



Designation: E352 – 13

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 E352; 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.

1. Scope

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

Element	Composition 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:

Test Method	Sections
Carbon, Total, by the Combustion—Thermal Conductivity Method— <i>Discontinued 1986</i>	
Carbon, Total, by the Combustion Gravimetric Method— <i>Discontinued</i>	
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— <i>Discontinued 1980</i>	
Cobalt by the Ion-Exchange—Potentiometric Titration Method	(2 % to 14 %) 52
Cobalt by the Nitroso-R-Salt Spectrophotometric Method	(0.10 % to 5.0 %) 60
Copper by the Neocuproine Spectrophotometric Method	(0.01 % to 2.00 %) 89

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 Feb. 1, 2013. Published May 2013. Originally approved in 1968. Last previous edition approved in 2006 as E352 – 93 (2006). DOI: 10.1520/E0352-13.

Test Method	Sections
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 0.01 %) 99
Nickel by the Dimethylglyoxime Gravimetric Method	(0.1 % to 4.0 %) 144
Manganese by the Periodate Spectrophotometric Method	(0.10 % to 5.00 %) 8
Molybdenum by the Ion Exchange—8-Hydroxyquinoline Gravimetric Method	203
Molybdenum by the Spectrophotometric Method	(0.01 % to 1.50 %) 162
Phosphorus by the Alkalimetric Method	(0.01 % to 0.05 %) 136
Phosphorus by the Molybdenum Blue Spectrophotometric Method	(0.002 % to 0.05 %) 18
Silicon by the Gravimetric Method	(0.10 % to 2.50 %) 45
Sulfur by the Gravimetric Method— <i>Discontinued 1988</i>	
Sulfur by the Combustion-Iodate Titration Method— <i>Discontinued</i>	
Sulfur by the Chromatographic Gravimetric Method— <i>Discontinued 1980</i>	
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 carbon and sulfur not included in this standard can be found in Test Methods E1019.

1.4 Some of the composition ranges given in 1.1 are too broad to be covered by a single 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.

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

2. Referenced Documents

2.1 *ASTM Standards*:²

- D1193** Specification for Reagent Water
 - E29** Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
 - E50** Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
 - E60** Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
 - E135** Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
 - E173** Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)³
 - E350** Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron
 - E351** Test Methods for Chemical Analysis of Cast Iron—All Types
 - E353** Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys
 - E882** Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
 - E1019** Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Fusion Techniques
 - E1024** Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry (Withdrawn 2004)³
 - E1806** Practice for Sampling Steel and Iron for Determination of Chemical Composition
- ### 2.2 *Other Document*:⁴
- ISO 5725** Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests

3. Terminology

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

4. Significance and Use

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

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

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

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

skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide **E882**.

5. Apparatus, Reagents, and Instrumental Practices

5.1 *Apparatus*—Specialized apparatus requirements are listed in the “Apparatus” Section in each method.

5.2 *Reagents*:

5.2.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the “Reagent Grade” Specifications of the American Chemical Society.⁵ 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.”

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

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

6. Hazards

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

7. Sampling

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

8. Interlaboratory Studies and Rounding Calculated Values

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

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

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

9. Scope

9.1 This method covers the determination of manganese in compositions from 0.10 % to 5.00 %.

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

10. Summary of Method

10.1 Manganous ions are oxidized to permanganate ions by treatment with periodate. Tungsten when present at compositions greater than 0.5 % is kept in solution with phosphoric acid. Solutions of the samples are fumed with HClO_4 so that the effect of periodate is limited to the oxidation of manganese. Spectrophotometric measurement is made at approximately 545 nm.

11. Concentration Range

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

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

12. Stability of Color

12.1 The color is stable for at least 24 h.

13. Interferences

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

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

13.3 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.

14. Reagents

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

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

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

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

15. Preparation of Calibration Curve

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

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

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

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

15.4 Spectrophotometry:

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

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

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

16. Procedure

16.1 *Test 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.

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

16.1.1.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO₃ as needed to hasten dissolution, and then add 3 mL to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of 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-mL or 500-mL volumetric flask as indicated in 16.1. Proceed to 16.1.3.

16.1.1.2 For samples whose dissolution is hastened by HF, add 8 mL 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 mL 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-mL or 500-mL volumetric flask as indicated in 16.1. Proceed to 16.1.3.

16.1.2 For Samples Containing More Than 0.5 % Tungsten:

16.1.2.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 mL to 6 mL of H₂SO₄, and 3 mL to 4 mL of HNO₃. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 min 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-mL or 500-mL volumetric flask as directed in 16.1. Proceed to 16.1.3.

16.1.2.2 For samples whose dissolution is hastened by HF, add 8 mL to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 mL to 6 mL of H₂SO₄, 3 mL 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 min 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-mL or 500-mL volumetric flask as directed in 16.1. Proceed to 16.1.3.

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

16.1.4 Using a pipet, transfer 10 mL to 20 mL aliquots, as specified in 16.1 to two 50-mL borosilicate glass volumetric flasks. Treat one portion as directed in 16.3. Treat the other portion as directed in 16.4.1.

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

16.3 Color Development—Proceed as directed in 15.3.

16.4 Reference Solutions:

16.4.1 Background Color Solution—To one of the sample aliquots in a 50-mL volumetric flask, add 10 mL of nitric-

phosphoric acid mixture, and heat the solution at not less than 90 °C for 20 min to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

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

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

17. Calculation

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

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

where:

A = manganese, mg, found in 50 mL of the final test solution,

B = apparent manganese, mg, found in 50 mL of the final background color solution, and

C = sample weight, g, represented in 50 mL of the final test solution.

18. Precision and Bias

18.1 Precision—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 1.

18.2 Bias—No information on the accuracy of this method is known. The accuracy of this method may be judged by

TABLE 1 Statistical Information—Manganese by the Metaperiodate Spectrophotometric Method

Test Specimen	Manganese Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
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

comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

PHOSPHORUS BY THE MOLYBDENUM BLUE SPECTROPHOTOMETRIC METHOD

19. Scope

19.1 This test method covers the determination of phosphorus in compositions from 0.002 % to 0.05 %.

20. Summary of Method

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

21. Concentration Range

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

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

22. Stability of Color

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

23. Interferences

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

24. Apparatus

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

25. Reagents

25.1 *Ammonium Molybdate Solution* (20 g/L)—Cautiously, while stirring and cooling, add 300 mL of H_2SO_4 to 500 mL of water and cool. Add 20 g of ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), cautiously dilute to 1 L, and mix.

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

25.3 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ($(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4$) in water, dilute to 1 L, and mix. Discard any unused solution after 24 h.

25.4 *Phosphorus Standard Solution A* (1 mL = 1.0 mg P)—Transfer 2.292 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4), previously dried to constant weight at 105 °C, to a 500-mL volumetric flask; dissolve in about 100 mL of water, dilute to volume, and mix.

25.5 *Phosphorus Standard Solution B* (1 mL = 0.01 mg P)—Using a pipet, transfer 10 mL of Solution A (1 mL = 1.0 mg P) to a 1-L volumetric flask, add 50 mL of HClO_4 (1 + 5), dilute to volume, and mix.

25.6 *Phosphorus Standard Solution C* (1 mL = 0.10 mg P)—Using a pipet, transfer 50 mL of Solution A (1 mL = 1.0 mg P) to a 500-mL volumetric flask, add 50 mL of HClO_4 (1 + 5), dilute to volume, and mix.

25.7 *Sodium Sulfite Solution* (100 g/L)—Dissolve 100 g of sodium sulfite (Na_2SO_3) in water, dilute to 1 L, and mix.

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

26.1 *Calibration Solutions*—Using pipets, transfer 5 mL, 10 mL, 15 mL, 25 mL, and 50 mL of Phosphorus Standard Solution B (1 mL = 0.01 mg P) to 100-mL volumetric flasks. Add 20 mL of HClO_4 , dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 100-mL borosilicate glass volumetric flask. Proceed in accordance with 26.3.

26.2 *Reagent Blank*—Transfer 12 mL of HClO_4 (1 + 5) to a 100-mL borosilicate glass volumetric flask.

26.3 Color Development:

26.3.1 Add 15 mL of Na_2SO_3 solution, boil gently for 30 s, and add 50 mL of ammonium molybdate-hydrazine sulfate solution that has been prepared within the hour.

26.3.2 Heat the solutions at not less than 90 °C for 20 min, quickly cool, dilute to volume, and mix.

NOTE 4—Immersing the flasks in a boiling water bath is the preferred means of heating them for complete color development.

26.4 Reference Solution—Water.

26.5 Spectrophotometry:

26.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) versus the reference solution (26.4) using absorption cells with a 1-cm light path and using a light band centered at approximately 825 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions versus the reference solution.

26.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (26.4) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting using a light band centered at approximately 825 nm. While maintaining this adjustment, take the spectrophotometric readings of the reagent blank solution and of the calibration solutions.

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

27. Procedure

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

27.1.1 *Test Solution:*

27.1.1.1 Transfer a 1.0-g sample, weighed to the nearest 0.5 mg, to a 250-mL Erlenmeyer flask.

27.1.1.2 Add 15 mL of a freshly prepared mixture of 1 volume of HNO₃ and 3 volumes of HCl, slowly and in small portions. When the reaction has ceased, add 10 mL of HClO₄ and evaporate to fumes. Remove the flask immediately to avoid undue loss of HClO₄, cool, and add 20 mL of HBr (1 + 4). Evaporate the solution to copious white fumes and then, without delay, fume strongly enough to cause the white fumes to clear the neck of the flask, and continue at this rate for 1 min.

27.1.1.3 Cool the solution, add 60 mL of HClO₄ (1 + 5), and swirl to dissolve the salts. Transfer to a 100-mL volumetric flask, cool, dilute to volume, and mix. Allow insoluble matter to settle or dry filter the solution. Using a pipet, transfer 10-mL portions to two 100-mL borosilicate glass volumetric flasks; treat one in accordance with 27.1.3 and the other in accordance with 27.1.4.2.

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

27.1.3 *Color Development*—Proceed with one of the 10-mL portions obtained in 27.1.1.3, in accordance with 26.3.

27.1.4 *Reference Solutions:*

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

27.1.4.2 *Background Color Reference Solution*—Add 15 mL of Na₂SO₃ solution to the second 10-mL portion obtained in 27.1.1.3. Boil gently for 30 s, add 50 mL of H₂SO₄ (3 + 37), cool, dilute to volume, and mix. Use this as the reference solution for the test solution.

27.1.5 *Spectrophotometry*—Take the spectrophotometric readings of the reagent blank solution and of the test solution (using the respective reference solutions) in accordance with 26.5.

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

27.2.1 *Test Solution:*

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

27.2.1.2 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.

27.2.1.3 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 27.2.3 and the other as directed in 27.2.4.

27.2.2 *Reagent Blank Solution*—Proceed as directed in 27.2.1.2 and 27.2.1.3.

27.2.3 *Color Development*—Proceed as directed in 26.3.

27.2.4 *Reference Solutions:*

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

27.2.4.2 *Background Color Reference Solution*—Add 15 mL of Na₂SO₃ solution to the second 10-mL portion obtained in 27.2.1.3. Boil gently for 30 s, add 50 mL of H₂SO₄ (3 + 37), cool, dilute to volume, and mix. Use this as the reference solution for the test solution.

27.2.5 *Spectrophotometry*—Proceed as directed in 27.1.5.

28. Calculation

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

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

where:

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

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

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

29. Precision

29.1 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

(This method, which consisted of Sections 36 through 44 of this standard, was discontinued in 2012.)

SILICON BY THE GRAVIMETRIC METHOD

45. Scope

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

TABLE 2 Statistical Information—Phosphorus

Test Specimen	Phosphorus Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
1. Tool steel 5Mo-6W-4Cr-2V (NIST 132a, 0.029 P)	0.029	0.011	0.008
2. Tool steel 8Co-9Mo-2W-4Cr-2V (NIST 153a, 0.023 P)	0.023	0.008	0.007
3. Tool steel 18W-4Cr-1V (NIST 50c, 0.022 P)	0.022	0.005	0.007

46. Summary of Method

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

47. Interferences

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

48. Reagents

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

48.2 Perchloric Acid:

48.2.1 Select a lot of HClO_4 that contains not more than 0.0002 % silicon for the analysis of samples containing silicon in the range from 0.02 % to 0.10 % and not more than 0.0004 % silicon for samples containing more than 0.10 % by determining duplicate values for silicon in accordance with 48.2.2 – 48.2.6.

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

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

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

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

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

48.2.6 Calculate the percent of silicon as follows:

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

where:

A = initial weight of crucible plus impure SiO_2 when 65 mL of HClO_4 was taken, g,

B = final weight of crucible plus impurities when 65 mL of HClO_4 was taken, g,

C = initial weight of crucible plus impure SiO_2 when 15 mL of HClO_4 was taken, g,

D = final weight of crucible plus impurities when 15 mL of HClO_4 was taken, g, and

E = nominal weight (80 g) of 50 mL of HClO_4 .

48.3 *Sodium Silicate Solution*—Transfer 11.0 g of sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) to a 400-mL beaker. Add 150 mL of water and dissolve the salt. Filter through a medium paper, collecting the filtrate in a 1-L volumetric flask, dilute to volume, and mix. Store in a polyethylene bottle. Use this solution to determine the suitability of the HClO_4 .

48.4 *Tartaric Acid Solution* (20.6 g/L)—Dissolve 20.6 g of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) in water, dilute to 1 L, and filter.

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

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_2SO_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. Proceed in accordance with 49.2 if tungsten is greater than 0.5% or if tungsten is less than 0.5%, proceed in accordance with 49.2 or 49.3.

49.2 Sulfuric Acid Dehydration:

49.2.1 Add amounts of HCl or HNO_3 , or mixtures and dilutions of these acids, that are sufficient to dissolve the sample; and then add the H_2SO_4 (1 + 4) as specified in 49.1, and cover. Heat until dissolution is complete. Remove and rinse the cover glass; substitute a ribbed cover glass.

49.2.2 Evaporate until salts begin to separate; at this point evaporate the solution rapidly to the first appearance of fumes and fume strongly for 2 min to 3 min. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat, if necessary, but do not boil. Proceed immediately in accordance with 49.4.

49.3 Perchloric Acid Dehydration:

49.3.1 Add amounts of HCl or HNO_3 , or mixtures and dilutions of these acids, which are sufficient to dissolve the sample, and cover. Heat until dissolution is complete. Add HNO_3 to provide a total of 35 mL to 40 mL, followed by HClO_4 as specified in the table in 49.1. Remove and rinse the cover glass; substitute a ribbed cover glass.

49.3.2 Evaporate the solution to fumes and heat for 15 min to 20 min at such a rate that the HClO_4 refluxes on the sides of the container. Cool sufficiently and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat to boiling. If the

sample solution contains more than 100 mg of chromium, add, while stirring, 1 mL of tartaric acid solution for each 25 mg of chromium.

49.4 Add paper pulp and filter immediately, on a low-ash 11-cm medium-porosity filter paper. Collect the filtrate in a 600-mL beaker. Transfer the precipitate to the paper, and scrub the container thoroughly with a rubber-tipped rod. Wash the paper and precipitate alternately with 3 mL to 5 mL portions of hot HCl (1 + 19) and hot water until iron salts are removed but for not more than a total of ten washings. If the HClO₄ dehydration method was followed, wash the paper twice more with H₂SO₄ (1 + 49), but do not collect these washings in the filtrate; discard the washings. Transfer the paper to a platinum crucible and reserve.

49.5 Add 15 mL of HNO₃ to the filtrate, stir, and evaporate in accordance with either 49.2 or 49.3, depending upon the dehydrating acid used. Filter immediately, using a low-ash, 9-cm 100-porosity filter paper, and wash in accordance with 49.4.

49.6 Transfer the paper and precipitate to the reserved platinum crucible. Dry the papers and then heat the crucible at 600 °C until the carbon is removed. Finally ignite at 1100 °C to 1150 °C to constant weight (at least 30 min). Cool in a desiccator and weigh.

49.7 Add enough H₂SO₄ (1 + 1) to moisten the impure SiO₂, and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H₂SO₄ is removed. Ignite at 1100 °C to 1150 °C for 15 min, cool in a desiccator, and weigh. If the sample contains more than 0.5 % tungsten, ignite at 750 °C instead of 1100 °C to 1150 °C after volatilization of SiO₂.

50. Calculation

50.1 Calculate the percent of silicon as follows:

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

where:

- A = initial weight of crucible and impure SiO₂, g,
- B = final weight of crucible and residue, g, and
- C = sample used, g.

51. Precision and Bias

51.1 Eleven laboratories cooperated in testing this method and obtained the data summarized in Table 3. 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.

TABLE 3 Statistical Information—Silicon

Test Specimen	Silicon Found, %	Repeatability (R ₁ , E173)	Reproducibility (R ₂ , E173)
H ₂ SO ₄ Dehydration			
1. Tool steel 5Mo-6W-4Cr-2V (NIST 132a, 0.19 Si)	0.193	0.019	0.031

**COBALT BY THE ION-EXCHANGE—
POTENTIOMETRIC TITRATION METHOD**

52. Scope

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

53. Summary of Method

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

54. Interferences

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

55. Apparatus

55.1 *Ion-Exchange Column*, approximately 25 mm in diameter and 300 mm in length, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. A Jones Reductor (Fig. 1) may be adapted to this method. A reservoir for the eluants may be added at the top of the column.

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

56. Reagents

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

56.2 *Cobalt, Standard Solution* (1mL = 1.5 mg of Co):

56.2.1 *Preparation*—Dry a weighing bottle in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer 3.945 g of cobalt sulfate (CoSO₄)⁶ that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in desiccator, stopper the bottle, and weigh. The difference in weight is the amount of CoSO₄ taken. Transfer the weighed CoSO₄ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 20 mL of HNO₃, and heat to dissolve the salts. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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

$$\text{Cobalt, mg/mL} = \text{weight of CoSO}_4, \text{ g} \times 0.38026 \quad (5)$$

56.3 *Ion-Exchange Resin*:⁷

56.3.1 Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a nominal crosslinkage of 8 %, and 200-nominal to 400-nominal mesh size. To remove those beads greater than about 180-µm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a

⁶ Cobalt sulfate (99.9 % minimum) prepared from the hexamine salt by G. Frederick Smith Chemical Co., Columbus, OH, is satisfactory for this purpose.

⁷ Available from the Dow Chemical Co., Midland, MI.

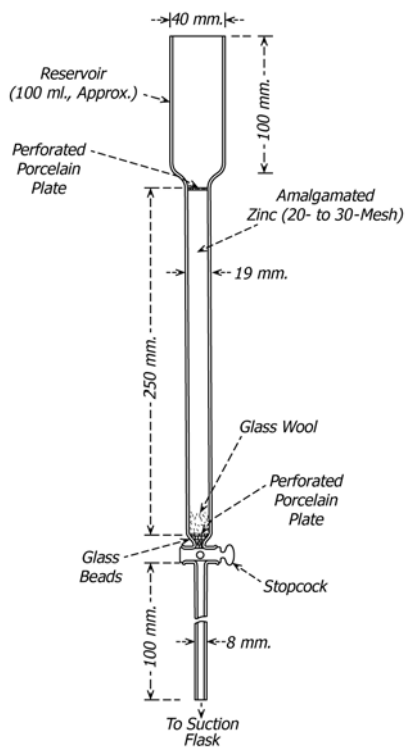


FIG. 1 Jones Reductor

beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a No. 80 (180- μ m) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 min to 6 min, decant 150 mL 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.

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

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

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

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

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

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

where:

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

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

57. Procedure

57.1 Transfer a 0.50-g sample, weighed to the nearest 0.1 mg, to a 150-mL beaker. Add 20 mL of a mixture of 5 parts of HCl and 1 part of HNO_3 (Note 8). Cover the beaker and digest

at 60 °C to 70 °C until the sample is decomposed. Rinse and remove the cover. Place a ribbed cover glass on the beaker, and evaporate the solution nearly to dryness, but do not bake. Cool, add 20 mL of HCl (7 + 5), and digest at 60 °C to 70 °C until salts are dissolved (approximately 10 min).

NOTE 8—Some alloys are decomposed more readily by a mixture of 5 mL of bromine, 15 mL of HCl, and 1 drop to 2 drops of HF.

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

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

57.3 Add HCl (1 + 2) to the column and collect 165 mL to 175 mL of the solution while maintaining the 3.0 mL/min flow rate. Reserve the solution. If the sample solution did not contain more than 0.200 g of iron, substitute a 250-mL beaker and precondition the column for the next sample as follows: Drain the remaining solution in the column to 10 mm to 20 mm above the resin bed, pass 35 mL to 50 mL of HCl (7 + 5) through the column until 10 mm to 20 mm of the solution remains above the resin bed, then close the lower stopcock. If the sample solution contained more than 0.200 g of iron, or if the column is not to be used again within 3 h, discard the resin and recharge the column as directed in 56.3.

57.4 Add 30 mL of HNO₃ and 15 mL of HClO₄ to the solution from 57.3 and evaporate to fumes of HClO₄. Cool, add 25 mL to 35 mL of water, boil for 1 min to 2 min, cool, and add 10 mL of ammonium citrate solution.

57.5 Using a 50-mL buret, transfer to a 400-mL beaker a sufficient volume of K₃Fe(CN)₆ solution to oxidize the cobalt and to provide an excess of about 5 mL to 8 mL. Record the buret reading to the nearest 0.01 mL. Add 50 mL of NH₄OH and cool to 5 °C to 10 °C. Transfer the beaker to the potentiometric titration apparatus and maintain the 5 °C to 10 °C temperature during the titration.

57.6 While stirring, add the sample solution to the solution from 57.5, rinse the beaker with water, and add the rinsings to the solution (Note 10). Using a 50-mL buret, titrate the excess K₃Fe(CN)₆ with the cobalt solution (1 mL = 1.5 mg Co), at a fairly rapid rate until the end point is approached, and then add the titrant in 1-drop increments through the end point. After the

TABLE 4 Statistical Information—Cobalt

Test Specimen	Cobalt Found, %	Repeatability (R_1 , E173)	Reproducibility (R_2 , E173)
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 (NIST 153a, 8.47 Co)	8.46	0.03	0.07
4. No. 4, E354	11.27	0.06	0.16
5. No. 5, E354	13.88	0.09	0.18

addition of each increment, record the buret reading and voltage when equilibrium is reached. Estimate the buret reading at the end point to the nearest 0.01 mL by interpolation.

NOTE 10—For a successful titration, the sample solution must be added to the excess K₃Fe(CN)₆ solution.

58. Calculation or Interpretation of Results

58.1 Calculate the percentage of cobalt as follows:

$$\text{Cobalt, \%} = [(A B - C D)/E] \times 100 \quad (7)$$

where:

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

59. Precision and Bias

59.1 Ten laboratories cooperated in testing the method and obtained the data summarized in Table 4 for specimens 1, 2, and 3. Although samples covered by this method with cobalt compositions 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 SPECTROPHOTOMETRIC METHOD

60. Scope

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

61. Summary of Method

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

62. Concentration Range

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

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

63. Stability of Color

63.1 The color is stable for at least 3 h.

64. Interferences

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

65. Reagents

65.1 *Cobalt, Standard Solution* (1 mL = 0.06 mg Co)—Dry a weighing bottle and stopper in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer approximately 0.789 g of cobalt sulfate (CoSO₄)⁸ that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in a desiccator, stopper the bottle, and weigh. The difference in weight is the exact amount of CoSO₄ taken. Transfer the weighed CoSO₄ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 10 mL of HCl, and heat to dissolve the salts. Cool, transfer to a 500-mL volumetric flask, dilute to volume, and mix. By means of a pipet, transfer a 50-mL aliquot of this solution to a 500-mL volumetric flask, dilute to volume, and mix. The exact concentration (in milligrams of cobalt per millilitre) of the final solution is the exact weight of CoSO₄ taken multiplied by 0.076046.

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

65.3 *Sodium Acetate Solution* (500 g/L)—Dissolve 500 g of sodium acetate trihydrate (CH₃COONa·3H₂O) in about 600 mL of water, filter, and dilute to 1 L.

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

66. Preparation of Calibration Curve

66.1 *Calibration Solutions*—Using pipets, transfer 2 mL, 5 mL, 10 mL, 15 mL, 20 mL, and 25 mL of cobalt standard solution (1 mL = 0.06 mg Co) to six 100-mL volumetric flasks, dilute to volume, and mix. Using a pipet, transfer 10 mL of each solution to a 50-mL borosilicate glass volumetric flask. Proceed in accordance with 66.3.

66.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed in accordance with 66.3.

⁸ Cobalt sulfate (99.9 % minimum) prepared from the hexamine salt by G. Frederick Smith Chemical Co., Columbus, OH, is satisfactory for this purpose.

66.3 *Color Development*—Add 5 mL of sodium acetate solution, and mix. Using a pipet, add 10 mL of nitroso-R-salt solution, and mix. Place the flask in a boiling water bath. After 6 min to 10 min, add 5 mL of HNO₃ (1 + 2), and mix. Continue the heating for 2 min to 4 min. Cool the solution to room temperature, dilute to volume, and mix.

66.4 Spectrophotometry:

66.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction with water using absorption cells with a 1-cm light path and using a light band centered at approximately 520 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions versus the reference solution (66.2).

66.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (66.2) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at approximately 520 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

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

67. Procedure

67.1 Test Solution:

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

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

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

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

67.1.3 Add ZnO suspension in portions of about 5 mL until the iron is precipitated and a slight excess of ZnO is present. Shake thoroughly after each addition of the precipitant and avoid a large excess (Note 12). Dilute to volume, and mix. Allow the precipitate to settle; filter a portion of the solution through a dry, fine-porosity filter paper and collect it in a dry, 150-mL beaker after having discarded the first 10 mL to 20 mL. Using a pipet, transfer 10 mL of the filtrate to a 50-mL borosilicate glass volumetric flask. Proceed as in accordance with 67.3.

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

NOTE 13—Other ratios and concentrations of acids, with or without the addition of 1 mL to 2 mL of HF, are used for the decomposition of special grades of alloys. 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 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed in accordance with 67.3.