



Designation: E 352 – 93 (Reapproved 2000)^{e1}

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.

^{e1} 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:

Section	Section
Carbon, Total, by the Combustion—Thermal Conductivity Method	2a
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	2b
Cobalt by the Ion-Exchange—Potentiometric Titration Method	(2 to 14 %) 52

Section	Section
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 ^{2c}
Sulfur by the Gravimetric Method	
Sulfur by the Combustion-Iodate Titration Method	(0.005 to 0.4 %) 36
Sulfur by the Chromatographic Gravimetric Method	2b
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

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.

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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.

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

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.

acid. Solutions of the samples are fumed with perchloric acid 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:

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

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.

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

20. Concentration Range

20.1 See Section 20 of Test Methods E 350.

21. Stability of Color

21.1 See Section 21 of Test Methods E 350.

22. Interferences

22.1 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 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

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

TABLE 3 Statistical Information—Sulfur

Test Specimen	Sulfur Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)	Dehydrating Acid, mL	
				H ₂ SO ₄ (1 + 4)	HClO ₄
Induction Furnace					
1. High-alloy steel 8Co-9Mo-2W-4Cr-2V (NBS 153a, 0.007S)	0.006 ^A	0.002	0.003	0.1 to 0.1	4.0
2. Tool steel 18W-4Cr-1V (NBS 50c, 0.010S)	0.008 ^A	0.001	0.004	1.0 to 1.75	3.0
3. No. 3, E 350	0.014 ^A	0.003	0.003	1.75 to 2.50	2.0
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.

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.

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

TABLE 4 Statistical Information—Silicon

Test Specimen	Silicon Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. Tool steel 5Mo-6W-4Cr-2V (NBS 132a, 0.19 Si)	0.193	0.019	0.031

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

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

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

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.

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

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

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

74.3 *Sulfamic Acid* (H(NH₂)SO₃).

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 HNO₃ 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 HNO₃ and 10 mL of HClO₄, heat moderately to oxidize organic matter, and finally heat to mild fumes of HClO₄. Cool the solution, add 1 to 2 mL of HF, and repeat the fuming.

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 HNO₃ and 1 to 2 mL of HF, and evaporate to dryness. Add 10 mL of HNO₃(1+1) and digest at 90 to 100°C for 5 min. Transfer the contents of the crucible to the original flask, add 10 mL of HClO₄, and heat to mild fumes of HClO₄.

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 NH₄OH and 20 g of tartaric acid. When the tartaric acid has

dissolved, again add a slight excess of NH₄OH and digest near the boiling point until dissolution is complete, or nearly so.

75.6 Add 5 mL of H₂SO₄ and heat at 85 to 95°C for 30 min. If insoluble matter persists, repeat the steps as directed in 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 H₂S; admit the gas at a rate sufficient to cause a steady stream of bubbles to leave the solution. Continue passing the gas into the solution for at least 1 h. Allow to stand until the supernatant solution becomes clear, but not longer than 12 to 15 h.

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 H₂SO₄, and heat to char the paper. Add 20 mL of HNO₃, and evaporate to fumes to destroy organic matter. Add HNO₃ in 1-mL increments and heat to fumes after each addition to oxidize the last traces of organic matter.

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

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

NOTE 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 HNO₃, and evaporate at low heat until salts begin to appear. Remove the beaker from the hot plate and while the solution is still hot add 5 mL of HNO₃. When the reaction has subsided, add another 5 mL of HNO₃ and again wait until the reaction subsides. Continue adding 5-mL increments of HNO₃ in this manner until there is no further reaction with the chloride ions. Cover the beaker with a ribbed cover glass and warm gently until the vigorous evolution of gas ceases. Evaporate to fumes of SO₃. Cool, add 25 mL of water, and heat to dissolve the salts. Cool, transfer to a 250-mL beaker, add 3 mL of HNO₃, and dilute to 175 mL.

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/dm². Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 to 3 A/dm²(Note 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/dm², 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.

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

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.

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, cupellet, 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

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.

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

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

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.