Designation: E352 – 13

# Standard Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels[1]

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:

| | | Sections |
|---|---|---|
| Carbon, Total, by the Combustion—Thermal Conductivity Method—*Discontinued 1986* | | |
| Carbon, Total, by the Combustion Gravimetrical Method—*Discontinued* | | |
| 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—*Discontinued 1980* | | |
| 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 |
| 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—*Discontinued 1988* | | |
| Sulfur by the Combustion-Iodate Titration Method—*Discontinued* | | |
| Sulfur by the Chromatographic Gravimetric Method—*Discontinued 1980* | | |
| 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.

[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. 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 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 %.

[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.

[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 $HNO_3$ 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 $HClO_4$; 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 $HNO_3$ and a few drops of HF as needed to hasten dissolution, and then add 3 mL to 4 mL of $HNO_3$. When dissolution is complete, cool, then add 10 mL of $HClO_4$, 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 $H_3PO_4$, 10 mL of $HClO_4$, 5 mL to 6 mL of $H_2SO_4$, and 3 mL to 4 mL of $HNO_3$. 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 $SO_3$. 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 $H_3PO_4$, 10 mL of $HClO_4$, 5 mL to 6 mL of $H_2SO_4$, 3 mL to 4 mL of $HNO_3$, 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 $SO_3$. 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 ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), 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 ($(NH_2)_2\cdot H_2SO_4$) 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 $HNO_3$ and 3 volumes of HCl, slowly and in small portions. When the reaction has ceased, add 10 mL of $HClO_4$ and evaporate to fumes. Remove the flask immediately to avoid undue loss of $HClO_4$, 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 $HClO_4$ (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 $Na_2SO_3$ solution to the second 10-mL portion obtained in 27.1.1.3. Boil gently for 30 s, add 50 mL of $H_2SO_4$ (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 $HNO_3$ and 3 volumes of HCl. When the reaction has ceased, add 2.5 mL of $HClO_4$ 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 $Na_2SO_3$ solution to the second 10-mL portion obtained in 27.2.1.3. Boil gently for 30 s, add 50 mL of $H_2SO_4$ (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:

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

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 ($Na_2SiO_3 \cdot 9H_2O$) 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 ($C_4H_6O_6$) 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:

| | | | Dehydrating Acid, mL | |
|---|---|---|---|---|
| Silicon, % | Sample Weight, g | Tolerance in Sample Weight, mg | $H_2SO_4$ (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 $HClO_4$ dehydration method was followed, wash the paper twice more with $H_2SO_4$ (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 $HNO_3$ 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 $H_2SO_4$ (1 + 1) to moisten the impure $SiO_2$, 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 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 $SiO_2$.

## 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 $SiO_2$, 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 $HClO_4$ dehydration procedure; neither were samples available with tungsten greater than 0.5 % for testing the $H_2SO_4$ 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) |
|---|---|---|---|
| $H_2SO_3$ 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 ($CoSO_4$)[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 $CoSO_4$ taken. Transfer the weighed $CoSO_4$ 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 $HNO_3$, 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.

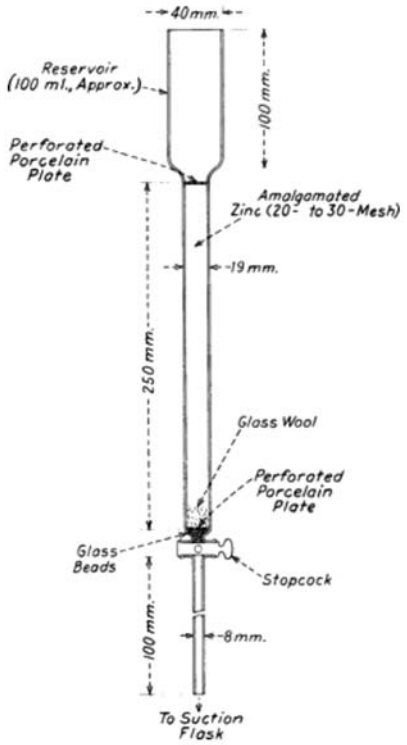


**FIG. 1 Jones Reductor**

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

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

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 $HNO_3$ and 15 mL of $HClO_4$ to the solution from 57.3 and evaporate to fumes of $HClO_4$. 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 $K_3Fe(CN)_6$ 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 $NH_4OH$ 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 $K_3Fe(CN)_6$ with the cobalt solution (1 mL = 1.5 mg Co), at a fairly rapid rate until the end point is approached, and then add the titrant in 1-drop increments through the end point. After the addition of each increment, record the buret reading and voltage when equilibrium is reached. Estimate the buret reading at the end point to the nearest 0.01 mL by interpolation.

NOTE 10—For a successful titration, the sample solution must be added to the excess $K_3Fe(CN)_6$ solution.

**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 |

## 58. Calculation or Interpretation of Results

58.1 Calculate the percentage of cobalt as follows:

$$\text{Cobalt},\% = [(AB - CD)/E] \times 100 \quad (7)$$

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 ($CoSO_4$)[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 $CoSO_4$ taken. Transfer the weighed $CoSO_4$ 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 $CoSO_4$ 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 ($CH_3COONa{\cdot}3H_2O$) 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.

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 $HNO_3$ (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 $HNO_3$ 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.

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

**TABLE 5 Statistical Information—Cobalt**

| Test Specimen | Cobalt Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 2, E353 | 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 (NIST 438, 4.9 Co) | 4.94 | 0.08 | 0.17 |

67.3 *Color Development*—Proceed in accordance with 66.3.

67.4 *Spectrophotometry*—Take the spectrophotometric reading of the test solution in accordance with 66.4.

## 68. Calculation

68.1 Convert the net spectrophotometric reading of the test solution to milligrams of cobalt by means of the calibration curve. Calculate the percent of cobalt as follows:

$$\text{Cobalt},\% = A/(B \times 10) \quad (8)$$

where:

$A$ = cobalt found in 50 mL of the final test solution, mg, and
$B$ = sample represented in 50 mL of the final test solution, g.

## 69. Precision

69.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 5 for specimens 2 and 3. Although a sample covered by this method with cobalt composition of approximately 0.1 % was not available for testing, the precision data obtained for specimen 1 by Test Methods E353 should apply.

# COPPER BY SULFIDE PRECIPITATION-ELECTRODEPOSITION GRAVIMETRIC METHOD

## 70. Scope

70.1 This method covers the determination of copper in compositions 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 14). Chloride ions are removed from the filtrate, and copper, as the metal, is deposited on a platinum cathode.

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

## 72. Interferences

72.1 Ammonium salts may cause the copper deposit to be spongy and subject to air oxidation while drying in the oven. If this occurs the copper should be dissolved from the platinum cathode and redeposited (Note 16).

## 73. Apparatus

73.1 *Electrodes*—Platinum electrodes of the stationary type are recommended as described in 73.1.1 and 73.1.2, but strict adherence to the exact size and shape of the electrodes is not mandatory. When agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes, generally available, may be employed. The surface of the platinum electrodes should be smooth, clean, and bright to promote uniform deposition and good adherence. Sandblasting is not recommended.

73.1.1 *Cathodes*—Platinum cathodes may be formed either from plain or perforated sheets or from wire gauze, and may be either open or closed cylinders. Gauze cathodes are recommended, and shall be made preferably from 50-mesh gauze woven from wire approximately 0.21 mm (0.0085 in.) in diameter. The cathode should be stiffened by doubling the gauze for about 3 mm at the top and the bottom of the cylinder or by reinforcing the gauze at the top and bottom with a platinum band or ring. The cylinder should be approximately 30 mm in diameter and 50 mm in height. The stem should be made from a platinum alloy wire such as platinum-iridium, platinum-rhodium, or platinumruthenium, having a diameter of approximately 1.30 mm. It should be flattened and welded the entire length of the gauze. The over-all height of the cathode should be approximately 130 mm. A cathode of these dimensions will have a surface area of 135 $cm^2$ exclusive of the stem.

73.1.2 *Anodes*—Platinum anodes may be of the spiral type when anodic deposits are not being determined, or if the deposits are small (as in the electrolytic determination of lead when it is present in amounts not over 0.2 %). When used in analyses where both cathodic and anodic plates are to be determined, the anodes should be of wire gauze. Spiral anodes should be made from 1.00-mm or larger platinum wire formed into a spiral of seven turns having a height of approximately 50 mm and a diameter of 12 mm, the over-all height being approximately 130 mm. A spiral anode of this description will have a surface area of 9 $cm^2$. Platinum gauze anodes should be made of the same material and of the same general design as platinum gauze cathodes. The anode cylinder should be approximately 12 mm in diameter and 50 mm in height and the over-all height of the anode should be approximately 130 mm. A gauze anode of these dimensions will have a surface area of 54 $cm^2$. Both areas are exclusive of the stem.

## 74. Reagents

74.1 *Ammonium Sulfate-Hydrogen Sulfide Solution*—Dissolve 50 g of ammonium sulfate ($(NH_4)_2SO_4$) in about 800 mL of $H_2SO_4$ (1 + 99), dilute to 1 L with $H_2SO_4$ (1 + 99) and saturate with hydrogen sulfide ($H_2S$).

74.2 *Ferric Chloride Solution* (2 g Fe/L)—Dissolve 10 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in about 800 mL of HCl (1 + 99) and dilute to 1 L with HCl (1 + 99).

74.3 *Sulfamic Acid* ($H(NH_2)SO_3$).

## 75. Procedure

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

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

Transfer it to a 1-L Erlenmeyer flask.

75.2 Add 115 mL of HCl (1 + 2) plus an additional 9 mL of HCl (1 + 2) and 1 mL of $HNO_3$ for each gram of sample. Heat until dissolution is complete, and then boil the solution for 2 min to 3 min. If the solution is clear, proceed as directed in 75.3 and 75.4 through 75.4.14. If the solution contains insoluble matter proceed as directed in 75.3 and 75.5 through 75.20.

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

75.4 For clear solutions proceed as follows.

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

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

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

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

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

75.4.6 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.

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

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

75.4.9 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.

75.4.10 Stir the solution with an automatic stirrer; start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1 A/dm$^2$. Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 A/dm$^2$ to 3 A/dm$^2$ (Note 15). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 15—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm$^2$, and 2 h to 3 h should be allowed for complete deposition.

75.4.11 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 min to 15 min to ensure complete deposition of the copper.

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

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

NOTE 16—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of $HNO_3$ and 5 mL of $H_2SO_4$ 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/dm$^2$ until the copper has been removed from the original electrode. Reverse the polarity and redeposit the copper on the original electrode as directed in 75.4.9 and 75.4.10. Proceed as directed in 75.4.11 and 75.4.12.

75.4.14 Allow the electrode to cool to room temperature undesiccated, and weigh.

NOTE 17—To prepare the electrode for reuse, immerse it in $HNO_3$ (1 + 1) to dissolve the deposit of copper, rinse thoroughly with water and then with acetone or ethanol. Dry in an oven, cool to room temperature, and weigh.

75.5 If the solution contains insoluble matter, add paper pulp, digest 15 min 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 times or 5 times with water. Reserve the filtrate. Proceed as directed in 75.5.1 or 75.5.2 according to preference, bearing in mind that the latter procedure may be the easier to apply when copious amounts of insoluble matter are encountered.

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

75.5.2 Transfer the paper and precipitate to a platinum crucible. Dry the paper and heat at 600 °C until the carbon is

removed. Finally ignite for 30 min at 1100 °C. Cool, add 3 drops of $HNO_3$ and 1 mL to 2 mL of HF, and evaporate to dryness. Add 10 mL of $HNO_3$ (1 + 1) and digest at 90 °C to 100 °C for 5 min. Transfer the contents of the crucible to the original flask, add 10 mL of $HClO_4$, and heat to mild fumes of $HClO_4$.

75.5.3 Cool the solution from 75.5.1 or 75.5.2, add 100 mL of water and digest at or near boiling for about 45 min.

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

75.7 Add 5 mL of $H_2SO_4$ and heat at 85 °C to 95 °C for 30 min. If insoluble matter persists, repeat the steps as directed in 75.5 through 75.7. When dissolution is complete, combine the solution with the filtrate reserved in 75.5.

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

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

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

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

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

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

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

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

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

75.17 Stir the solution with an automatic stirrer, start the electrolysis and increase the voltage until the ammeter indicates a current which is equivalent to about 1 A/dm$^2$. Electrolyze at this current density until the cathode is covered with copper, and then increase the current density to 2.5 A/dm$^2$ to 3 A/dm$^2$ (Note 18). Continue the electrolysis until the absence of color in the solution indicates that most of the copper has been deposited.

NOTE 18—If the solution is not stirred during electrolysis, the current density should be limited to about 0.5 A/dm$^2$, and 2 h to 3 h should be allowed for complete deposition.

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

75.19 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.

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

NOTE 19—If the deposit appears dark, showing evidence of copper oxide, reassemble the electrodes in a fresh electrolyte consisting of 3 mL of $HNO_3$ and 5 mL of $H_2SO_4$ 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/dm$^2$ until the copper has been removed from the original electrode. Reverse the polarity and redeposit the copper on the original electrode as directed in 75.16 and 75.17. Proceed as directed in 75.18 and 75.19.

## 76. Calculation

76.1 Calculate the percentage of copper as follows:

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

**TABLE 6 Statistical Information—Copper**

| Test Specimen | Copper Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 1, E350 | 0.020 | 0.005 | 0.006 |
| 2. Tool steel 18W-4Cr-1V (NIST 50c, 0.079 Cu) | 0.079 | 0.003 | 0.006 |
| 3. No. 2, E351 | 1.49 | 0.02 | 0.03 |

where:

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

### 77. Precision

77.1 Six laboratories cooperated in testing this method and obtained eight sets of data summarized in Table 6 for specimen 2. Although samples covered by this method with copper composition at the lower and upper limits of the scope were not available for testing, the precision data obtained using the methods indicated should apply.

## TOTAL CARBON BY THE COMBUSTION GRAVIMETRIC METHOD

(This method, which consisted of Sections 78 through 88 of this standard, was discontinued in 2012.)

## COPPER BY THE NEOCUPROINE SPECTROPHOTOMETRIC METHOD

### 89. Scope

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

### 90. Summary of Method

90.1 Copper is separated as cuprous copper from other metals by extraction of the copper-neocuproine complex with chloroform. Spectrophotometric measurement is made at approximately 455 nm.

### 91. Concentration Range

91.1 The recommended concentration range is from 0.01 mg to 0.30 mg of copper per 50 mL of solution, using a 1-cm cell.

NOTE 20—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.

### 92. Stability of Color

92.1 The color develops within 5 min and the extracted complex is stable for at least 1 week; however, because of the volatile nature of the solvent, it is advisable to take spectrophotometric readings promptly.

### 93. Interferences

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

### 94. Reagents

94.1 *Chloroform* ($CHCl_3$).

94.2 *Citric Acid Solution* (300 g/L)—Dissolve 300 g of citric acid in water and dilute to 1 L. The addition of 1 g of benzoic acid per litre will prevent bacterial growth.

94.3 *Copper, Standard Solution* (1 mL = 0.01 mg Cu)—Transfer 0.4000 g of copper (purity: 99.9 % minimum) to a 250-mL Erlenmeyer flask, and dissolve in 20 mL of $HNO_3$ (1 + 1). Add 10 mL of $HClO_4$ and evaporate to $HClO_4$ fumes to expel $HNO_3$. Cool, add 100 mL of water, transfer to a 1-L volumetric flask, dilute to volume, and mix. Using a pipet, transfer 25 mL to a 1-L volumetric flask, dilute to volume, and mix. Do not use a solution that has stood more than one week.

94.4 *2,9-Dimethyl-1,10-Phenanthroline (Neocuproine) Solution* (1 g/L)—Dissolve 0.1 g of neocuproine in 100 mL of absolute ethanol.

NOTE 21—In addition to absolute ethanol, 95 % ethanol or denatured No. 30 or 3A alcohol have been found suitable for preparing this solution.

94.5 *Hydroxylamine Hydrochloride Solution* (100 g/ L)—Dissolve 5.0 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 50 mL of water. Prepare fresh as needed.

94.6 *Water*—Use deionized water or water distilled in all-glass or all-quartz apparatus.

### 95. Preparation of Calibration Curve

95.1 *Calibration Solutions*—Using pipets, transfer 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 30 mL of copper solution (1 mL = 0.01 mg Cu) to 150-mL beakers, and dilute to 50 mL. Proceed in accordance with 120.3.

95.2 *Reagent Blank Solution*—Transfer 50 mL of water to a 150-mL beaker. Proceed in accordance with 95.3.

95.3 *Color Development:*

95.3.1 Add 5 mL of $NH_2OH{\cdot}HCl$ solution and 10 mL of citric acid solution. Stir for 30 s. Using a pH meter (Note 22), adjust the pH to 5.0 ± 1.0 with $NH_4OH$ (1 + 1). Add 10 mL of neocuproine solution.

NOTE 22—Test paper may be used, except for highly colored solutions, by affixing it to the inner wall of the beaker, and rinsing it with water before removing it.

95.3.2 Transfer the solution to a 125-mL conical separatory funnel, rinsing the beaker with 10 mL to 15 mL of water. Add 15 mL of $CHCl_3$ and shake for 30 s. Allow the phases to separate. Place a small roll of filter paper which has been washed with $CHCl_3$, in the stem of a small funnel. Drain the $CHCl_3$ layer through the funnel into a 50-mL volumetric flask containing 6 mL to 7 mL of ethanol. Add 10 mL of $CHCl_3$ to the separatory funnel, extract as before, and drain the $CHCl_3$ layer through the funnel into the 50-mL volumetric flask. Repeat the extraction just described. Wash the paper and the funnel with 4 mL to 5 mL of ethanol, and collect the washings in the volumetric flask. Dilute to volume with ethanol, and mix.

95.4 *Reference Solution*—$CHCl_3$.

95.5 *Spectrophotometry:*

95.5.1 *Multiple-Cell Spectrophotometer*—Measure the reagent blank (which includes the cell correction) using absorption cells with a 1-cm light path and a light band centered at approximately 455 nm. Using the test cell, take the spectrophotometric readings of the calibration solutions.

95.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution 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 455 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions.

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

## 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 $HNO_3$, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample (Note 23). Heat as required to hasten dissolution. Add $HNO_3$ to provide an excess of 3 mL to 4 mL, a sufficient amount of HF to volatilize the silica, and 15 mL of $HClO_4$.

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

96.1.3 Heat to fumes, and continue fuming until chromium, if present, is oxidized and the white $HClO_4$ vapors are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming the solution until the volume has been reduced to about 10 mL. Cool, add 7 mL of water, and digest if necessary to dissolve the salts. Cool to room temperature, add 1 mL of HCl, and transfer the solution (Note 24) to a volumetric flask that provides for the dilution in accordance with 96.1.1. Dilute to volume and mix.

NOTE 24—If silver is present in the alloy it must be removed by filtration at this point.

96.1.4 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 the aliquot. Using a pipet, transfer a portion as specified in 96.1.1 to a 150-mL beaker, and dilute to 50 mL. Proceed as directed in 96.4.

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

96.3 *Reference Solution*—$CHCl_3$.

96.4 *Color Development*—Proceed in accordance with 95.3.

96.5 *Spectrophotometry*—Take the spectrophotometric reading of the test solution in accordance with 95.5.

**TABLE 7 Statistical Information—Copper**

| Test Specimen | Copper Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 1, E354 | 0.006 | 0.001 | 0.004 |
| 2. No. 2, E354 | 0.014 | 0.002 | 0.006 |
| 3. No. 3, E350 | 0.021 | 0.004 | 0.010 |
| 4. No. 3, E354 | 0.033 | 0.005 | 0.004 |
| 5. Tool steel 18W-4Cr-1V (NIST 50c, 0.079 Cu) | 0.078 | 0.005 | 0.010 |
| 6. Tool steel 5Mo-6W-4Cr-2V (NIST 132a, 0.120 Cu) | 0.118 | 0.007 | 0.016 |
| 7. No. 8, E353 | 0.221 | 0.013 | 0.022 |
| 8. No. 9, E353 | 0.361 | 0.015 | 0.036 |
| 9. No. 5, E351 | 1.51 | 0.04 | 0.05 |

## 97. Calculation

97.1 Convert the net spectrophotometric readings of the test solution and of the reagent blank solution to milligrams of copper by means of the calibration curve. Calculate the percent of copper as follows:

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

where:

$A$ = copper found in 50 mL of the final test solution, mg,
$B$ = copper found in 50 mL of the final reagent blank solution, mg, and
$C$ = sample represented in 50 mL of the final test solution, g.

## 98. Precision

98.1 Ten laboratories cooperated in testing this method and obtained the data summarized in Table 7. Although samples covered by this method with copper compositions near the lower and upper limits of the scope were not available for testing, the precision data obtained for the other specimens by the methods indicated should apply.

# LEAD BY THE ION-EXCHANGE—ATOMIC ABSORPTION METHOD

## 99. Scope

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

## 100. Summary of Method

100.1 A HCl solution of the sample is passed through an ion-exchange column to separate the lead from most of the other elements, including iron. After elution of lead, the solution is aspirated into an air-acetylene flame. Spectral energy at 217.0 nm from a lead hollow-cathode tube is passed through the flame, and the absorbance is measured. The spectrometer is calibrated with solutions of known concentrations of lead.

## 101. Concentration Range

101.1 The recommended concentration range is from 0.002 mg to 0.030 mg of lead per millilitre of solution.

## 102. Interferences

102.1 All interfering elements normally present are removed by the ion-exchange separation.

## 103. Apparatus

103.1 *Atomic Absorption Spectrometer,* capable of resolving the 217.0 nm line, equipped with a neon-filled hollow-cathode tube whose radiant energy is modulated, with a detector system tuned to the same frequency, and with a premix air-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (0.030 mg/mL) produces an absorbance of 0.300 or higher, and a calibration curve whose deviation from linearity is within the limits in accordance with 105.3.

103.2 *Ion-Exchange Column,* approximately 25 mm in diameter and 300 mm in length, tapered at one end, and provided with a stopcock or other means to stop the flow. The Jones reductor may be adapted to this test method and has the dimensional requirements shown in Fig. 1. It consists of a column 19 mm in diameter and 250 mm in length, of 20-mesh to 30-mesh amalgamated zinc. To amalgamate the zinc, shake 800 g of zinc (as free of iron as possible) with 400 mL of $HgCl_2$ solution (25 g/L) in a 1-L flask for 2 min. Wash several times with $H_2SO_4$ (2 + 98), and then thoroughly with water. The reductor, when idle, should always be kept filled with distilled water to above the top of the zinc.

## 104. Reagents

104.1 *Ion-Exchange Resin:*

104.1.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a nominal cross-linkage of 8 % and 100-nominal to 200-nominal mesh size.[9]

104.1.2 Transfer a supply of the resin (Note 25) to a beaker, cover with water, and allow at least 30 min for the beads to undergo maximum swelling. Place a No. 60 (250-µm) screen, 150 mm in diameter, over a 2-L beaker. Prepare a thin slurry of the resin and pour a portion of it onto the screen. Wash the fine beads through the screen using a small stream of water. Continue adding small portions of the resin to the screen and washing with a small stream of water until all of the resin has been screened. Discard the large resin beads retained on the screen periodically, if necessary to avoid undue clogging of the openings.

NOTE 25—One pound of resin (45 % moisture) provides enough material for approximately 5 ion-exchange columns.

104.1.3 Allow the bulk of the collected resin to settle for 4 min to 6 min and then decant the excess water. Add 1 L of water, stir vigorously, allow the resin to settle for 4 min to 6 min, decant 900 mL to 950 mL of the suspension, and discard. Repeat the treatment twice more, and reserve the coarser resin for the column preparation.

104.1.4 Prepare the column (Note 26) 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 sufficient 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 solution is added. Add 150 mL of HCl to the column, and when the solution level is 10 mm to 20 mm above the resin bed, add a minimum of 50 mL of HCl (1 + 11) to the column. Drain to 10 mm to 20 mm above the top of the resin bed and close the stopcock.

NOTE 26—If necessary, prepare at least 4 columns, as this number or more of test solutions can be conveniently processed simultaneously through the ion-exchange separation.

104.2 *Lead, Standard Solution* (1 mL = 0.1 mg Pb)—Transfer 0.2500 g of lead (purity: 99.9 % minimum) to a 250-mL borosilicate glass volumetric flask. Add 10 mL of $HNO_3$ (1 + 1) and heat gently. When dissolution is complete, cool to room temperature, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 200-mL volumetric flask, dilute to volume, and mix.

## 105. Preparation of Calibration Curve

105.1 *Calibration Solutions*—Using pipets, transfer 2 mL, 5 mL, 10 mL, 15 mL, 20 mL, 25 mL, and 30 mL of lead solution (1 mL = 0.1 mg Pb) to 100-mL volumetric flasks, add 2 mL $HNO_3$, dilute to volume, and mix. Do not use solutions that have stood more than two weeks.

NOTE 27—Prepare the test solution (106.1) and the reagent blank solution (106.2), and have them ready to aspirate immediately after aspirating the calibration solutions.

105.2 *Spectrometry:*

105.2.1 With the lead hollow-cathode tube in position, energized, and stabilized, locate the wavelength setting that gives maximum response to radiant energy at 217.0 nm.

105.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the lead solution with the highest concentration from the series prepared in accordance with 105.1, and adjust the height of the burner, the air and fuel pressures and flow rates, the aspiration rate of the solution, and the position of the capillary to obtain maximum response. Adjust the slit setting and the gain to obtain optimum signal-to-noise ratio.

NOTE 28—Recalibration is required whenever these parameters are changed.

105.2.3 Aspirate the lead solution used in 105.2.2 a sufficient number of times to establish that the absorbance reading is not drifting. Record six readings, and calculate the standard deviation, $s$, of the readings as follows:

$$s = (A - B) \times 0.40 \quad (11)$$

where:

$A$ = highest of the six values found, and
$B$ = lowest of the six values found.[10]

105.2.4 Beginning with the calibration solution containing the lowest concentration of lead, aspirate each calibration

[9] Dowex 1, manufactured by The Dow Chemical Co., Midland, MI, has been found satisfactory for this purpose.

[10] The value 0.40, which is used to estimate the standard deviation from the range of six values, is derived from Dixon, W. J., and Massey, F. J., *Introduction to Statistical Analysis*, McGraw-Hill, New York, NY, 1957, p. 404, Table 8b (1).

solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of the six values recorded in 105.2.3 by more than twice the standard deviation, *s*, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposits in the burner or clogged capillary), correct it; and repeat 105.2.1-105.2.4.

105.2.5 Proceed immediately as directed in 106.3.

105.3 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \qquad (12)$$

where:

$C$ = absorbance value for 0.03 mg Pb/mL,
$D$ = absorbance value for 0.025 mg Pb/mL, and
$E$ = absorbance value for 0.005 mg Pb/mL.

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

## 106. Procedure

106.1 *Test Solution:*

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

| Lead, % | Sample Weight, g | Tolerance in Sample Weight, mg | Dilution (after separation), mL |
|---|---|---|---|
| 0.0004 to 0.006 | 5.00 | 5 | 10 |
| 0.005 to 0.015 | 5.00 | 5 | 25 |
| 0.010 to 0.030 | 5.00 | 5 | 50 |
| 0.025 to 0.060 | 5.00 | 5 | 100 |
| 0.050 to 0.12 | 2.50 | 2 | 100 |
| 0.10 to 0.24 | 2.50 | 2 | 200 |
| 0.20 to 0.50 | 2.50 | 2 | 500 |

Transfer the sample to a 600-mL beaker.

106.1.2 Add 40 mL of HCl and 10 mL of $HNO_3$, or other ratios and concentrations of these acids as required for the decomposition of certain grades of alloys. Add bromine and HCl to decompose alloys that require this treatment. Heat as required until action ceases. If $HNO_3$ was not used for sample decomposition, add a sufficient amount to oxidize the iron, and evaporate the solution to dryness. Add 40 mL of HCl (1 + 1) and digest until soluble salts are dissolved.

106.1.3 Dilute to 50 mL and filter through a medium paper into a 250-mL Erlenmeyer flask. Wash the paper and residue alternately 3 times or 4 times with 3 mL to 5 mL portions of hot HCl (1 + 9) and hot water. Evaporate the filtrate to a volume between 15 mL and 20 mL. Cool, pour the solution into a 25-mL graduated cylinder without rinsing, and note the volume. Return the solution to the flask and rinse the cylinder with a volume of water equivalent to 5 times the noted volume. Add the rinsings to the solution in the flask.

106.1.4 Place a beaker under the ion-exchange column and open the stopcock. Transfer portions of the sample solution to the column. When the solution has been transferred and has drained to a level 10 mm to 20 mm above the resin bed, rinse the flask with 8 mL to 10 mL of HCl (1 + 11). Add these rinsings to the column in such a manner as to wash the upper part of the column at the same time. Allow the solution to reach a level of 10 mm to 20 mm above the resin bed and then repeat the rinsing of the flask and upper part of the column twice more. Add 80 mL more of HCl (1 + 11) to the column. Allow the solution to reach a level of 10 mm to 20 mm above the resin bed, close the stopcock, and discard the eluate.

106.1.5 Open the stopcock, add 75 mL of concentrated HCl to the column, and collect the eluate in a 150-mL beaker. When the solution level has reached 10 mm to 20 mm above the resin bed, close the stopcock and place a 250-mL beaker under the column. Open the stopcock, mix the solution in the 150-mL beaker, and add it to the column (Note 29). When the solution level is 10 mm to 20 mm above the top of the resin bed, rinse the 150-mL beaker 2 times or 3 times with 5-mL portions of HCl and add the rinsings to the column. Continue to add HCl to the column until 150 mL of eluate has been collected. Reserve the 250-mL beaker.

NOTE 29—This is required in order to remove the residual iron present after the first pass through the column.

106.1.6 Precondition the column for the next test solution as follows: Drain the remaining solution in the column to 10 mm to 20 mm above the resin bed, pass 100 mL of water, 200 mL of $HNO_3$ (1 + 9), 100 mL of water, 150 mL of HCl, and a minimum of 50 mL of HCl (1 + 11) through the column. Drain to 10 mm to 20 mm above the top of the resin bed and close the stopcock.

106.1.7 Cover the 250-mL beaker reserved in 106.1.5 with a ribbed cover glass and evaporate the solution to dryness. Dissolve the residue with 0.5 mL of $HNO_3$ and 5 mL of water. Digest 2 min to 3 min, cool, and transfer to a volumetric flask, selecting the size in accordance with the dilution specified in 106.1.1 (Note 30). Cool, dilute to volume, and mix.

NOTE 30—Use a 10-mL volumetric flask for the reagent blank.

106.2 *Reagent Blank*—Carry a reagent blank through the entire procedure, using the same amounts of all reagents but with the sample omitted; take the reagents from the same lots as used to prepare the test solution.

106.3 *Spectrometry*—Aspirate the test solution and the reagent blank solution, and record the absorbance values. Measure the absorbance of the calibration solution with the highest concentration of lead. If the value differs from the average of the six values recorded in 105.2.3 by more than twice the standard deviation, *s*, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause, correct it, repeat the calibration procedure, and recheck the readings of the test solution (or solutions).

NOTE 31—A group comprised of as many as four test solutions, together with the reagent blank solution, may be aspirated before applying this test for drift.

## 107. Calculation

107.1 Convert the absorbance of the test solution and of the reagent blank to milligrams of lead per millilitre of final solution by means of the calibration curve. Calculate the percent of lead as follows:

$$\text{Lead},\% = [((A \times B) - (C \times 10))/(D \times 10)] \qquad (13)$$

**TABLE 8 Statistical Information—Lead**

| Test Specimen | Lead Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 1, E353 | 0.0004 | 0.0002 | 0.0003 |
| 2. No. 2, E353 | 0.0010 | 0.0001 | 0.0005 |
| 3. No. 3, E353 | 0.0029 | 0.0004 | 0.0004 |
| 4. No. 4, E353 | 0.0063 | 0.0009 | 0.0010 |
| 5. No. 5, E353 | 0.0126 | 0.0012 | 0.0028 |
| 6. No. 6, E353 | 0.106 | 0.023 | 0.031 |
| 7. No. 7, E350 | 0.217 | 0.010 | 0.049 |

where:

$A$ = lead per millilitre of the final test solution, mg,
$B$ = final test solution, mL,
$C$ = lead per millilitre of the final reagent blank solution, mg, and
$D$ = sample used, g.

### 108. Precision

108.1 Although samples covered by this method were not available for testing, the precision data obtained for other types of alloys, using the methods indicated in Table 8, should apply.

## SULFUR BY THE CHROMATOGRAPHIC GRAVIMETRIC METHOD

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

## CHROMIUM BY THE PEROXYDISULFATE-OXIDATION TITRIMETRIC METHOD

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

## TOTAL CARBON BY THE COMBUSTION-THERMAL CONDUCTIVITY METHOD

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

## PHOSPHORUS BY THE ALKALIMETRIC METHOD

### 136. Scope

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

### 137. Summary of Method

137.1 Phosphorus is separated as ammonium phosphomolybdate. The precipitate is dissolved in standard NaOH solution, and the excess sodium hydroxide is titrated with standard $HNO_3$.

### 138. Interferences

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

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

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

### 139. Apparatus

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

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

### 140. Reagents

140.1 *Ammonium Molybdate Solution (Acidic):*

140.1.1 *Solution No. 1*—Transfer 100 g of molybdic acid (85 % $MoO_3$) to a 600-mL beaker containing 240 mL of water and mix thoroughly. Add 140 mL of $NH_4OH$ while stirring vigorously. When dissolution is complete, filter through a medium paper, add 60 mL of $HNO_3$, and cool.

140.1.2 *Solution No. 2*—Add 400 mL of $HNO_3$ to 960 mL of water in a 2-L beaker and cool.

140.1.3 Add Solution No. 1 to Solution No. 2 while stirring constantly. Add 0.1 g of ammonium phosphate, dibasic ($(NH_4)_2HPO_4$), and let stand at least 24 h before using. Use only the clear supernatant liquid. Filter just prior to use.

140.2 *Ferrous Sulfate Solution* (100 g/L)—Dissolve 100 g of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in 1 L of $H_2SO_4$ (5 + 95).

140.3 *Nitric Acid, Standard Solution* (1 mL = approximately 0.00013 g P)—Transfer 6.3 mL of $HNO_3$ to a 1-L volumetric flask containing 500 mL of water. Dilute to volume, and mix. Standardize the solution as follows: Using a pipet, transfer 20 mL of NaOH standard solution (1 mL = approximately 0.00013 g P), described in 140.7, to a 125-mL Erlenmeyer flask. Add 3 drops of phenolphthalein indicator solution and titrate with the $HNO_3$ until 1 drop causes the pink color to disappear. Calculate the phosphorus equivalent as follows:

$$\text{Phosphorus equivalent, g P/mL} = (A \times B)/C \qquad (14)$$

where:

$A$ = NaOH solution, mL,
$B$ = phosphorus equivalent of the NaOH solution, and

$C$ = $HNO_3$ solution, mL.

140.4 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %).

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

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

140.7 *Sodium Hydroxide, Standard Solution* (1 mL = approximately 0.00013 g P)—Transfer 4.0 g of sodium hydroxide (NaOH) to a 1-L volumetric flask, and dissolve in freshly boiled water that has been cooled to room temperature. Dilute to volume with the boiled water and mix. Standardize the solution as follows: Transfer to a 300-mL Erlenmeyer flask 0.5000 g of the NIST standard sample of potassium acid phthalate ($KHC_8H_4O_4$) previously dried for 2 h at 105 °C. Add 100 mL of freshly boiled water that has been cooled to room temperature and 3 drops of phenolphthalein indicator solution. Swirl to dissolve the salt. Titrate with the NaOH solution until one drop produces a pink color. Calculate the phosphorus equivalent as follows:

$$\text{Phosphorus equivalent, g P/mL} = (A \times 0.001347)/(B \times 0.2042) \quad (15)$$

where:

$A$ = potassium acid phthalate, g, and
$B$ = NaOH solution, mL.

## 141. Procedure

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

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

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

141.4 Evaporate the solution to 100 mL, and cool to room temperature. While swirling the flask, slowly add 20 mL of $NH_4OH$, so that no precipitate forms (Note 32). Adjust the temperature to 45 °C.

NOTE 32—The quantity of $NH_4OH$ specified should result in a pH of 0.1 to 0.6 after the addition of the $NH_4OH$ and a pH of 0.2 after the addition of ammonium molybdate solution to the flask. Care must be exercised in the dissolution step to prevent excessive loss of acid. An excessive amount of $NH_4OH$ will precipitate iron as ferric hydroxide. Failure to carefully control the acidity will retard the precipitation of the ammonium phosphomolybdate.

141.5 Add 40 mL of ammonium molybdate solution, stopper the flask, and shake 10 min on a mechanical shaker. If the vanadium composition is less than 0.1 %, allow the precipitate to settle at least 20 min at room temperature; for samples containing higher compositions of vanadium, cool the solution to 10 °C to 20 °C, add 5 mL of ferrous sulfate solution and, 2 drops to 3 drops of $H_2SO_3$, and allow the precipitate to settle at least 20 min at 10 °C to 20 °C.

141.6 Filter the solution with the aid of suction using a Hirsch porcelain crucible (139.1) or a glass funnel fitted with a perforated porcelain filtering disk (139.2). Rinse the flask 3 times to 5 times with a total volume of approximately 40 mL of $KNO_3$ solution, transferring all the precipitate to the filter. Wash the filter paper 12 times to 15 times with a total volume of approximately 100 mL of $KNO_3$ solution (Note 33). Discard the filtrate.

NOTE 33—Analysts not having experience with this method should familiarize themselves with the proper washing technique. Blanks obtained by the method as written should not be measurable provided the reagents are of the quality specified in Recommended Practices E50.

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

141.8 Remove and rinse the stopper. Dilute the solution to 150 mL with freshly boiled water that has been cooled to room temperature and add 3 drops of phenolphthalein indicator solution. Using a 25-mL buret, titrate the excess NaOH with the standard $HNO_3$ solution until 1 drop causes the disappearance of the pink color. Record the buret reading.

## 142. Calculation

142.1 Calculate the percentage of phosphorus as follows:

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

where:

$A$ = NaOH solution, mL, used for the sample (141.7),
$B$ = phosphorus equivalent of the NaOH solution,
$C$ = $HNO_3$ solution, mL, required by the sample (141.8),
$D$ = phosphorus equivalent of the $HNO_3$ solution,
$E$ = NaOH solution, mL, used for the blank,
$F$ = $HNO_3$ solution required by the blank, mL, and
$G$ = sample used, g.

**TABLE 9 Statistical Information—Phosphorus**

| Test Specimen | Phosphorus Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 1, E353 | 0.017 | 0.001 | 0.006 |
| 2. No. 2, E353 | 0.017 | 0.004 | 0.007 |
| 3. No. 3, E353 | 0.024 | 0.003 | 0.011 |
| 4. No. 4, E353 | 0.024 | 0.003 | 0.009 |
| 5. No. 5, E353 | 0.125 | 0.008 | 0.018 |
| 6. No. 6, E353 | 0.151 | 0.015 | 0.015 |

### 143. Precision[11]

143.1 Nine laboratories cooperated in testing this method and obtained the data summarized in Table 9. Although samples of this E designation were not tested, the precision data obtained for E353 type of alloys using the method indicated in Table 9 should apply.

## NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD

### 144. Scope

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

### 145. Summary of Method

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

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

### 146. Interferences

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

### 147. Apparatus

147.1 *Anion-Exchange Column,* approximately 25 mm in diameter and 300 mm 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. The Jones Reductor, Fig. 1 may be adapted to this method. A reservoir for the eluants may be added at the top of the column.

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

147.3 *pH Meter.*

### 148. Reagents

148.1 *Ammonium Citrate Solution* (200 g/L)—Dissolve 200 g of diammonium hydrogen citrate [$(NH_4)_2HC_6H_5O_7$] in 600 mL of water. Filter and dilute to 1 L.

148.2 *Anion Exchange Resin:*

148.2.1 Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a crosslinkage of 8 % and a 200-nominal to 400-nominal mesh size.[12] To remove those beads greater than 180 µm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a No. 80 (180-µm) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 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.

148.2.2 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 100 mL of HCl (3 + 1) through the column, with the hydrostatic head 100 mm above the top of the resin bed, adjust the flow rate, by means of the upper stopcock, to not more than 3.0 mL/min. Drain to 5 mm to 10 mm above the top of the resin bed and then close the lower stopcock.

148.3 *Dimethylglyoxime Solution in Alcohol* (10 g/L)—Dissolve 10 g of dimethylglyoxime in ethanol, methanol, or No. 30 specially denatured alcohol and dilute to 1 L with alcohol. Filter before using. This solution keeps almost indefinitely.

### 149. Procedure

149.1 *Double Precipitation:*

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

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

Transfer it to a 600-mL beaker.

149.1.2 Add 60 mL of HCl (1 + 1) and 10 mL of $HNO_3$. Heat to dissolve the sample and boil to expel oxides of nitrogen. Cool the solution and add 30 mL of $HClO_4$. Heat to strong fumes of $HClO_4$ and continue fuming for 5 min. Cool, and dilute to 100 mL with water.

149.1.3 Filter the solution through an 11-cm coarse paper into a 600-mL beaker. Transfer any insoluble matter to the

[11] Supporting data are available from ASTM International Headquarters. Request RR:E03-1002.

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

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

149.1.4 Add 200 mL of water and 20 mL of ammonium citrate solution. Using a pH meter adjust the pH to at least 7.5 with $NH_4OH$. Acidify the solution with HCl to pH 3 ± 0.1.

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

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

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

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

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

149.2 *Anion-Exchange Separation:*

149.2.1 Proceed as directed in 149.1.1.

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

149.2.3 Filter the solution obtained in 149.2.2 through an 11-cm coarse paper, collecting the filtrate in a 250-mL beaker. Transfer any insoluble matter to the paper with hot HCl (5 + 95). Wash the paper alternately with hot water and hot HCl (5 + 95) until iron salts are removed. Finally, wash the paper 3 times with 5-mL portions of hot water. Discard the residue.

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

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

**TABLE 10 Statistical Information—Nickel**

| Test Specimen | Nickel Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. Tool Steel 5 Mo-6W-4Cr-2V (NIST 132a, 0.137 Ni) | 0.135 | 0.012 | 0.015 |
| 2. Ni-Mo steel 2 Ni-0.3 Mo (NIST 111b, 1.81 Ni) | 1.81 | 0.09 | 0.08 |
| 3. Ni-Mo steel 4 Ni-0.3 Mo (NIST 33d, 3.58 Ni) | 3.58 | 0.11 | 0.07 |
| 4. No. 3 E354 | 4.22 | 0.06 | 0.05 |

149.2.6 Place a clean 600-mL beaker under the ion-exchange column and open the bottom stopcock. Transfer the solution from 149.2.4 to the column. Allow the sample solution to drain to 5 mm to 10 mm from the top of the resin bed. Rinse the 250-mL beaker with a 5-mL portion of HCl (3 + 1) and transfer the rinsing to the column. When it has drained to 5 mm to 10 mm above the resin bed, add a second 5-mL rinse portion from the 250-mL beaker. Repeat this operation 3 more times and allow the level to drop to 5 mm to 10 mm above the resin bed before adding the next. Add sufficient HCl (3 + 1) at the top of the column to collect a total of 200 mL in the 600-mL beaker. Close the lower stopcock and reserve the solution.

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

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

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

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

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

149.6 With the aid of suction, filter using a weighed (Note 34) fritted glass crucible. Wash the beaker and precipitate 6 times with cold water.

NOTE 34—Heat the crucible at 150 °C, and cool in a desiccator before weighing.

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

## 150. Calculation

150.1 Calculate the percentage of nickel as follows:

$$\text{Nickel},\% = [((A - B) \times 0.2032)/C] \times 100 \quad (17)$$

where:

$A$ = weight of crucible and precipitate, g,
$B$ = weight of crucible, g, and
$C$ = sample taken, g.

## 151. Precision

151.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 10. Although a

sample covered by this method near the higher end of the scope was not tested, the data obtained for other types of alloys using the methods indicated in Table 10 should apply.

## TIN BY THE SOLVENT EXTRACTION—ATOMIC ABSORPTION METHOD

### 152. Scope

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

### 153. Summary of Method

153.1 Tin is extracted from a dilute HCl solution of the sample, containing ascorbic acid and potassium iodide, into a solution of trioctylphosphine oxide (TOPO) in methyl isobutyl ketone (MIBK). The MIBK extract is aspirated into the nitrous oxide-acetylene flame. Spectral energy at 286.3 nm from a tin hollow-cathode lamp or tin electrodeless discharge lamp is passed through the flame and the absorbance is measured.

### 154. Concentration Range

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

### 155. Interferences

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

### 156. Apparatus

156.1 *Atomic Absorption Spectrometer,* capable of resolving the 286.3 nm line, equipped with a tin hollow-cathode lamp or tin electrodeless discharge lamp whose radiant energy is modulated, with a detector system tuned to the same frequency and a premix nitrous oxide-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (40 µg/mL) produces an absorbance of 0.15 or higher, and a calibration curve whose deviation from linearity is within the limits specified in 158.4.

### 157. Reagents

157.1 *Ascorbic Acid.*

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

157.3 *Methyl Isobutyl Ketone* (MIBK).

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

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

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

### 158. Preparation of Calibration Curve

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

NOTE 35—Volumetric flasks with ground glass stoppers must be used.

158.2 *Extraction:*

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

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

NOTE 36—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

158.3 *Spectrometry:*

158.3.1 With a tin hollow-cathode lamp or electrodeless discharge lamp in position, energized and stabilized, adjust the wavelength setting to the location that gives the maximum detector response in the immediate vicinity of 286.3 nm.

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

NOTE 37—From this point on, only MIBK solutions should be aspirated until all test and calibration solution measurements have been completed. If the burner slot shows any sign of blockage, shut off the flame according to the instrument manufacturer's approved procedures, clean the slot, and relight as in 158.3.2.

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

NOTE 38—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 39—Due to the small amount of extract available for making this test, the number of readings and the time between readings must be kept to a minimum.

158.3.4 Beginning with the calibration solution to which no tin was added, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration (40 µg Sn/mL) differs from the average values obtained in 158.3.3 by more than 0.03 multiplied by the

average of the values, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposit in the burner or clogged capillary), correct it, and repeat the procedure in 158.3.1-158.3.4.

158.3.5 Proceed immediately as directed in 159.3.

158.4 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (A - B)/C \quad (18)$$

where:

$A$ = absorbance value for 40 µg Sn/mL,
$B$ = absorbance value for 30 µg Sn/mL, and
$C$ = absorbance value for 10 µg Sn/mL.

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

## 159. Procedure

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

159.2 *Test Solution:*

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

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

Transfer it to a 250-mL polytetrafluorethylene beaker.

159.2.2 Add 50 mL of HCl (1 + 1) and 5 drops of HF. Cover the beaker with a polytetrafluorethylene cover and heat at a low temperature (approximately 90 °C) until dissolution is complete.

NOTE 40—If silicon is above 0.5 %, use 10 drops to 12 drops of HF.

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

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

NOTE 41—If tungsten composition is high, a yellow precipitate of $WO_3$ may form. Extract such samples as directed with minimal delay.

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

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

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

159.3 *Spectrometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 38) and record the absorbance values. Take three readings on each solution (Note 39). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drift as in 159.3.4 and 159.3.5.

## 160. Calculation

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

$$\text{Tin, \%} = [(D - E)/F \times 1000] \quad (19)$$

where:

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

## 161. Precision and Bias[13]

161.1 *Precision*—Eleven laboratories cooperated in testing this method and obtained the precision data listed as No. 3 and 5 in Table 11. This method differs only slightly from the method for tin, Test Methods E350, in that the amounts of reagents used to dissolve the sample have been increased. The fact that the precision data obtained for No. 3 and 5 correspond closely with that obtained for No. 2 and 4, Test Methods E350, suggests that the precision of the two methods is the same.

161.2 *Bias*—Table 11 lists the test results obtained for two high-speed tool steel standards and their certified values. The accuracy of this method may be judged by comparing the arithmetic average obtained for this test with the certified values.

**TABLE 11 Statistical Information—Tin**

| Test Specimen | Tin Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 1, E350 | 0.0034 | 0.0006 | 0.0007 |
| 2. No. 3, E350 | 0.011 | 0.001 | 0.002 |
| 3. Tool steel 18W-4Cr-1V (NIST 50c) 0.018 Sn | 0.017 | 0.001 | 0.003 |
| 4. No. 4, E350 | 0.031 | 0.003 | 0.004 |
| 5. Tool steel 18W-4Cr-1V (NIST 50a) 0.025 Sn | 0.025 | 0.004 | 0.006 |
| 6. No. 6, E350 | 0.097 | 0.011 | 0.011 |

# MOLYBDENUM BY THE SPECTROPHOTOMETRIC METHOD

## 162. Scope

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

[13] Supporting data are available from ASTM International Headquarters. Request RR:E03-1022.

## 163. Summary of Method

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

## 164. Concentration Range

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

NOTE 42—This method has been written for cells having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

## 165. Stability of Color

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

## 166. Interferences

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

## 167. Reagents

167.1 *Butyl Acetate.*

NOTE 43—Operations with this chemical should be carried out away from heat and open flame and are best done in a well ventilated hood. Avoid prolonged breathing of vapor.

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

167.3 *Iron*[14]—Purity: 99.8 % minimum, molybdenum 0.001 % maximum.

167.4 *Iron Solution A* (1 mL = 70 mg Fe)—Dissolve 25 g of ferric sulfate ($Fe2(SO_4)3{\cdot}H_2O$) in 75 mL of hot water. Cool and add 10 mL of $H_2SO_4$. Cool, and dilute to 100 mL.

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

167.6 *Molybdenum, Standard Solution A* (1 mL = 0.2 mg Mo)—Transfer 0.2000 g of molybdenum metal (purity: 99.8 % min) to a 150-mL beaker and dissolve in 10 mL of HCl and $HNO_3$ added dropwise. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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

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

167.9 *Sodium Thiocyanate Solution* (100 g/L)—Dissolve 100 g of sodium thiocyanate (NaSCN) in about 500 mL of water, filter, and dilute to 1 L. Store in a dark bottle.

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

NOTE 44—This solution is used for color development in 168.3, 169.3, 170.3, and 171.3. When an absorption cell is used sequentially for a number of spectrophotometric measurements, a white film of an insoluble tin compound may adhere to the inside of the cell and must be removed before further measurements are made.

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

168.1 *Calibration Solutions:*

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

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

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

168.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 168.1.2, 168.1.3, and 168.3.

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

NOTE 45—This funnel should be cleaned thoroughly after each filtration to avoid development of a pink color that would contaminate the filtrate.

168.4 *Reference Solution*—Butyl acetate.

168.5 *Spectrophotometry:*

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

168.5.2 *Single Cell Spectrophotometer*—Transfer a suitable portion of the reference solution 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 475 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank.

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

[14] Johnson-Matthey JMC 847 sponge iron has been found suitable for this purpose.

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

169.1 *Calibration Solutions:*

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

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

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

169.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 169.1.2, 169.1.3, and 169.3.

169.3 *Color Development*—Using a pipet, transfer 50 mL to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of $SnCl_2$ solution, and 50 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of $H_2SO_4$ (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 45.)

169.4 *Reference Solution*—Butyl acetate.

169.5 *Spectrophotometry:*

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

169.5.2 *Single Cell Spectrophotometer*—Transfer a suitable portion of the reference solution 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 475 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank.

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

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

170.1 *Calibration Solutions:*

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

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

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

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

170.3 *Color Development*—Using a pipet, transfer 25 mL of iron solution B and 25 mL of the calibration solution to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of $SnCl_2$ solution, and 100 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of $H_2SO_4$ (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 45.)

170.4 *Reference Solution*—Butyl acetate.

170.5 *Spectrophotometry:*

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

170.5.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution 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 475 nm. While maintaining this adjustment, take the spectrophotometric readings of the calibration solutions and the reagent blank.

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

## 171. Procedure

171.1 *Test Solution:*

171.1.1 Transfer a 0.3-g sample, weighed to the nearest milligram, to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving acid. Add HCl, or $HNO_3$, or combinations of the two with or without several drops of HF, and heat until dissolution is complete.

171.1.2 Increase the temperature and heat to $HClO_4$ fumes. Continue fuming until chromium, if present, is oxidized and the white $HClO_4$ fumes are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl, allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been volatilized. Continue fuming the solution until the volume has been reduced to about 15 mL. Cool, add 50 mL of water and 70 mL of $H_2SO_4$ (1 + 1), heat to boiling, and cool in a water bath. If the solution is not clear, filter the solution through an 11-cm fine filter paper, collecting the filtrate in a volumetric flask that provides for dilution in accordance with the guide given in 171.1.3. Wash the paper

with five 5-mL portions of $H_2SO_4$ (1 + 99) collecting these in the same volumetric flask. Proceed as directed in 171.3. If the solution is clear, proceed to 171.1.3.

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

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

Proceed as directed in 171.3.

171.2 *Reagent Blank Solution*—Transfer 0.3 g of iron to a 250-mL Erlenmeyer flask. Add 30 mL of dissolving solution and heat until dissolution is complete. Proceed as directed in 171.1.2, 171.1.3, and 171.3, using the same dilution and aliquots used for the test solution.

171.3 *Color Development*—Using a pipet, transfer the appropriate aliquot to a 250-mL separatory funnel containing the appropriate amount of iron solution for the specified aliquot. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of $SnCl_2$ solution, and, measured with a pipet, the amount of butyl acetate specified in the aliquot guide. Stopper the separatory funnel and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of $H_2SO_4$ (1 + 6), 5 mL of NaSCN solution, and 5 mL of $SnCl_2$ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, drain off, and discard the aqueous phase. Drain enough of the solvent layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 45.)

171.4 *Reference Solution*—Butyl acetate.

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

## 172. Calculation

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

$$\text{Molybdenum, \%} = \frac{A}{B \times 10} \quad (20)$$

**TABLE 12 Statistical Information—Molybdenum**

| Test Specimen | Molybdenum Found, % | Repeatability $R_1$, E173 | Reproducibility $R_2$, E173 |
|---|---|---|---|
| 1. Cr-W steel (NIST 155, 0.039 Mo) | 0.037 | 0.002 | 0.006 |
| 2. No. 3, E350 | 0.163 | 0.012 | 0.03 |
| 3. Tool steel T-15 4Cr-13W-5V-5Co (0.45 Mo not certified) | 0.442 | 0.027 | 0.055 |
| 4. No. 4, E350 | 0.51 | 0.02 | 0.06 |
| 5. Tool steel H-12 1W-5Cr (1.5 Mo not certified) | 1.47 | 0.053 | 0.058 |

where:

$A$ = molybdenum, mg, found in 25 mL, 50 mL, or 100 mL, as appropriate of butyl acetate, and the aliquot volume used, and

$B$ = sample, in g, represented in 25 mL, 50 mL, or 100 mL, as appropriate, of butyl acetate and the aliquot used (see aliquot guide 171.1.3).

## 173. Precision and Bias[15]

173.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 12. This method is identical with molybdenum in accordance with Test Methods E350, E351, and E353. The fact that the precision for different materials is comparable suggests that the precision of these methods is the same.

173.2 *Bias*—The accuracy of a method can be judged by comparing the certified value of a standard with the arithmetic average of the test data. The specified values for No. 3 and 5 (Table 12), while not certified, were obtained by other methods and are believed to be reliable.

# CHROMIUM BY ATOMIC ABSORPTION METHOD

## 174. Scope

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

## 175. Summary of Method

175.1 The sample is dissolved in mineral acids and the residue fused, dissolved, and solution combined. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 357.9 nm from a chromium hollow-cathode lamp is passed through the flame and the absorbance is measured. The spectrometer is calibrated with solutions of known chromium concentrations.

## 176. Concentration Range

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

## 177. Interferences

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

## 178. Apparatus

178.1 *Atomic Absorption Spectrometer,* capable of resolving the 357.9 nm line, equipped with a chromium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it meets the limits defined in 180.4. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this method.

[15] Supporting data are available from ASTM International Headquarters. Request RR:E03-1023.

## 179. Reagents

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

179.2 *Iron,*[16] Low Chromium—Cr < 0.0001 %.

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

## 180. Preparation of Calibration Curves

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

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

180.3 *Spectrometry:*

180.3.1 With the chromium hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 357.9 nm line. The wavelength setting in the vicinity of 428.9 nm may be used provided that the instrument meets the performance requirements.

180.3.2 Light the burner, allow it to thermally equilibrate, and adjust the instrument to zero while aspirating water. Aspirate the chromium solution with the highest concentration from the series prepared as directed in 180.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is required.

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

$$s = (A - B) \times 0.40 \quad (21)$$

where:

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

180.3.4 Using water as a reference, and beginning with the solution to which no addition of chromium was made in 180.1 and 180.2, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of 6 values calculated in 180.3.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the 6 values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, correct it, and repeat the steps in 180.3.1-180.3.4.

180.3.5 Proceed immediately as directed in Section 181.

180.4 *Calibration for Compositions from 0.005 % to 0.10 %*—Follow the instrument manufacturer's instructions for generating the calibration curve. Calculate the deviation from linearity of the curve as follows:

$$\text{Deviation from linearity} = (C - D)/E \quad (22)$$

where:

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

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

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

## 181. Procedure

181.1 *Test Solution:*

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

| Chromium, % | Sample Weight, g | Tolerance in Sample Weight, mg | Dilution after Dissolution, mL | Aliquot Required, mL | HCl to be added to Aliquot, mL | Final Dilution, mL |
|---|---|---|---|---|---|---|
| 0.005–0.10 | 1 | 0.10 | 100 | 0 | 0 | 100 |
| 0.010–1.00 | 1 | 0.10 | 100 | 10 | 9 | 100 |

Transfer it to a 250-mL borosilicate beaker.

181.1.2 Add 20 mL HCl, 10 mL $HNO_3$, and 5 drops of HF. Heat to dissolve. Remove from the hot plate and dilute to approximately 50 mL. Add a small amount of filter pulp and filter the solution through 11-cm fine filter paper into a 250-mL borosilicate beaker. Wash the paper 5 times with HCl (1 + 99), and reserve the filtrate.

181.1.3 Transfer the paper and contents to a platinum crucible. Dry on a hot plate, and transfer to a muffle furnace

[16] Johnson-Matthey sponge iron or Spex iron has been found suitable for this purpose.

that is less than 400 °C. Gradually heat to 600 °C and hold at this temperature for 1 h. Cool, add 0.5 g of $K_2CO_3$, and carefully fuse over a free flame until a clear melt is obtained (see Note 46). Cool and add 15 mL of water. Add HCl dropwise until reaction ceases. Add 5 drops of HCl in excess and warm on a hot plate, if necessary to obtain a clear solution.

NOTE 46—Fusion of the residue is made in order to include in the sample solution any chromium that might exist in the sample in an acid insoluble form.

181.1.4 Transfer this solution to the filtrate from 181.1.2 and evaporate just to dryness. Add 10 mL HCl and warm to dissolve salts. Transfer quantitatively to a 100-mL volumetric flask, dilute to volume, and mix. For samples with expected chromium compositions less than 0.10 % proceed as directed in 181.3. For samples with expected chromium composition greater than 0.10 %, transfer by pipet 10 mL to a 100-mL volumetric flask, add 9 mL of HCl, dilute to volume, and mix.

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

181.3 *Spectrometry*—Using water as a reference solution, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of 4 or fewer test solutions and reagent blank solutions has been aspirated, apply the test using the standard solution as directed in 180.3.4, depending on the concentration range. If the value differs from the average of the 6 values by more than twice the standard deviation, *s*, found in 180.3.3, or more than 0.01 multiplied by the average of 6 values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration and aspiration of test solutions.

## 182. Calculation

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

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (23)$$

where:

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

**TABLE 13 Statistical Information—Chromium**

| Test Specimen | Chromium Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 3, E350 | 0.149 | 0.028 | 0.025 |
| 2. No. 4, E350 | 0.693 | 0.019 | 0.024 |
| 3. No. 5, E350 | 0.961 | 0.036 | 0.093 |

## 183. Precision and Bias[17]

183.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the precision data summarized in Table 13.

183.2 *Bias*—The accuracy can be inferred from the data in Table 13 by comparing the certified values for chromium with the average value obtained by using this method.

# CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

## 184. Scope

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

## 185. Summary of Method

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

NOTE 47—In the dichromate titration, the vanadium is not oxidized along with the excess ferrous ions and, therefore, the volume of dichromate added reflects the total of vanadium and chromium and the calculated value for percent Cr is high. In the permanganate titration, the $V^{IV}$ is oxidized to $V^{V}$, thereby compensating for the reduction of vanadium by ferrous sulfate in a previous step.

## 186. Interferences

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

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

$$(2.6A + 0.05B + 0.01C)\ D \quad (24)$$

where:

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

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

## 187. Apparatus

187.1 *Apparatus for Potentiometric Titrations*—pH meter with a saturated calomel reference and platinum indicator electrode.

[17] Supporting data are available from ASTM International Headquarters. Request RR:E03-1030.

## 188. Reagents

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

188.2 *Ferrous Ammonium Sulfate, Standard Solution (0.05 N and 0.10 N)*—Dissolve 20 g and 40 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) in 500 mL of cold $H_2SO_4$ (5 + 95) and dilute to 1 L with $H_2SO_4$ (5 + 95). Standardize the solution as directed in 189.1, 189.2, or 189.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

188.3 *Potassium Dichromate, Standard Solution (0.05 N and 0.10 N)*—Dissolve 2.4518 g and 4.9036 g of NIST 136c standard potassium dichromate ($K_2Cr_2O_7$) or equivalent primary standard grade in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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

188.5 *Potassium Permanganate, Standard Solution (0.05 N and 0.10 N):*

188.5.1 *Preparation*—Dissolve 1.6 g and 3.2 g of potassium permanganate ($KMnO_4$) in 1 L of water. Let stand in the dark for 2 weeks. Filter, without washing, through a Gooch crucible or a fine porosity fritted-glass crucible. Avoid contact with rubber or other organic material. Store in a dark-colored glass-stoppered bottle.

188.5.2 *Standardization*—Dry a portion of the NIST 40h or equivalent primary standard grade sample of sodium oxalate at 105 °C. Transfer 0.1500 g of the sodium oxalate to a 600-mL beaker. Add 250 mL of $H_2SO_4$ (5 + 95), previously boiled for 10 min to 15 min and then cooled to 27 °C ± 3 °C, and stir until the oxalate has dissolved. Add 39 mL to 40 mL of the $KMnO_4$ solution, at a rate of 25 mL/min to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s). Heat to 55 °C to 60 °C and complete the titration by adding $KMnO_4$ solution until a faint pink color persists for 30 s. Add the last 0.5 mL to 1 mL dropwise, allowing each drop to become decolorized before adding the next drop. To determine the blank: Titrate 250 mL of $H_2SO_4$ (5 + 95), treated as above, with $KMnO_4$ solution to a faint pink color. The blank correction is usually equivalent to 0.03 mL × 0.05 mL.

188.6 *Silver Nitrate Solution* (8 g/L)—Dissolve 8 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

188.7 *Sodium Diphenylamine Sulfonate Indicator Solution* (2.0 g/L):

188.7.1 *Preparation from Barium Diphenylamine Sulfonate*—Dissolve 0.32 g of barium diphenylamine sulfonate in 100 mL of hot water. Add 0.5 g of sodium sulfate ($Na_2SO_4$), stir, and filter through a fine paper to remove the $BaSO_4$. Store in a dark-colored bottle.

188.7.2 *Preparation from Sodium Diphenylamine Sulfonate*—Dissolve 0.20 g of sodium diphenylamine sulfonate in 100 mL of water. Store in a dark-colored bottle.

188.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 M)—Dissolve 1.485 g of 1,10-phenanthroline monohydrate in 100 mL of ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$).

## 189. Standardization of Ferrous Ammonium Sulfate Solution

189.1 *Against Potassium Permanganate Solution:*

189.1.1 Transfer 180 mL of water, 12 mL of $H_2SO_4$ (1 + 1), and 5 mL of $H_3PO_4$ into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 *N* or 0.10 *N* $Fe(NH_4)_2(SO_4)_2$ (188.2) with either 0.05 *N* or 0.10 *N* $KMnO_4$ solution (188.5) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 1 drop to 2 drops of 1,10 phenanthroline indicator solution. Using a 25-mL buret, titrate the ferrous ions with 0.05 *N* $KMnO_4$ standard solution (188.5) while swirling the flask. As the end point is approached, add $KMnO_4$ dropwise. Continue until the pink color changes to clear green and persists for at least 60 s.

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

$$\text{Normality} = AB/C \tag{25}$$

where:

$A$ = normality of $KMnO_4$ solution (188.5),
$B$ = $KMnO_4$ solution, mL, and
$C$ = $Fe(NH_4)_2(SO_4)_2$ solution, mL.

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

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

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

$$\text{Normality} = \left(0.05 \text{ or } 0.10\ (A - B)\right)/C \tag{26}$$

where:

$A$ = 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution, mL, used in the first titration,
$B$ = mL equivalent to the indicator blank, and
$C$ = $Fe(NH_4)_2(SO_4)_2$ solution, mL, used in the first titration.

189.3 *Against Potassium Dichromate Using Potentiometric End Point:*

189.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution into a 600-mL beaker. Reserve the remaining 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution in the buret for

the back-titration. Add 150 mL of water, 10 mL of $H_2SO_4$ (1 + 1), and 5 mL of $H_3PO_4$. Insert the saturated calomel reference electrode and the platinum indicator electrode into the beaker and connect them to the potentiometer apparatus. While stirring the solution, add $Fe(NH_4)_2(SO_4)_2$ until the dichromate ion yellow color disappears and then a slight excess. Record the volume of the $Fe(NH_4)_2(SO_4)_2$ solution to the nearest 0.01 mL. Back-titrate with the remaining 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution by adding the solution in 0.1-mL increments as the end point is approached. Record the voltage when equilibrium is reached after each 0.1-mL increment. Inspect the data for the maximum voltage change per 0.1-mL increment. Determine the voltage change for the 0.1-mL increments before and after this maximum change. Determine the two differences between the three voltage readings corresponding to the volume (0.1-mL) increment before the maximum, the maximum, and after the maximum. This is a very close approximation of the second derivative of the volume versus change in voltage curve corresponding to the maximum inflection if this curve were plotted. Sum the two voltage differences. Determine the ratio of the first of these two differences to the sum and multiply 0.1 mL by this ratio to obtain the volume to be added to the smaller volume between the two incremental additions that the maximum change in voltage occurred. See the following example:

| Volume of 0.05 *N* $K_2Cr_2O_7$ Back Titrant (mL) | Voltage (mV) | Δ Voltage (mV) | Difference Before and After Maximum |
|---|---|---|---|
| 20.80 | 555 | | |
| 20.90 | 570 | 50 | 50 |
| 21.00 | 620 | 100 | 20 |
| 21.10 | 720 | 80 | |
| 21.20 | 800 | | |
| 21.30 | 835 | | |
| 21.40 | 854 | | |

Maximum voltage change occurred between 21.00 mL and 21.10 mL of $K_2Cr_2O_7$ solution. The changes in voltage were 50 mV before the maximum, 100 mV at the maximum, and 80 mV after the maximum. The two differences between the maximum corresponding to before and after the maximum were 50 mV and 20 mV, respectively. Their sum equals 70 and the ratio of the first to the sum equals 50/70. Thus 50/70 times 0.1 mL must be *added* to smaller volume between the two increments where the maximum change in voltage occurred. The end point is 21.07 mL.

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

$$\text{Normality} = 0.05 \text{ or } 0.10\, A/B \quad (27)$$

where:

$A$ = 0.05 *N* or 0.10 *N* $K_2Cr_2O_7$ solution, mL, and
$B$ = $Fe(NH_4)_2(SO_4)_2$ solution, mL.

## 190. Procedure

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

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

[A] Use 50 mL burets for this composition range instead of the 25 mL burets specified in the procedure.

Transfer it to a 600-mL beaker.

190.2 Add 80 mL of $H_2SO_4$ (1 + 5) and 5 mL of $H_3PO_4$. Cover the beaker with a ribbed cover glass and heat at 85 °C to 100 °C until the sample is decomposed. Add sufficient $HNO_3$ in small increments to oxidize iron. Boil 2 min to expel oxides of nitrogen.

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

190.4 Transfer the paper and residue to a platinum crucible, char the paper, and ignite at 850 °C to 900 °C for 15 min. Cool, add sufficient $H_2SO_4$ (1 + 1) to moisten the residue, and then 3 mL to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until $H_2SO_4$ is removed. Fuse the residue with a minimum amount of either fused sodium hydrogen sulfate (sodium pyrosulfate–$Na_2S_2O_7$) or potassium pyrosulfate ($K_2S_2O_7$). Cool the crucible, place in a 250-mL beaker, and dissolve the melt in 20 mL of $H_2SO_4$ (1 + 10). Remove the crucible, rinse with water, transfer the solution to the reserved filtrate (190.3), and dilute to 200 mL.

190.5 Add 5 mL of $AgNO_3$ solution and 20 mL of $(NH_4)_2S_2O_8$ solution. If a beaker is used, cover it with a ribbed cover glass. Boil the solution 8 min to 10 min maintaining the volume at 200 mL by additions of hot water. If the color due to permanganate ions does not develop, or develops but does not persist, add 2 drops of $KMnO_4$ solution (188.4), 5 mL more of $AgNO_3$ solution, and 20 mL more of $(NH_4)_2S_2O_8$ solution, and boil an additional 8 min to 10 min. Add hot water to maintain the volume at 200 mL during this operation and the operations that follow in 190.6.

190.6 Reduce the permanganate ions as follows: Add 5 mL of HCl (1 + 3) and continue boiling for 10 min after the disappearance of permanganate color. If the permanganate ions

have not been completely reduced or if $MnO_2$ is present, add 2 mL of HCl (1 + 3) and boil again for 10 min. Repeat the addition of HCl and boiling until all manganese is present as colorless manganous ions. Cool to room temperature and dilute to 200 mL. If vanadium is present or its absence has not been confirmed, proceed as directed in 190.7. If vanadium is absent and the criteria of 186.2 are met, proceed as directed in 190.8. If vanadium is absent and the criteria of 186.2 are not met, or if potentiometric titration is preferred and vanadium is absent, proceed as directed in 190.9.

190.7 *Titration With Potassium Permanganate*—While swirling the flask, add 1 drop to 2 drops of 1,10 phenanthroline indicator solution and then add sufficient $Fe(NH_4)_2(SO_4)_2$ solution to effect a change in color from clear green to pink. Add 1 mL to 2 mL more and record the buret reading to the nearest 0.01 mL. Using a 25-mL buret, back-titrate the excess ferrous ions with 0.05 *N* $KMnO_4$ standard solution. Add $KMnO_4$ dropwise as the end point is approached. Continue the titration until the pink color has changed to clear green which persists for 60 s. Record the buret reading to the nearest 0.01 mL.

190.8 *Titration with Potassium Dichromate to the Diphenylamine Sulfonate End Point*—While swirling the flask, add $Fe(NH_4)_2(SO_4)_2$ solution from a 25-mL buret until the disappearance of the yellow color. Then add 1 mL to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using another 25-mL buret back-titrate the excess ferrous ions with 0.05 *N* $K_2Cr_2O_7$ standard solution. Add the $K_2Cr_2O_7$ solution dropwise as the end point is approached. Continue the titration until a blue color appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL.

190.9 *Titration with Potassium Dichromate and Potentiometric End Point Detection*—Stir the sample solution in the 600-mL beaker with a magnetic stirrer and insert the saturated calomel reference and platinum indicator electrodes. With the electrodes connected to the potentiometer apparatus, add from a 25-mL buret the $Fe(NH_4)_2(SO_4)_2$ solution, while stirring, until the yellow color disappears. Add 1 mL to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Using another 25-mL buret add 0.05 *N* $K_2Cr_2O_7$ standard solution in 0.1-mL increments recording the voltage after equilibrium is reached for each increment. Inspect the data for the maximum voltage change between increments of the standard dichromate solution (see 189.3). Determine the voltage change for the increments before and after the maximum change and interpolate the end point to the nearest 0.01 mL as described in 189.3.

**TABLE 14 Statistical Information—Chromium**

| Test Specimen | Chromium Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| 1. No. 2, E350 | 0.481 | 0.015 | 0.053 |
| 2. No. 2, E351 | 1.96 | 0.10 | 0.16 |
| 3. Tool Steel 8Mo, 2W, 3Cr (NIST 134a 3.67Cr) | 3.68 | 0.16 | 0.48 |
| 4. No. 5, E353 | 12.87 | 0.26 | 0.28 |

## 191. Calculation

191.1 If $KMnO_4$ was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (28)$$

where:

$A$ = $Fe(NH_4)_2(SO_4)_2$ solution, mL,
$B$ = normality of $Fe(NH_4)_2(SO_4)_2$ solution,
$C$ = $KMnO_4$ solution used, mL,
$D$ = normality of the $KMnO_4$ solution, and
$E$ = sample taken, in g.

191.2 If $K_2Cr_2O_7$ was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (29)$$

where:

$A$ = $Fe(NH_4)_2(SO_4)_2$ solution mL,
$B$ = normality of $Fe(NH_4)_2(SO_4)_2$ solution,
$C$ = $K_2Cr_2O_7$ solution, mL,
$D$ = normality of $K_2Cr_2O_7$ solution, and
$E$ = sample taken, in g.

## 192. Precision and Bias[18]

192.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 14. Although only one sample was tested in the midrange of the scope, the precision data for other types of alloys using the methods indicated in Table 14 should apply.

192.2 *Bias*—No information on the accuracy of this method is known. The accuracy of this method may be judged, however, by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing (see Table 14).

# VANADIUM BY THE ATOMIC ABSORPTION METHOD

## 193. Scope

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

## 194. Summary of Method

194.1 The sample is dissolved in HCl, $HNO_3$, and $HClO_4$. An aluminum solution is added as a spectrochemical buffer. The sample solution is aspirated into a nitrous oxide-acetylene flame of an atomic absorption spectrometer. Spectral energy at approximately 318.4 nm from a vanadium hollow cathode lamp is passed through the flame, and the absorbance is measured. This absorbance is compared with the absorbance of a series of standard calibration solutions.

## 195. Concentration Range

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

[18] Supporting data are available from ASTM International Headquarters. Request RR:E03-1036.

## 196. Interferences

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

## 197. Apparatus

197.1 *Atomic Absorption Spectrometer,* capable of resolving the 318.4 nm line, equipped with a vanadium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it is suitable for use as described in Guide E1024.

## 198. Reagents

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

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

NOTE 48—As an alternative to vanadium metal, ammonium metavanadate may be used to prepare the standard vanadium solution. It is prepared as follows: Dry several grams of ammonium metavanadate ($NH_4VO_3$), minimum purity 99.9 %, in an air oven at 105 °C to 110 °C for at least 1 h and cool to room temperature in a desiccator. Weigh 0.4592 g of the dried product into a 600-mL beaker, add 400 mL of hot water, and gently simmer to dissolve. Cool, transfer to a 1000-mL volumetric flask, dilute to volume, and mix (1 mL = 0.20 mg V).

## 199. Preparation of Calibration Curve

199.1 *Calibration Solutions*—To each of five, 250-mL borosilicate beakers, add 10 mL of $HClO_4$. Using a microburet, transfer 0.0 mL, 1.0 mL, 2.0 mL, 4.5 mL, and 8.0 mL of vanadium standard solution to each beaker, respectively. Cover with a watch glass, heat, and evaporate to fumes. Continue heating until solutions are near dryness (Note 49). Cool, dissolve the salts with 10 mL of HCl and 20 mL of water. Filter through a medium-porosity filter paper into a 100-mL volumetric flask, wash well with warm HCl (2 + 100). Cool, add 10 mL of $AlCl_3$ solution (198.1), dilute to volume, and mix.

NOTE 49—The remaining amount of $HClO_4$ must be at a minimum.

199.2 *Spectrometry:*

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

199.2.2 Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero while aspirating water. Aspirate the vanadium solution with the highest concentration from the series prepared as directed 199.1, and adjust the burner, nitrous oxide, and fuel pressures and flow rates to obtain maximum response. Whenever one or more of these parameters are changed, recalibration is necessary.

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

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

where:

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

199.2.4 Using water as a reference, and beginning with the solution to which no addition of vanadium was made in 199.1, aspirate each calibration solution in turn and record its absorbance. If the value for the solution with the highest concentration differs from the average of six values calculated in 199.2.3 by more than twice the standard deviation, or by more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If a problem is indicated, determine the cause, take appropriate corrective measures, and repeat 199.2.1-199.2.4.

199.2.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Test for linearity as given in Guide E1024.

## 200. Procedure

200.1 *Test Solution:*

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

200.1.2 Add 20 mL of HCl, 4 mL of $HNO_3$, and cover with a cover glass. Heat until dissolution is complete. Add 10 mL of $HClO_4$ and evaporate to fumes. Continue heating until solutions are near dryness (Note 49). Cool, dissolve the salts with 10 mL of HCl and 20 mL of water. Filter through a medium-porosity filter paper into a 100-mL volumetric flask, and wash well with warm HCl (2 + 100). Cool, add 10 mL of $AlCl_3$ solution (198.1), dilute to volume, and mix.

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

200.2 *Spectrometry*—Using water as a reference, aspirate and record the absorbance of the calibration, sample, and reagent blank solutions. After each group of four or fewer samples and reagent blank solutions have been aspirated, apply the test using the standard solution as directed in 199.2.4. If the value differs from the average of the six values by more than twice the standard deviation, *s*, found in 199.2.3, or more than 0.01 multiplied by the average of six values used to calculate *s*, whichever is greater, determine the cause and repeat the calibration, sample, and reagent blank measurements.

**TABLE 15 Statistical Information—Vanadium**

| Test Specimen | Vanadium Found, % | Repeatability ($R_1$, E173) | Reproducibility ($R_2$, E173) |
|---|---|---|---|
| Tool Steel (JSS601-7, 0.033 V) | 0.032 | 0.002 | 0.004 |
| Tool Steel (JSS605-7, 0.160 V) | 0.161 | 0.007 | 0.011 |
| No. 1, E350 | 0.107 | 0.008 | 0.014 |
| No. 1, E351 | 0.008 | 0.002 | 0.003 |
| No. 1, E353 | 0.038 | 0.003 | 0.005 |

### 201. Calculation

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

$$\text{Vanadium, \%} = ((A - B) \times 10)/C \quad (31)$$

where:

$A$ = vanadium, mg, per mL of the final sample solution,
$B$ = vanadium, mg, per mL of the final reagent blank solution, and
$C$ = weight of sample in g.

### 202. Precision and Bias[19]

202.1 *Precision*—Twenty-three laboratories participated in testing this method under the auspices of WG-9 of ISO Committee TC 17/SC 1 and obtained the data summarized in Table 15. All testing meets the requirements of Practice E173.

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

## MOLYBDENUM BY THE ION EXCHANGE—8-HYDROXYQUINOLINE GRAVIMETRIC METHOD

### 203. Scope

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

### 204. Summary of Method

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

### 205. Interferences

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

### 206. Apparatus

206.1 *Ion Exchange Column, Polystyrene,* approximately 400 mm in length and 25 mm in inside diameter, the bottom tapered to a 2-mm bore outlet, fitted with a hosecock or stopcock to control the liquid flow. All parts of the apparatus must be constructed of HF-resistant plastic, such as polytetrafluoroethylene, polyethylene, or polyvinyl chloride (Note 50).

NOTE 50—The ion exchange column system must be carefully assembled and checked to avoid possible leakage of solutions containing HF.

### 207. Reagents

207.1 *Ammonium Chloride Solution* (240 g/L)—Dissolve 240 g of ammonium chloride ($NH_4Cl$) in 800 mL of water. Warm to room temperature, dilute to 1 L and mix.

207.2 *Ammonium Fluoride* ($NH_4F$).

207.3 *Ammonium Oxalate* ($NH_4OCOCOONH_4 \cdot H_2O$).

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

207.5 *Eluent Solutions*—See Note 51.

NOTE 51—**Warning:** HF causes serious burns which may not be immediately painful; read the paragraph about HF in the Hazards section of Practices E50).

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

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

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

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

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

207.6 *8-Hydroxyquinoline Solution* (30 g/L)—Dissolve 30 g of 8-hydroxyquinoline in 120 mL of glacial acetic acid ($CH_3COOH$). Cautiously add water, with stirring to a total solution volume of 600 mL. Warm to 40 °C. Add $NH_4OH$ (1 + 1) dropwise with stirring until a slight permanent precipitate is formed. Carefully add glacial $CH_3COOH$ with stirring until the precipitate first dissolves. Dilute to 1 L.

207.7 *Ion-Exchange Resin:*

207.7.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and of 200-nominal to 400-nominal U.S. mesh size.[20] To remove those beads greater than about 180 µm in diameter, as well as the very small diameter

[19] Supporting data are available from ASTM International Headquarters. Request RR:E03-1040.

[20] AG 1-X8 (catalog number 140-1451), 200 mesh to 400 mesh, chloride form, which is available from Bio-Rad Laboratories, Hercules, CA, 94547, has been found satisfactory (www.bio-rad.com).

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

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

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

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

## 208. Procedure

208.1 Transfer 1 g of sample weighed to the nearest 0.1 mg to a 20-mL polytetrafluoroethylene beaker marked at the 100 mL level on the outside. Add 10 mL of HF and cover with a polytetrafluoroethylene watchglass. Warm the solution with low heat and cautiously add $HNO_3$ in 1-mL increments allowing the reaction to subside between additions. High chromium samples may also require cautious dropwise additions of HCl. When dissolution is complete, cool the beaker, remove the cover with platinum-tipped tongs and cautiously rinse it into the solution with water.

208.2 Over a steam bath or other low temperature arrangement evaporate the solution to dryness. Cool, wash down the sides of the beaker with HCl (1 + 1) and again evaporate to dryness over low heat. Cool, add 5 mL HF and 25 mL water. Warm over low heat until all salts are dissolved (Note 52). Cool to room temperature and dilute to 100 mL with water.

NOTE 52—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

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

208.4 Place an 800-mL plastic beaker under the column. Place a small plastic funnel holding a high-porosity hard-surface filter paper in the top of the column. Ensure that an air seal does not form between the funnel and the column. Cautiously filter the sample solution onto the column. Adjust the effluent flow to about 2 mL/min. Rinse the beaker with HF/HCl/water (4 + 1 + 95) transferring the washings to the paper. Cautiously police the beaker with a polytetrafluoroethylene policeman, if necessary, and rinse onto the paper with HF/HCl/water (4 + 1 + 95). Wash the paper well with HF/HCl/water (4 + 1 + 95). Cautiously, remove and discard paper (Note 53).

NOTE 53—If insoluble molybdenum compounds are suspected or known to be present, halt the flow from the column when the washing of the paper is complete. Cautiously transfer the paper to a platinum crucible and ignite at 500 °C (no higher) in a muffle furnace. Cool in a desiccator, add 1 g anhydrous sodium carbonate powder ($Na_2CO_3$) and fuse over a burner. Cool, add 20 mL of water and heat to dissolve the melt. Carefully acidify with dropwise additions of HCl (1 + 4) until effervescence ceases plus 10 drops excess. Evaporate to dryness, cool, add 20 mL HF/HCl/water (4 + 1 + 95), heat to dissolve, cool, and transfer this solution to the column. Resume the 2 mL/min flow from the column.

208.5 Continue to add HF/HCl/water (4 + 1 + 95) until 650 mL have been collected in the 800-mL plastic beaker (Note 54). Drain solution to the top of the resin bed. Cautiously discard this solution.

NOTE 54—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper, and manganese.

208.6 Place an 800-mL plastic beaker under the column and elute 500 mL of HF/HCl/water (1 + 5 + 4) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 55).

NOTE 55—This solution contains all the tungsten, titanium, zirconium, and hafnium.

208.7 Place an 800-mL polytetrafluoroethylene beaker under the column and elute the molybdenum with 500 mL of HF/HCl/water (20 + 25 + 55) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Proceed with this eluent solution as described in paragraph 208.11.

208.8 Place an 800-mL plastic beaker under the column and elute 300 mL of HF/$NH_4Cl$/water (4 + 60 + 36) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 56).

NOTE 56—This solution contains all the niobium.

208.9 Place an 800-mL plastic beaker under the column and elute 350 mL of $NH_4F/NH_4Cl$ solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 57).

NOTE 57—This solution contains all the tantalum.

208.10 Place an 800-mL plastic beaker under the column and elute 100 mL of water, then 100 mL of HCl (1 + 3), stopping the flow when the liquid level is 10 mm to 20 mm above the resin bed. Cautiously discard the solution. The column is now ready to be stored for future use or to be preconditioned for another sample (see 208.3).

208.11 To the eluent containing the molybdenum (from 208.7) cautiously add 15 mL of $H_2SO_4$ (1 + 1) and evaporate to light fumes on a steam bath or other carefully controlled heat source (Note 58). Cool and cautiously rinse into a 400-mL borosilicate glass beaker. Heat to low volume (about 10 mL), cool, add 2 mL of $HNO_3$, and evaporate to strong fumes of $SO_3$.

NOTE 58—**Warning:** Ensure that the applied temperature does not exceed the softening point of polytetrafluoroethylene.

208.12 Cool to room temperature, dilute to about 30 mL with water, add 5 mL of $HNO_3$ and 5 mL of HCl. Cover and heat for 10 min.

208.13 Dilute to 100 mL. Heat to boiling and while hot, cautiously add NaOH solution (100 g/L) until litmus paper moistened with the solution turns blue, then add 10 mL excess. Boil for 1 min. If a precipitate is present, filter through high porosity, surface hardened filter paper and wash paper thoroughly with warm NaOH solution (10 g/L). Discard paper. If no precipitate is present, proceed directly to 208.14.

208.14 Adjust the volume of the solution or filtrate obtained in 208.13 to about 200 mL. Add 10 mL of EDTA solution (10 g/L) and 3 g of ammonium oxalate. Warm gently to obtain a clear solution and cool to room temperature. Adjust the pH to 4.0 using a pH meter and dropwise additions of HCl (1 + 1) and NaOH solution (10 g/L).

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

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

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

## 209. Calculation

209.1 Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, } \% = [(A - B) \times 23.05]/C \quad (32)$$

where:

A = weight of crucible plus precipitate, in g,
B = weight of crucible, in g, and
C = sample weight, in g.

## 210. Precision and Bias

210.1 *Precision*—Seven laboratories cooperated in testing this method and obtained the data summarized in Table 16. While the testing range exceeds the upper limit of the Scope, the data for Test Specimen 4 were included to illustrate the ruggedness of the method's precision at levels near the upper limit of the Scope.

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

## 211. Keywords

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

**TABLE 16 Statistical Information—Molybdenum Ion Exchange–8 Hydroxyquinoline Gravimetric Method**

| Test Material | Molybdenum Found, % | Repeatability ($R_1$, E173)[A] | Reproducibility ($R_2$, E173)[A] |
|---|---|---|---|
| 1. No. 1, E351 | 1.48 | 0.070 | 0.086 |
| 2. No. 2, E354 | 3.92 | 0.219 | 0.250 |
| 3. mod. M34 high speed 8Co-4Cr-2V-2W-1C (NIST 153a, 8.85 Mo) | 8.85 | 0.180 | 0.188 |
| 4. No. 4, E354 | 17.49 | 0.285 | 0.641 |

[A] This test was conducted in accordance with the 1980 version of Practice E173.