No. 9, E 353	0.361	0.015	0.036
9. No. 5, E 351	1.51	0.04	0.05

lower and upper limits of the scope were not available for testing, the precision data obtained for the other specimens by the methods indicated should apply.

LEAD BY THE ION-EXCHANGE—ATOMIC ABSORPTION METHOD

99. Scope

99.1 This method covers the determination of lead in concentrations from 0.001 to 0.01 %.

100. Summary of Method

100.1 See Section 133 of Test Methods E 350.

101. Concentration Range

101.1 See Section 134 of Test Methods E 350.

102. Interferences

102.1 See Section 135 of Test Methods E 350.

103. Apparatus

103.1 See Section 136 of Test Methods E 350.

104. Reagents

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

105. Preparation of Calibration Curve

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

106. Procedure

106.1 *Test Solution:*

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

106.1.2 Add 40 mL of HCl and 10 mL of HNO₃, or other ratios and concentrations of these acids as required for the decomposition of certain grades of alloys. Add bromine and HCl to decompose alloys that require this treatment. Heat as required until action ceases. If HNO₃ was not used for sample decomposition, add a sufficient amount to oxidize the iron, and evaporate the solution to dryness. Add 40 mL of HCl (1 + 1) and digest until soluble salts are dissolved.

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

106.2 *Reagent Blank*—Proceed as directed in 139.2 of Test Methods E 350.

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

107. Calculation

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

108. Precision ⁶

108.1 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 10, should apply.

TABLE 10 Statistical Information—Lead

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

SULFUR BY THE CHROMATOGRAPHIC GRAVIMETRIC METHOD

(This method, which consisted of Sections 109 through 116 of this standard, was discontinued in 1980.)

CHROMIUM BY THE PEROXYDISULFATE-OXIDATION TITRIMETRIC METHOD

(This method, which consisted of Sections 117 through 124 of this standard, was discontinued in 1980.)

TOTAL CARBON BY THE COMBUSTION-THERMAL CONDUCTIVITY METHOD

(This method, which consisted of Sections 125 through 135 of this standard, was discontinued in 1986.)

PHOSPHORUS BY THE ALKALIMETRIC METHOD

136. Scope

136.1 This method covers the determination of phosphorus in concentrations from 0.01 to 0.05 % in samples containing not more than 0.5 % tungsten.

137. Summary of Method

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

138. Interferences

138.1 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.

138.2 To eliminate interference of silicon, HF is added during dissolution of samples containing silicon in concentrations greater than 0.5 %.

138.3 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.

139. Apparatus

139.1 *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 on the funnel, moisten it with KNO₃ 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.

139.2 *Funnel, Glass, 60°*, fitted with a 25-mm diameter perforated porcelain filtering disk. Place a 5.5-cm fine qualitative paper, over the perforated plate. Place an 11-cm fine 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.

140. Reagents

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

140.2 *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 $\text{H}_2\text{SO}_4(5 + 95)$.

140.3 *Nitric Acid, Standard Solution (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 140.7, 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:

$$\text{Phosphorus equivalent, g P/mL} = (A \times B)/C \quad (8)$$

where:

A = NaOH solution, mL

B = phosphorus equivalent of the NaOH solution, and

C = HNO_3 solution, mL.

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

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

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

140.7 *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 one drop produces a pink color. Calculate the phosphorus equivalent as follows:

$$\text{Phosphorus equivalent, g P/mL} = (A \times 0.001347)/(B \times 0.2042) \quad (9)$$

where:

A = potassium acid phthalate, g, and

B = NaOH solution, mL.

141. Procedure

141.1 Transfer a 2-g sample, weighed to the nearest 5 mg, to a 400-mg beaker.

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

141.3 Add 35 mL of HNO_3 and 40 mL of HCl and, if the silicon concentration is greater than 0.5 %, add 3 to 5 drops of HF. Cover the beaker and heat, as required, to hasten dissolution. Add 15 mL of HClO_4 . Remove and rinse the cover. Place a ribbed cover glass on the beaker and evaporate to fumes. Continue heating for 5 min until the chromium is oxidized. Cool slightly, and add 40 mL of water and paper pulp. Filter through an 11-cm fine paper into a 300-mL Erlenmeyer flask. Wash the beaker and paper containing the residue with 75 mL of $\text{HNO}_3(1 + 3)$. Heat the solution, add KMnO_4 dropwise until a permanent brown precipitate forms, and boil 3 min. Add H_2SO_3 dropwise until the precipitate dissolves, and boil 3 min to expel the oxides of nitrogen.

141.4 Evaporate the solution to 100 mL, and cool to room temperature. While swirling the flask, slowly add 20 mL of NH_4OH , so that no precipitate forms (Note 8). Adjust the temperature to 45°C.

NOTE 24—The quantity of NH_4OH specified should result in a pH of 0.1 to 0.6 after the addition of the NH_4OH 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 NH_4OH will precipitate iron as ferric hydroxide. Failure to carefully control the acidity will retard the precipitation of the ammonium phosphomolybdate.

141.5 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 H_2SO_3 , and allow the precipitate to settle at least 20 min at 10 to 20°C.

141.6 Filter the solution with the aid of suction using a Hirsch porcelain crucible (139.1) or a glass funnel fitted with a perforated porcelain filtering disk (139.2). Rinse the flask 3 to 5 times with a total volume of approximately 40 mL of KNO_3 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 KNO_3 solution (Note 9). Discard the filtrate.

NOTE 25—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 Recommended Practices E 50.

141.7 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, 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.

141.8 Remove and rinse the stopper. Dilute the solution to 150 mL with freshly boiled water that 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 standard HNO₃ solution until 1 drop causes the disappearance of the pink color. Record the buret reading.

142. Calculation

142.1 Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, \%} = (AB - CF) - (EB - FD)/G \times 100 \quad (10)$$

where:

- A* = NaOH solution, mL, used for the sample (141.7),
- B* = phosphorus equivalent of the NaOH solution,
- C* = HNO₃ solution, mL, required by the sample (141.8).
- D* = phosphorus equivalent of the HNO₃ solution,
- E* = NaOH solution, mL, used for the blank,
- F* = HNO₃ solution required by the blank, mL, and
- G* = sample used, g.

143. Precision¹²

143.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 11. Although samples of this E designation were not tested, the precision data obtained for E 353 type of alloys using the method indicated in Table 11 should apply.

NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD

144. Scope

144.1 This method covers the determination of nickel in concentrations from 0.1 to 4.0 %.

145. Summary of Method

145.1 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.

145.2 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.

146.1 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.

146. Interferences

146.1 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.

147. Apparatus

147.1 *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.

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

147.3 *pH Meter*—Apparatus No. 3A.

148. Reagents

148.1 *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.

148.2 *Anion Exchange Resin*:

148.2.1 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.¹³ To remove those beads greater than 180 μm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a No. 80 (180-μm) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 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.

148.2.2 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

¹² Supporting data are available from ASTM Headquarters. Request RR:E03-1002.

TABLE 11 Statistical Information—Phosphorus

Test Specimen	Phosphorus Found, %	Repeatability (<i>R</i> ₁ , E 173)	Reproducibility (<i>R</i> 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 353	0.125	0.008	0.018
6. No. 6, E 353	0.151	0.015	0.015

¹³ Dowex 1, manufactured by the Dow Chemical Co., Midland, MI, has been found satisfactory for this purpose.

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.

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

149. Procedure

149.1 Double Precipitation:

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

Nickel, %	Sample Weight, g	Tolerance Sample Weight, mg
0.1 to 1.0	3.0	1.0
1.0 to 4.0	1.0	0.5

Transfer it to a 600-mL beaker.

149.1.2 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.

149.1.3 Filter the solution through an 11-cm coarse paper into a 600-mL beaker. Transfer any insoluble matter to the paper with hot HCl (5 + 95). Wash the beaker and paper alternately with hot HCl (5 + 95) and hot water until iron salts are removed. Finally, wash the paper 3 times with 5-mL portions of hot water. Discard the residue.

149.1.4 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 NH₄OH. Acidify the solution with HCl to pH 6.3 ± 0.1.

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

149.1.6 Using a pH meter, adjust the pH to 7.4 ± 0.1 with NH₄OH. 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.

149.1.7 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.

149.1.8 Add 30 mL of HNO₃ and 15 mL of HClO₄. Evaporate to strong fumes and continue fuming for 5 min. Cool and add 50 mL of water.

149.1.9 Filter through an 11-cm coarse paper into a 600-mL beaker. Wash the paper 5 times with HCl (5 + 95) and 3 times with water. Dilute the filtrate to 200 mL with water and proceed as directed in 149.3–149.7.

149.2 Anion-Exchange Separation:

149.2.1 Proceed as directed in 149.1.1.

149.2.2 Proceed as directed in 149.1.2, but dilute with only 50 mL of water.

149.2.3 Filter the solution obtained in 149.2.2 through an 11-cm coarse paper, collecting the filtrate in a 250-mL beaker. Transfer any insoluble matter to the paper with hot HCl

(5 + 95). Wash the paper alternately with hot water and hot HCl (5 + 95) until iron salts are removed. Finally, wash the paper 3 times with 5-mL portions of hot water. Discard the residue.

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

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

149.2.6 Place a clean 600-mL beaker under the ion-exchange column and open the bottom stopcock. Transfer the solution from 149.2.4 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.

149.2.7 Precondition the column for the next sample as follows: Open the lower stopcock. Drain any remaining solution in the column to 5 to 10 mm from the top of the resin bed. Add HCl (1 + 19) in 50-mL increments until iron has been eluted and the eluate is visibly free of color (approximately 300-mL). Drain the solution to 5 to 10 mm from the top of the resin bed and close the lower stopcock. If the column is not to be used immediately, cover, and store. If another sample solution is to be put through the column, proceed as directed in 149.2.5.

149.2.8 Heat the solution reserved in 149.2.6 to boiling and evaporate to 60 mL to remove excess HCl. Cool and dilute to 200-mL.

149.3 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 NH₄OH. Remove and rinse the electrodes with water, collecting the rinsings in the original beaker.

149.4 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.

149.5 Using a pH meter, adjust the pH to 7.4 ± 0.1 with NH₄OH. 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.

149.6 With the aid of suction, filter using a weighed (Note 14) fritted glass crucible. Wash the beaker and precipitate 6 times with cold water.

NOTE 26—Heat the crucible at 150°C, and cool in a desiccator before weighing.

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

150. Calculation

150.1 Calculate the percentage of nickel as follows:

$$\text{Nickel, \%} = [(A - B) \times 0.2032 / C] \times 100 \quad (11)$$

where:

A = weight of crucible and precipitate, g,

B = weight of crucible, g, and

C = sample taken, g.

151. Precision ⁶

151.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 12. Although a sample covered by this method near the higher end of the scope was not tested, the data obtained for other types of alloys using the methods indicated in Table 12 should apply.

TIN BY THE SOLVENT EXTRACTION—ATOMIC ABSORPTION METHOD

152. Scope

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

153. Summary of Method

153.1 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.

154. Concentration Range

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

155. Interferences

155.1 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.

156. Apparatus

156.1 *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 158.4.

157. Reagents

157.1 *Ascorbic Acid*.

157.2 *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.

157.3 *Methyl Isobutyl Ketone (MIBK)*.

157.4 *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.

157.5 *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.

157.6 *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.

158. Preparation of Calibration Curve

158.1 *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 27—Volumetric flasks with ground glass stoppers must be used.

158.2 *Extraction*:

158.2.1 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.

158.2.2 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 28—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

158.3 *Photometry*:

158.3.1 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.

158.3.2 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

TABLE 12 Statistical Information—Nickel

Test Specimen	Nickel Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. Tool Steel 5 Mo-6W-4Cr-2V (NBS 132a, 0.137 Ni)	0.135	0.012	0.015
2. Ni-Mo steel 2 Ni-0.3 Mo (NBS 111b, 1.81 Ni)	1.81	0.09	0.08
3. Ni-Mo steel 4 Ni-0.3 Mo (NBS 33d, 3.58 Ni)	3.58	0.11	0.07
4. No. 3 E354	4.22	0.06	0.05

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 29—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 158.3.1.

158.3.3 Aspirate the solution with the highest concentration (40 µg Sn/mL) from the series prepared in 158.1 a sufficient number of times to establish that the absorbance is not drifting.

NOTE 30—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 31—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.

158.3.4 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 158.3.3 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 158.3.1–158.3.4.

158.3.5 Proceed immediately as directed in 159.3.

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

$$\text{Deviation from linearity} = (A - B)/C \quad (12)$$

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.

159. Procedure

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

159.2 *Test Solution:*

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

Tin, %	Sample Weight, g
0.002 to 0.005	3.00
0.004 to 0.010	2.00
0.009 to 0.050	1.00
0.045 to 0.100	0.50

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

159.2.2 Add 50 mL of HCl (1 + 1) and 5 drops of HF. Cover

the beaker with a poly(tetrafluorethylene) cover and heat at a low temperature (approximately 90°C) until dissolution is complete.

NOTE 32—If silicon is above 0.5 %, use 10 to 12 drops of HF.

159.2.3 Remove the cover with platinum-tipped tongs and cautiously rinse into the beaker with water. Cautiously evaporate the solution at a low temperature (approximately 90°C) to 15 mL. Rinse the sides of the beaker with water, add 20 mL HCl (1 + 1), and again evaporate to 15 mL.

159.2.4 Rinse the sides of the beaker with about 5 mL of water and cool.

NOTE 33—If tungsten concentration is high, a yellow precipitate of WO₃ may form. Extract such samples as directed with minimal delay.

159.2.5 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.

159.2.6 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.

159.2.7 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.

159.3 *Photometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 18) and record the absorbance values. Take three readings on each solution (Note 19). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drift as in 159.3.4 and 159.3.5.

160. Calculation

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

$$\text{Tin, \%} = [(D - E)/F \times 1000] \quad (13)$$

where:

- D = µg tin per mL of the final test solution,
- E = µg tin per mL of the final reagent blank solution, and
- F = sample used, g.

TABLE 13 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. No. 3, E 350	0.011	0.001	0.002
3. Tool steel 18W-4Cr-1V (NBS 50c) 0.018 Sn	0.017	0.001	0.003
4. No. 4, E 350	0.031	0.003	0.004
5. Tool steel 18W-4Cr-1V (NBS 50a) 0.025 Sn	0.025	0.004	0.006
6. No. 6, E 350	0.097	0.011	0.011

161. Precision and Bias¹⁴

161.1 *Precision*—Eleven laboratories cooperated in testing this method and obtained the precision data listed as No. 3 and 5 in Table 13. This method differs only slightly from the method for tin, Test Methods E 350, in that the amounts of reagents used to dissolve the sample have been increased. The fact that the precision data obtained for No. 3 and 5 correspond closely with that obtained for No. 2 and 4, Test Methods E 350, suggests that the precision of the two methods is the same.

161.2 *Bias*—Table 13 lists the test results obtained for two high-speed tool steel standards and their certified values. The accuracy of this method may be judged by comparing the arithmetic average obtained for this test with the certified values.

MOLYBDENUM BY THE PHOTOMETRIC METHOD

162. Scope

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

163. Summary of Method

163.1 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.

164. Concentration Range

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

NOTE 34—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.

165. Stability of Color

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

166. Interferences

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

167. Reagents

167.1 *Butyl Acetate*:

NOTE 35—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.

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

167.3 *Iron*¹⁵—Purity: 99.8 % minimum, molybdenum 0.001 % maximum.

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

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

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

167.7 *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.

167.8 *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.

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

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

NOTE 36—This solution is used for color development in 168.3, 169.3, 170.3, and 171.3. 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.

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

168.1 *Calibration Solutions*:

168.1.1 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.

168.1.2 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.

168.1.3 Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 168.3.

168.2 *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 168.1.2, 168.1.3, and 168.3.

168.3 *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

¹⁴ Supporting data are available from ASTM Headquarters. Request RR:E03-1022.

¹⁵ Johnson-Matthey JMC 847 sponge iron has been found suitable for this purpose.

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

168.4 *Reference Solution*—Butyl acetate.

168.5 *Photometry*:

168.5.1 *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.

168.5.2 *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.

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

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

169.1 *Calibration Solutions*:

169.1.1 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.

169.1.2 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.

169.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 169.3.

169.2 *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 169.1.2, 169.1.3, and 169.3.

169.3 *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 SnCl₂ 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 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, 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 25.)

169.4 *Reference Solution*—Butyl acetate.

169.5 *Photometry*:

169.5.1 *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.

169.5.2 *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.

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

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

170.1 *Calibration Solutions*:

170.1.1 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.

170.1.2 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.

170.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 170.3.

170.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 300 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 170.1.2, 170.1.3, and 170.3.

170.3 *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, 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 25.)

170.4 *Reference Solution*—Butyl acetate.

170.5 *Photometry*:

170.5.1 *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.

170.5.2 *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.

170.6 *Calibration Curve*—Plot the net photometric readings

of the calibration solutions against milligrams of molybdenum per 100 mL of butyl acetate.

171. Procedure

171.1 Test Solution:

171.1.1 Transfer a 0.3-g sample, weighed to the nearest milligram, to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving acid. Add HCl, or HNO₃, or combinations of the two with or without several drops of HF, and heat until dissolution is complete.

171.1.2 Increase the temperature and heat to HClO₄ fumes. Continue fuming until chromium, if present, is oxidized and the white HClO₄ 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. If the solution is not clear, filter the solution through an 11-cm fine filter paper, collecting the filtrate in a volumetric flask that provides for dilution in accordance with the guide given in 171.1.3. Wash the paper with five 5-mL portions of H₂SO₄(1 + 99) collecting these in the same volumetric flask. Proceed as directed in 171.3. If the solution is clear, proceed to 171.1.3.

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

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

Proceed as directed in 171.3.

171.2 *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 171.1.2, 171.1.3, and 171.3, using the same dilution and aliquots used for the test solution.

171.3 *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, 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 25.)

171.4 *Reference Solution*—Butyl acetate.

171.5 *Photometry*—Take the photometric reading of the test solution and of the reagent blank solution as directed in 169.5.

172. Calculation

172.1 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:

$$\text{Molybdenum, \%} = \frac{A}{B \times 10} \tag{14}$$

where:

- A = molybdenum, mg, found in 25, 50, or 100 mL, as appropriate of butyl acetate, and the aliquot volume used, and
- B = sample, in g, represented in 25, 50, or 100 mL, as appropriate, of butyl acetate and the aliquot used (see aliquot guide 171.1.3).

173. Precision and Bias ¹⁶

173.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 14. This method is identical with molybdenum in accordance with Test Methods E 350, E 351, and E 353. The fact that the precision for different materials is comparable suggests that the precision of these methods is the same.

173.2 *Bias*—The accuracy of a method can be judged by comparing the certified value of a standard with the arithmetic average of the test data. The specified values for No. 3 and 5 (Table 14), while not certified, were obtained by other methods and are believed to be reliable.

CHROMIUM BY ATOMIC ABSORPTION METHOD

174. Scope

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

175. Summary of Method

175.1 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 3579 Å from a chromium hollow-cathode lamp is

¹⁶ Supporting data are available from ASTM Headquarters. Request RR:E03-1023.

TABLE 14 Statistical Information—Molybdenum

Test Specimen	Molybdenum Found, %	Repeatability R ₁ , E 173	Reproducibility R ₂ , E 173
1. Cr-W steel (NBS 155, 0.039 Mo)	0.037	0.002	0.006
2. No. 3, E 350	0.163	0.012	0.03
3. Tool steel T-15 4Cr-13W-5V-5Co (0.45 Mo not certified)	0.442	0.027	0.055
4. No. 4, E 350	0.51	0.02	0.06
5. Tool steel H-12 1W-5Cr (1.5 Mo not certified)	1.47	0.053	0.058

passed through the flame and the absorbance is measured. The spectrophotometer is calibrated with solutions of known chromium concentrations.

176. Concentration Range

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

177. Interferences

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

178. Apparatus

178.1 *Atomic Absorption Spectrophotometer*, capable of resolving the 3579 Å 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 180.4. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this method.

179. Reagents

179.1 *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.

179.2 *Iron*,¹⁷ *Low Chromium*—Cr < 0.0001 %.

179.3 *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.

180. Preparation of Calibration Curves

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

180.2 *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 flask 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.

180.3 Photometry:

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

180.3.2 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 180.1, 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.

180.3.3 Aspirate the chromium solutions used in 180.3.2 to assure that the absorbance reading is repeatable. Record 6 readings, and calculate the standard deviation, s , of the readings as follows:

$$s = (A - B) \times 0.40 \quad (15)$$

where:

A = the highest of 6 values found, and

B = the lowest of the 6 values found.¹⁸

180.3.4 Using water as a reference solution, and beginning with the solution to which no addition of chromium was made in 180.1 and 180.2, 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 180.3.3 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 180.3.1–180.3.4.

180.3.5 Proceed immediately as directed in Section 181.

180.4 *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:

$$\text{Deviation from linearity} = (C - D)/E \quad (16)$$

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.

¹⁷ Johnson-Matthey sponge iron or Spex iron has been found suitable for this purpose.

¹⁸ The value 0.40, which is used to estimate the standard deviation from the range of six values, was published by Dixon, W. J. and Massey, F. J., "Introduction to Statistical Analysis," McGraw-Hill, 1957, p. 404, Table 8b, (1).

180.5 Calibration for Concentrations from 0.10 to 1.00 %—Proceed as directed in 180.4.

181. Procedure

181.1 Test Solution:

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution after Dis-solution, mL	Aliquot Required, mL	HCl to be added to Ali-quot, mL	Final Dilu-tion, mL
0.005–0.10	1	0.10	100	0	0	100
0.010–1.00	1	0.10	100	10	9	100

Transfer it to a 250-mL borosilicate beaker.

181.1.2 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.

181.1.3 Transfer the paper and contents to a platinum crucible. Dry on a hot plate, and transfer to a muffle furnace that is less than 400°C. Gradually heat to 600°C and hold at this temperature for 1 h. Cool, add 0.5 g of K₂CO₃, and carefully fuse over a free flame until a clear melt is obtained (see Note 26). 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 38—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.

181.1.4 Transfer this solution to the filtrate from 181.1.2 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 181.3. 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.

181.2 Prepare for each concentration range a reagent blank by treating the same amount of all reagents as directed in 181.1.1–181.1.4, including the low chromium iron. Use reagents from the same lots for blank and test solutions.

181.3 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 180.3.4, 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 180.3.3, 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.

182. Calculation

182.1 Convert the absorbance of the test solution and the reagent blank to milligrams of chromium per millilitre of the

final test solution by means of the appropriate calibration curve. Calculate the percentage chromium as follows:

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \tag{17}$$

where:

A = chromium, mg, per mL of final test solution,

B = chromium, mg, per mL of final reagent blank solution,

C = final volume of test solution, and

W = weight of sample, in g, in final volume of test solution.

183. Precision and Bias ¹⁹

183.1 Precision—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 15.

183.2 Bias—The accuracy can be inferred from the data in Table 15 by comparing the certified values for chromium with the average value obtained by using this method.

CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

184. Scope

184.1 This method covers the determination of chromium in concentrations from 0.10 to 14.00 %.

185. Summary of Method

185.1 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 39—In the dichromate titration, the vanadium is not oxidized along with the excess ferrous ions and, therefore, the volume of dichromate added reflects the total of vanadium and chromium and the calculated value for percent Cr is high. In the permanganate titration, the V^{IV} is oxidized to V^V, thereby compensating for the reduction of vanadium by ferrous sulfate in a previous step.

186. Interferences

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

¹⁹ Supporting data are available from ASTM Headquarters. Request RR:E03-1030.

TABLE 15 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 3, E 350	0.149	0.028	0.025
2. No. 4, E 350	0.693	0.019	0.024
3. No. 5, E 350	0.961	0.036	0.093

186.2 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:

$$(2.6A + 0.05B + 0.01C)D \quad (18)$$

where:

A = tungsten, %, in the sample,

B = copper, %, in the sample,

C = nickel, %, in the sample, and

D = sample weight, g.

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

187. Apparatus

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

188. Reagents

188.1 *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.

188.2 *Ferrous Ammonium Sulfate, Standard Solution* (0.05 N and 0.10 N)—Reagent No. 5 (Practices E 50) but use 20 and 40 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, respectively, instead of the specified weight. Standardize the solution as directed in 189.1, 189.2, or 189.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

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

188.4 *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.

188.5 *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.

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

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

188.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 M)—Reagent No. 122 (Practices E 50).

189. Standardization of Ferrous Ammonium Sulfate Solution

189.1 *Against Potassium Permanganate Solution:*

189.1.1 Transfer 180 mL of water, 12 mL of H_2SO_4 (1+1),

and 5 mL of H_3PO_4 into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 or 0.10 N $Fe(NH_4)_2(SO_4)_2$ with either 0.05 or 0.10 N $KMnO_4$ solution (188.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 1 to 2 drops of 1,10 phenanthroline indicator solution. Using a 25-mL buret, titrate the ferrous ions with 0.05 N $KMnO_4$ standard solution (188.5) while swirling the flask. As the end point is approached, add $KMnO_4$ dropwise. Continue until the pink color changes to clear green and persists for at least 60 s.

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

$$\text{Normality} = AB/C \quad (19)$$

where:

A = normality of $KMnO_4$ solution (188.5),

B = $KMnO_4$ solution, mL, and

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

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

189.2.1 Transfer 180 mL of water, 12 mL of H_2SO_4 (1+1), and 5 mL of H_3PO_4 into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 or 0.10 N $Fe(NH_4)_2(SO_4)_2$ (188.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using a 25-mL buret, titrate the ferrous ions with either 0.05 or 0.10 N $K_2Cr_2O_7$ solution, while swirling the flask. As the end point is approached, add the $K_2Cr_2O_7$ titrant dropwise. Continue until a color blue appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL. Refill the burets, add the same volume of $Fe(NH_4)_2(SO_4)_2$ solution as before and again titrate with either 0.05 or 0.10 N $K_2Cr_2O_7$ solution to the blue end point. Subtract this volume of $K_2Cr_2O_7$ solution from the volume recorded for the first titration and record the difference as the indicator blank.

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

$$\text{Normality} = (0.05 \text{ or } 0.10 (A - B))/C \quad (20)$$

where:

A = 0.05 or 0.10 N $K_2Cr_2O_7$ solution, mL, used in the first titration,

B = mL equivalent to the indicator blank, and

C = $Fe(NH_4)_2(SO_4)_2$ solution, mL, used in the first titration.

189.3 *Against Potassium Dichromate Using Potentiometric End Point:*

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

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

Volume of 0.05 N K ₂ Cr ₂ O ₇ Back Titrant (mL)	Voltage (mV)	Δ Voltage (mV)	Difference Be- fore and After Maximum
20.80	555		
20.90	570	50	50
21.00	620	100	20
21.10	720	80	
21.20	800		
21.30	835		
21.40	854		

Maximum voltage change occurred between 21.00 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 times 0.1 mL must be added to smaller volume between the two increments where the maximum change in voltage occurred. The end point is 21.07 mL.

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

$$\text{Normality} = 0.05 \text{ or } 0.10 \text{ A/B} \quad (21)$$

where:

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

B = Fe(NH₄)₂(SO₄)₂ solution, mL.

190. Procedure

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

Chromium, %	Sample Weight, g	Tolerance in Sample		Normality of Titrants
		Weight, mg	Weight, mg	
0.10 to 0.50	3.50	2.0	0.05	0.05
0.40 to 1.00	2.00	1.0	0.05	0.05
0.80 to 1.60	1.25	0.3	0.05	0.05
1.50 to 3.50	0.50	0.1	0.05	0.05
3.30 to 8.00	0.25	0.1	0.05	0.05
8.00 to 14.00 ^A	0.50	0.1	0.10	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.

190.2 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.

190.3 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.

190.4 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 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, transfer the solution to the reserved filtrate (190.3), and dilute to 200 mL.

190.5 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 (188.4), 5 mL more of AgNO₃ solution, and 20 mL more of (NH₄)₂S₂O₈ solution, and boil 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 190.6.

190.6 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 190.7. If vanadium is absent and the criteria of 186.2 are met, proceed as directed in 190.8. If vanadium is absent and the criteria of 186.2 are not met, or if potentiometric titration is preferred and vanadium is absent, proceed as directed in 190.9.

190.7 *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.

190.8 *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.

190.9 *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, while stirring, until the yellow color disappears. 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 is reached for each increment. Inspect the data for the maximum voltage change between increments of the standard dichromate solution (see 189.3). 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 189.3.

191. Calculation

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

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (22)$$

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, in g.

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

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

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, in g.

192. Precision and Bias²⁰

192.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 16. Although only one sample was tested in the midrange of the

²⁰ Supporting data are available from ASTM Headquarters. Request RR:E03-1036.

TABLE 16 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 2, E 350	0.481	0.015	0.053
2. No. 2, E 351	1.96	0.10	0.16
3. Tool Steel 8Mo, 2W, 3Cr (NBS 134a 3.67Cr)	3.68	0.16	0.48
4. No. 5, E 353	12.87	0.26	0.28

scope, the precision data for other types of alloys using the methods indicated in Table 16 should apply.

192.2 *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 16).

VANADIUM BY THE ATOMIC ABSORPTION METHOD

193. Scope

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

194. Summary of Method

194.1 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.

195. Concentration Range

195.1 The recommended concentration range is from 0.002 to 0.016 mg of vanadium per milliliter of solution.

196. Interferences

196.1 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.

197. Apparatus

197.1 *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 the Operational Guide for Chemical Analysis of Metals and Metal Bearing Ores by Atomic Absorption Spectrophotometry.⁴

198. Reagents

198.1 *Aluminum Chloride Solution* (1 mL = 20 mg Al)—Dissolve 90 g of aluminum chloride (AlCl₃·6 H₂O) in approximately 300 mL of water, add 10 mL of HCl, and dilute to 500 mL.

198.2 *Vanadium, Standard Solution* (1 mL = 0.2 mg V)—Dissolve 0.200 g of vanadium (purity: 99.9 % minimum) in 20 mL of aqua regia (three volumes of HCl to one volume of HNO₃). Evaporate to near dryness and add 10 mL of HCl. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

NOTE 40—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 (NH₄VO₃), 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).

199. Preparation of Calibration Curve

199.1 *Calibration Solutions*—To each of five, 250-mL borosilicate beakers, add 10 mL of HClO₄. 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 29). 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 AlCl₃ solution (198.1), dilute to volume, and mix.

NOTE 41—The remaining amount of HClO₄ must be at a minimum.

199.2 Photometry:

199.2.1 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.

199.2.2 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 199.1, 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 necessary.

199.2.3 Aspirate the vanadium solution used in 199.2.2 to assure that the absorbance reading is repeatable. Record six absorbance readings, and calculate the standard deviation, *s*, of the readings as follows:

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

where:

A = the highest absorbance of the six values found, and
B = the lowest absorbance of the six values found.¹⁵

199.2.4 Using water as a reference, and beginning with the solution to which no addition of vanadium was made in 199.1, 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 199.2.3 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 199.2.1–199.2.4.

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

200. Procedure

200.1 Test Solution:

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

200.1.2 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 25). 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 (198.1), dilute to volume, and mix.

200.1.3 Prepare a reagent blank by using a 250-mL borosilicate beaker and proceeding as directed in 200.1.2. Use reagents from the same lots as those used for the sample solution.

200.2 *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 samples and reagent blank solutions have been aspirated, apply the test using the standard solution as directed in 199.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 199.2.3, 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.

201. Calculation

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

$$\text{Vanadium, \%} = ((A - B) \times 10)/C \quad (25)$$

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 in g.

202. Precision and Bias²¹

202.1 *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 17. All testing meets the requirements of Practice E 173.

202.2 *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.

²¹ Supporting data are available from ASTM Headquarters. Request RR: E03-1040.

TABLE 17 Statistical Information—Vanadium

Test Specimen	Vanadium Found, %	Repeatability (<i>R</i> ₁ , E173)	Reproducibility (<i>R</i> ₂ , E173)
Tool Steel (JSS 601-7, 0.033 V)	0.032	0.002	0.004
Tool Steel (JSS 605-7, 0.160 V)	0.161	0.007	0.011
No. 1, E 350	0.107	0.008	0.014
No. 1, E 351	0.008	0.002	0.003
No. 1, E 353	0.038	0.003	0.005

MOLYBDENUM BY THE ION EXCHANGE— 8-HYDROXYQUINOLINE GRAVIMETRIC METHOD

203. Scope

203.1 This method covers the determination of molybdenum in concentrations from 1.5 to 10 %.

204. Summary of Method

204.1 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.

205. Interferences

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

206. Apparatus

206.1 *Ion Exchange Column, Polystyrene*,²² 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 30).

NOTE 42—The ion exchange column system must be carefully assembled and checked to avoid possible leakage of solutions containing HF.

207. Reagents

207.1 *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.

207.2 *Ammonium Fluoride* (NH₄F).

207.3 *Ammonium Oxalate*—(NH₄OCOCOOH₄H₂O).

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

207.5 *Eluent Solutions*—See Note 31.

NOTE 43—**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).

207.5.1 *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.

207.5.2 *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.

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

207.5.4 *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 NH₄Cl on a weight/volume basis).

207.5.5 *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 NH₄F. 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 NH₄OH. Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH₄Cl and 4.1 % in NH₄F on a weight/volume basis.)

207.6 *8-Hydroxyquinoline Solution* (30 g/L)—Dissolve 30 g of 8-hydroxyquinoline in 120 mL of glacial acetic acid (CH₃COOH). Cautiously add water, with stirring to a total solution volume of 600 mL. Warm to 40°C. Add NH₄OH (1+1) dropwise with stirring until a slight permanent precipitate is formed. Carefully add glacial CH₃COOH with stirring until the precipitate first dissolves. Dilute to 1 L.

207.7 *Ion-Exchange Resin:*

207.7.1 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.²³ 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.

207.7.2 Prepare the column as follows: Place a 10 to 20-mm layer of poly(vinyl chloride) plastic fiber²⁴ 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 of HCl (1+3), turning off the

²² Columns available from Ledoux & Co., Inc., Teaneck, NJ, have been found satisfactory.

²³ AG1-X8, 200 to 400 mesh, chloride form, which is available from Bio-Rad Laboratories, Richmond, CA, has been found satisfactory.

²⁴ Dynel plastic wool, available from Union Carbide Corp., Chemical Division, Textile Fibers Department, Needham Heights, MA, has been found satisfactory.

stopcock when the solution level is 10 to 20 mm above the top of the resin bed.

207.8 *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.

207.9 *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.

208. Procedure

208.1 Transfer 1 g of sample weighed to the nearest 0.1 mg to a 20-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 HNO₃ 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.

208.2 Over a steambath or other low temperature arrangement evaporate the solution to dryness. Cool, wash down the sides of the beaker with HCl (1+1) and again evaporate to dryness over low heat. Cool, add 5 mL HF and 25 mL water. Warm over low heat until all salts are dissolved (Note 32). Cool to room temperature and dilute to 100 mL with water.

NOTE 44—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

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

208.4 Place an 800-mL plastic beaker under the column. Place a small plastic funnel holding a high-porosity hard-surface filter paper in the top of the column. Ensure that an air seal does not form between the funnel and the column. Cautiously filter the sample solution onto the column. Adjust the effluent flow to about 2 mL/min. Rinse the beaker with HF/HCl/water (4+1+95) transferring the washings to the paper. Cautiously police the beaker with a polytetrafluoroethylene policeman, if necessary, and rinse onto the paper with HF/HCl/water (4+1+95). Wash the paper well with HF/HCl/water (4+1+95). Cautiously, remove and discard paper (Note 33).

NOTE 45—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 of 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.

208.5 Continue to add HF/HCl/water (4+1+95) until 650 mL have been collected in the 800-mL plastic beaker (Note 34).

Drain solution to the top of the resin bed. Cautiously discard this solution.

NOTE 46—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper, and manganese.

208.6 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 35).

NOTE 47—This solution contains all the tungsten, titanium, zirconium, and hafnium.

208.7 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 208.11.

208.8 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 36).

NOTE 48—This solution contains all the niobium.

208.9 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 37).

NOTE 49—This solution contains all the tantalum.

208.10 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 (see 208.3).

208.11 To the eluent containing the molybdenum (from 208.7) cautiously add 15 mL of H₂SO₄(1+1) and evaporate to light fumes on a sandbath or other carefully controlled heat source (Note 39). Cool and cautiously rinse into a 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.

NOTE 50—**Warning:** Ensure that the applied temperature does not exceed the softening point of polytetrafluoroethylene.

208.12 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.

208.13 Dilute to 100 mL. Heat to boiling and while hot, cautiously add NaOH solution (100 g/L) until litmus paper moistened with the solution 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 208.14.

208.14 Adjust the volume of the solution or filtrate obtained in 208.13 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).

208.15 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.

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

208.17 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.

209. Calculation

209.1 Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, \%} = [(A - B) \times 23.05]/C \quad (26)$$

where:

A = weight of crucible plus precipitate, in g,

B = weight of crucible, in g, and

C = sample weight, in g.

210. Precision and Bias

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).

210.1 *Precision*—Seven laboratories cooperated in testing this method and obtained the data summarized in Table 18. While the testing range exceeds the upper limit of the Scope, the data for Test Specimen 4 were included to illustrate the ruggedness of the method’s precision at levels near the upper limit of the Scope.

210.2 *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.

211. Keywords

211.1 chromium; cobalt; combustion analysis; copper; high-alloy steel; induction furnace; infrared absorption; lead; nickel; manganese; molybdenum; phosphorus; silicon; sulfur; tin; tool steels; total carbon; vanadium

TABLE 18 Statistical Information—Molybdenum Ion Exchange–8 Hydroxyquinoline Gravimetric Method

Test Material	Molybdenum Found, %	Repeatability (R ₁ , E173) ^A	Reproducibility (R ₂ , E173) ^A
1. No. 1, E 351	1.48	0.070	0.086
2. No. 2, E 354	3.92	0.219	0.250
3. mod. M34 high speed 8Co-4Cr-2V-2W-1C (NBS 153a, 8.85 Mo)	8.85	0.180	0.188
4. No. 4, E 354	17.49	0.285	0.641

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