



Standard Test Methods for Chemical Analysis of Nickel, Cobalt, and High-Temperature Alloys¹

This standard is issued under the fixed designation E 1473; 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 describe the chemical analysis of nickel, cobalt, and high-temperature alloys having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	0.005 to 7.00
Beryllium	0.001 to 0.05
Boron	0.001 to 1.00
Calcium	0.002 to 0.05
Carbon	0.001 to 1.10
Chromium	0.10 to 33.00
Cobalt	0.10 to 75.00
Copper	0.01 to 35.00
Iron	0.01 to 50.00
Lead	0.001 to 0.01
Magnesium	0.001 to 0.05
Manganese	0.01 to 3.0
Molybdenum	0.01 to 30.0
Niobium (Columbium)	0.01 to 6.0
Nickel	0.10 to 98.0
Nitrogen	0.001 to 0.20
Phosphorus	0.002 to 0.08
Sulfur	0.002 to 0.10
Silicon	0.01 to 5.00
Tantalum	0.005 to 1.00
Tin	0.002 to 0.10
Titanium	0.01 to 5.00
Tungsten	0.01 to 18.00
Vanadium	0.01 to 3.25
Zinc	0.001 to 0.01
Zirconium	0.01 to 2.50

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

	Sections
Aluminum, Total by the 8-Quinolinol Gravimetric Method (0.20 to 7.00 %)²	62 to 69
Chromium by the Atomic Absorption Method (0.018 to 1.00 %)²	100 to 109
Chromium by the Peroxydisulfate Oxidation—Titration Method (0.10 to 33.00 %)²	110 to 118
Cobalt by the Ion-Exchange-Potentiometric Titration Method (2 to 75 %)²	34 to 41
Cobalt by the Nitroso-R-Salt Photometric Method (0.10 to 5.0 %)²	42 to 51
Copper by Neocuproine Photometric Method (0.010 to 10.00 %)²	52 to 61
Iron by the Silver Reduction Titrimetric Method (1.0 to 50.0 %)²	127 to 134

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Material and are the direct responsibility of Subcommittee E01.08 on Ni and Co and High-Temperature Alloys. Current edition approved December 1, 2003. Published January 2004. Originally approved in 1992. Last previous edition approved in 1998 as E 1473 – 94a (1998).

Manganese by the Metaperiodate Photometric Method (0.05 to 2.00 %)²	8 to 17
Molybdenum by the Ion Exchange—8-Hydroxyquinoline Gravimetric Method (1.5 to 30 %)²	119 to 126
Molybdenum by the Photometric Method (0.01 to 1.50 %)²	88 to 99
Nickel by the Dimethylglyoxime Gravimetric Method (0.1 to 84.0 %)²	70 to 77
Niobium by the Ion Exchange—Cupferron Gravimetric Method (0.5 to 6.0 %)	135 to 142
Silicon by the Gravimetric Method (0.05 to 5.00 %)²	27 to 33
Sulfur by the Combustion-Iodate Titration Method (0.006 to 0.1 %)²	18 to 26
Tantalum by the Ion Exchange—Pyrogallol Spectrophotometric Method (0.03 to 1.0%)	143 to 151
Tin by the Solvent Extraction-Atomic Absorption Method (0.002 to 0.10 %)²	78 to 87

1.3 Methods for the determination of several elements not included in these test methods can be found in Test Methods E 30, E 76, and E 1019.

1.4 Some of the concentration ranges given in 1.1 are too broad to be covered by a single method, and therefore, these test methods contain multiple methods for some elements. The user must select the proper test method by matching the information given in the scope and interference sections of each test method with the composition of the alloy to be analyzed.

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

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 7 and in special caution and warning paragraphs throughout these test methods.

2. Referenced Documents

- 2.1 *ASTM Standards:* ³
D 1193 Specification for Reagent Water

² These test methods were extracted from Test Methods E 354 and the references to Test Methods E 350, E 351, E 352, and E 353 contained therein.

³ 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.

- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E 30 Test Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals
- E 59 Practice for Sampling Steel and Iron for Determination of Chemical Composition
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals
- E 76 Test Methods for Chemical Analysis of Nickel-Copper Alloys
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals
- E 350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron
- E 351 Test Methods for Chemical Analysis of Cast Iron—All Types
- E 352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels
- E 353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys
- E 354 Test Methods for Chemical Analysis of High-Temperature, Electrical, Magnetic, and Other Similar Iron, Nickel, and Cobalt Alloys
- E 380 Practice for Use of the International System of Units (SI) (the Modernized Metric System)
- E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory
- E 1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel and in Iron, Nickel, and Cobalt Alloys
- E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry
- E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis

2.2 Other Document:

- ISO 5725 Precision of Test Methods—Determination of Repeatability and Reproducibility for Inter-Laboratory Tests⁴

3. Significance and Use

3.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with compositional specifications, particularly those under the jurisdiction of ASTM Committee B-2 on Nonferrous Metals and Alloys. It is assumed that all who use these test methods will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory under appropriate quality control practices such as those described in Guide E 882.

⁴ Available from American National Standards Institute, 11 West 42nd St., 13th Floor, New York, NY 10036.

4. Apparatus, Reagents, and Instrumental Practice

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

4.2 Reagents:

4.2.1 *Purity of Reagents*—Unless otherwise indicated, all reagents used in these test methods shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.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 Precision and Bias section.

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

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

5. Sampling

5.1 For procedures for sampling the material, reference shall be made to Method E 59.

6. Interlaboratory Studies and Rounding Calculated Values

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

6.2 Round calculated values to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

7. Hazards

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

MANGANESE BY THE METAPERIODATE PHOTOMETRIC METHOD

8. Scope

8.1 This test method covers the determination of manganese in concentrations from 0.05 to 2.00 %.

9. Summary of Test Method

9.1 Manganous ions are oxidized to permanganate ions by treatment with periodate. Tungsten when present at concentrations greater than 0.5 % is kept in solution with phosphoric acid. Solutions of the samples are fumed with perchloric acid so that the effect of periodate is limited to the oxidation of manganese. Photometric measurements are made at 545 nm.

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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

10. Concentration Range

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

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

11. Stability of Color

11.1 The color is stable for at least 24 h.

12. Interferences

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

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

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

13. Reagents

13.1 *Manganese, Standard Solution* (1 mL = 0.032 mg Mn)—Transfer the equivalent of 0.4000 g of assayed, high-purity manganese (purity: 99.99 % minimum), to a 500-mL volumetric flask and dissolve in 20 mL of HNO₃ by heating. Cool, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 500-mL volumetric flask, dilute to volume, and mix.

13.2 *Nitric-Phosphoric Acid Mixture*—Cautiously, while stirring, add 100 mL of HNO₃ and 400 mL of H₃PO₄ to 400 mL of water. Cool, dilute to 1 L, and mix. Prepare fresh as needed.

13.3 *Potassium Metaperiodate Solution* (7.5 g/L)—Dissolve 7.5 g of potassium metaperiodate (KIO₄) in 200 mL of hot HNO₃(1 + 1), add 400 mL of H₃PO₄, cool, dilute to 1 L, and mix.

13.4 *Water, Pretreated with Metaperiodate*—Add 20 mL of KIO₄ solution to 1 L of water, mix, heat at not less than 90°C for 20 to 30 min, and cool. Use this water to dilute solutions to volume that have been treated with KIO₄ solution to oxidize manganese, and thus avoid reduction of permanganate ions by

any reducing agents in the untreated water. **Caution**—Avoid the use of this water for other purposes.

14. Preparation of Calibration Curve

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

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

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

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

14.4 Photometry:

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

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

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

15. Procedure

15.1 *Test Solutions*—Select and weigh a sample in accordance with the following:

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

15.1.1 For Samples Containing Not More Than 0.5 % Tungsten:

15.1.1.1 To dissolve samples that do not require HF, add 8 to 10 mL of HCl (1 + 1), and heat. Add HNO₃ as needed to hasten dissolution, and then add 3 to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of HClO₄; evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, and digest if necessary to dissolve the salts. Cool and transfer the solution to a 100-mL volumetric flask. Proceed to 15.1.3.

15.1.1.2 For samples whose dissolution is hastened by HF, add 8 to 10 mL of HCl (1 + 1), and heat. Add HNO₃ and a few drops of HF as needed to hasten dissolution, and then add 3 to

4 mL of HNO₃. When dissolution is complete, cool, then add 10 mL of HClO₄, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to either a 100 or 500-mL volumetric flask as indicated in 15.1.5. Proceed to 15.1.3.

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

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

15.1.2.2 For samples whose dissolution is hastened by HF: Add 8 to 10 mL of H₃PO₄, 10 mL of HClO₄, 5 to 6 mL of H₂SO₄, 3 to 4 mL of HNO₃, and a few drops of HF. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO₃. Cool, add 50 mL of water, digest, if necessary, to dissolve the salts, cool, and transfer the solution to a 100 or 500-mL volumetric flask as directed in 15.1. Proceed to 15.1.3.

15.1.2.3 Cool the solution, dilute to volume, and mix. Allow insoluble matter to settle, or dry-filter through a coarse paper and discard the first 15 to 20 mL of the filtrate, before taking aliquots.

15.1.3 Using a pipet, transfer 20-mL aliquots to two 50-mL borosilicate glass volumetric flasks; treat one as directed in 15.3 and the other as directed in 15.4.1.

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

15.3 *Color Development*—Proceed as directed in 14.3.

15.4 *Reference Solutions:*

15.4.1 *Background Color Solution*—To one of the sample aliquots in a 50-mL volumetric flask, add 10 mL of nitric-phosphoric acid mixture, and heat the solution at not less than 90°C for 20 to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

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

15.5 *Photometry*—Establish the cell corrections with the reagent blank Reference solution to be used as a reference solution for background color solutions. Take the photometric readings of the background color solutions and the test solutions versus the respective reagent blank reference solutions as directed in 14.4

16. Calculation

16.1 Convert the net photometric reading of the test solution and of the background color solution to milligrams of manganese by means of the calibration curve. Calculate the percent of manganese as follows:

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

where:

- A = manganese found in 50 mL of the final test solution, mg,
- B = apparent manganese found in 50 mL of the final background color solution, mg, and
- C = sample weight represented in 50 mL of the final test solution, g.

17. Precision and Bias

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

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

SULFUR BY THE COMBUSTION-IODATE TITRATION METHOD

18. Scope

18.1 This test method covers the determination of sulfur in concentrations from 0.006 to 0.1 %.

19. Summary of Test Method

19.1 A major part of the sulfur in the sample is converted to sulfur dioxide (SO₂) by combustion in a stream of oxygen. During the combustion, the SO₂ is absorbed in an acidified starch-iodide solution and titrated with potassium iodate solution. The latter is standardized against steels of known sulfur content to compensate for characteristics of a given apparatus and for day-to-day variation in the percentage of sulfur recovered as SO₂. Compensation is made for the blank due to accelerators and boats (or crucibles).

20. Interferences

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

TABLE 1 Statistical Information—Manganese by the Metaperiodate Photometric Method

Test Specimen	Manganese Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. Nickel alloy, 77Ni-20Cr (NIST 169, 0.073 Mn)	0.074	0.002	0.008
2. High-temperature alloy 68Ni-14Cr-7Al-6Mo (NIST 1205, 0.29 Mn)	0.289	0.007	0.026
3. Cobalt alloy 41Co-20Ni-20Cr-4Mo-4W (NIST 168, 1.50 Mn)	1.49	0.03	0.08
4. Stainless steel 18Cr-9Ni (NIST 101e, 1.77 Mn)	1.79	0.07	0.07

21. Apparatus

21.1 Apparatus for Determination of Sulfur by Direct Combustion—The apparatus must be suitable for the combustion of the sample in oxygen to form sulfur dioxide (SO₂) and must provide an absorption vessel in which the SO₂ is titrated. A typical arrangement is shown in Fig. 1.

21.1.1 Oxygen Purifiers—The regular commercial tank oxygen is satisfactory. It must be passed through two pressure reduction valves (approximately 207 kPa (30 psig) and 14 to 28 kPa (2 to 4 psig), respectively) or a suitable two-stage reduction valve to provide an even and adequate flow of oxygen through a tower containing H₂SO₄ and through an absorption tower containing 20 to 30-mesh inert base impregnated with NaOH and anhydrous magnesium perchlorate (Mg(ClO₄)₂). A flowmeter and quick-acting shut-off valve for use during preheating periods must precede the resistance furnace assembly. A flowmeter must also precede the induction furnace assembly.

21.1.2 Combustion Furnace—An electric tube furnace capable of continuous operation at 1425 to 1450 °C is recommended, since this temperature is required for some alloys. The combustion may be accomplished either by resistance or induction heating. With the former, the temperature must be controlled as specified for each type of alloy. With the latter a rheostat to control the power input to the induction coil is required to avoid heating some types of samples too rapidly during the early stages of combustion. The combustion zone of the resistance furnace must be 200 to 250 mm (8 to 10 in.) in length and that of the induction furnace must amply provide for adequate heating of the sample.

21.1.3 Combustion Tube—The combustion tube of the resistance furnace must be of a low-sulfur refractory type that will withstand the maximum operating temperature without becoming porous. The tube must be of a suitable size to fit the particular furnace used and have an inside diameter large enough to accommodate the thimble, boat, and cover. A tapered-end tube is recommended.

21.1.4 Combustion Boats, Crucibles, and Covers—The boats and crucibles for use with the respective types of furnaces must be of adequate thickness to retain the molten

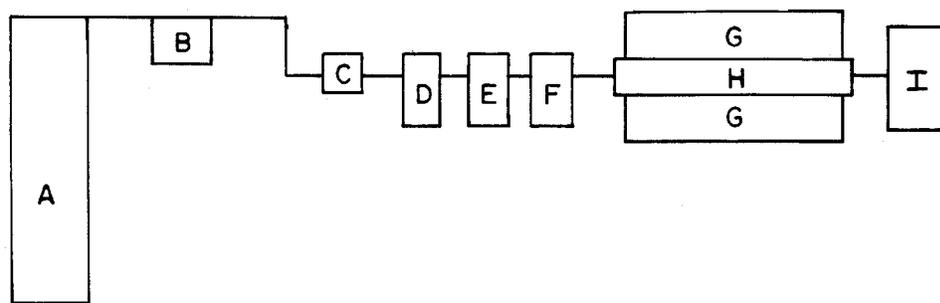
slag and have a blank as low and consistent as possible. The boats for use with resistance furnaces should be 90 to 100 mm (3.5 to 4 in.) in length and may be provided with suitable covers. The crucibles for use with induction furnaces must have adequate capacity and may be provided with suitable covers. The blank requirements that apply to the boats and crucibles also apply to their covers. Prior to use, the boats and covers must be pre-fired at least 15 min at 1100 °C and then stored in a desiccator.

21.1.5 Ceramic Thimble—A porous ceramic thimble or liner with a small orifice drilled in the closed end is placed (closed end first) in the hot zone of the tube of the resistance furnace to prolong the life of the combustion tube by absorbing spattered slag, and to act as a filter to remove metal oxide fumes from the gas stream.

21.1.6 Ceramic Filter—If a ceramic thimble is not available, a porous ceramic filter is placed in the hot zone of the furnace to remove metallic oxide fumes from the gas stream; it can be constructed from porous insulating fire brick capable of withstanding the operating temperatures. In induction furnaces suitable precautions must be taken to prevent metallic oxides from entering the titration vessel.

21.1.7 Connections—A metal breech connector at the entrance of the combustion tube is recommended. If a rubber stopper is used it must be protected by heat-reflecting baffles, preferably of the double-disk type. Connection between the outlet end of the combustion tube and the absorption and titration assembly must be as short and free of bends as possible, with glass connections butted to minimize areas of rubber tubing exposed to gases. All rubber stoppers and tubing must be essentially free of sulfur.

21.1.8 Absorption and Titration Apparatus—The apparatus should consist of an absorption and titration vessel of appropriate volume and containing an inlet bubbler tube for the sulfur gases with a float valve to prevent back flow of liquid when the sample is starting to consume oxygen. The vessel must be shaped to effect complete absorption of SO₂ in a small volume of solution. The buret should be approximately 10 mL in capacity. Automatic titrations which utilize a photoelectric



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| A — Oxygen tank | F — Flowmeter. |
| B — Reduction valve | G — Furnace, induction or resistance-type |
| C — Quick-acting shut-off valve | H — Combustion tube |
| D — Tower containing H ₂ SO ₄ | I — Absorption and titration assembly |
| E — Tower containing CO ₂ absorber and anhydrous Mg(ClO ₄) ₂ | |

FIG. 1 Typical Arrangement for Determination of Sulfur by the Direct-Combustion Method

cell to activate a solution inlet valve are commercially available and may be used.

22. Reagents

22.1 *Copper (Low-Sulfur) Accelerator*—Rectangular strips for combustion boats used with a resistance furnace, or rings for crucibles used with an induction furnace.

22.2 *Iron (Low-Sulfur) Accelerator*—Iron chips or iron powder.

22.3 *Potassium Iodate Standard Solution A* (Approximate sulfur equivalent = 0.1 mg S/mL)—Dissolve 0.2225 g of potassium iodate (KIO_3) in 900 mL of water containing 1 g of sodium hydroxide (NaOH) and dilute to 1 L.

22.4 *Potassium Iodate Standard Solution B*—(Approximate sulfur equivalent = 0.02 mg S/mL). Transfer 200 mL of KIO_3 Standard Solution A (Approximate sulfur equivalent = 0.1 mg S/mL) to a 1-L volumetric flask, dilute to volume, and mix.

NOTE 3—The stated sulfur equivalents are based on complete conversion of sulfur to SO_2 ; this is a phenomenon that seldom, if ever, occurs.

22.5 *Starch-Iodide Solution*—Transfer 9 g of soluble (or arrowroot) starch to a 50-mL beaker, add 5 to 10 mL of water, and stir until a smooth paste is obtained. Pour the mixture slowly into 500 mL of boiling water. Cool, add 15 g of potassium iodide (KI), and stir until the KI is dissolved. Dilute to 1 L.

22.6 *Tin (Low-Sulfur) Accelerator*, granular.

23. Calibration

23.1 Select a minimum of three standards (Note 6), two with sulfur contents near the high and low limits of the range for a given sample weight (24.1.3) and also one near the median. The median standard may be simulated, if necessary, by taking one half the sample weight of each of the other two.

NOTE 4—The accuracy of this test method is dependent to a large extent upon the accuracy of the methods used to certify the sulfur concentration in the calibration standards.

23.2 For sulfur concentrations greater than 0.02 % use KIO_3 Standard Solution A. For sulfur concentrations less than 0.02 % use KIO_3 Standard Solution B.

23.3 Select the standard with the lowest sulfur concentration and make several determinations as directed in 24.1 or 24.2 until the system is stabilized as shown by reproducible titrations.

23.4 Continue with multiple portions of each additional standard, as directed in 24.1 or 24.2, running the standards in ascending order of sulfur concentration.

23.5 Prepare a calibration curve by plotting the percentage of sulfur in each standard against the average of the milliliters of KIO_3 Standard Solution (or apparent percentage of sulfur for “direct-reading” burets). Prepare a separate calibration curve for each sample weight/sulfur range (24.1.3).

23.6 Repeat the calibration: (1) when another KIO_3 Standard Solution or another starch-iodide solution is used, (2) when a different lot of boats (or crucibles) is used, (3) when a different lot of accelerator is used, (4) when a different cylinder of oxygen is used, (5) when the system has not been in use for 1 h, or less than 1 h if the oxygen flow rate has not been maintained during that period, (6) when the system has been in

use continuously for 8 h, (7) when the operating temperature has been changed, and (8) when a change in sample weight as indicated in 24.1.3 is required.

24. Procedure

24.1 *Combustion with Resistance Furnace:*

24.1.1 Adjust the temperature of the furnace to 1400 to 1425°C.

24.1.2 Add 65 to 70 mL of HCl (1+99) and 2 mL of starch-iodide solution to the absorption vessel. Pass oxygen through the system at a constant rate which is the maximum compatible with the particular absorption system used but not less than 1.0 L/min and not more than 1.5 L/min. Add KIO_3 Standard Solution from the buret until the intensity of the blue color is that which is to be taken as the end point of the final titration. Read the buret and record as the initial reading, and refill the buret. Turn off the oxygen.

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

Sulfur, %	Sample Weight, g	Tolerance in Sample Weight, mg
0.005 to 0.10	1.000	1.0
0.10 to 0.25	0.500	0.5
0.25 to 0.60	0.250	0.5

Transfer the sample to a preignited combustion boat and spread it in a layer of uniform thickness.

24.1.4 Cover the sample with 0.5 g of iron accelerator and approximately 0.25 g of copper accelerator. Place a preignited cover on the boat and introduce it into the center of the combustion zone. Close the tube and allow the sample to heat for 1.5 min. Start the flow of oxygen at the rate used in 24.1.2.

24.1.5 Titrate the evolved SO_2 continuously with the appropriate KIO_3 Standard Solution at such a rate as to maintain as nearly as possible the initial intensity of the blue color. Continue the flow of oxygen for 10 min, record the buret reading, and subtract the initial reading obtained in 24.1.2. Drain the absorption vessel. If the net volume differs by more than a factor of three from that required for the sample previously analyzed, disregard the result and repeat the analysis a sufficient number of times to stabilize the system before proceeding as directed in 23.1.

24.2 *Combustion with Induction Furnace:*

24.2.1 Turn on the power of the induction furnace and allow the electronic circuit to heat to operating temperature. Depress the starting button until the ammeter indicates that the current is flowing through the induction coil.

24.2.2 Proceed as directed in 24.1.2.

24.2.3 Proceed as directed in 24.1.3 substituting a crucible for the combustion boat.

24.2.4 Add 0.5 g of iron accelerator, 1.0 g of tin, and approximately 0.5 g of copper accelerator. Place a preignited cover on the crucible and introduce it into the center of the combustion zone. Close the tube, start the flow of oxygen at the rate used in 24.2.2, turn on the power, and increase it to the maximum at such a rate that spattering of the molten sample is avoided.

24.2.5 Proceed as directed in 24.1.5, but discontinue the flow of oxygen after 4 to 5 min or when the titration is complete. Turn off the power to the induction coil.

25. Calculation

25.1 Read the percentage of sulfur in the sample from the appropriate curve plotted as directed in 23.5.

26. Precision and Bias

26.1 Although samples covered by this test method with appropriate sulfur concentrations for evaluation of the test method were not available, the precision data summarized in 45.1 of Test Methods E 353 should apply.

26.2 Twenty-two laboratories cooperated in testing this test method; six used resistance furnaces and reported eight sets of values (Note 5); sixteen used induction furnaces (Note 6). They obtained the data summarized in Table 2 for Material 7. Although samples covered by this test method with sulfur concentration near the lower limit of the scope were not available for testing, the precision data obtained using the test methods indicated in Table 2 should apply. None was available to permit a test near the upper limit of the scope.

NOTE 5—The recovery of sulfur as SO₂ ranged from 72 to 97 % with an average value of 83 % based on calibration standards designated *b*, *c*, and *d* in Table 3.

NOTE 6—The recovery of sulfur as SO₂ ranged from 80 to 96 % with an average value of 88 % based on calibration standards designated *b*, *c*, and *d* in Table 3.

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

TABLE 2 Statistical Information—Sulfur

Test Material	Sulfur Found, %	Repeatability (R ₁ , E 173 ^A)	Reproducibility (R ₂ , E 173 ^A)
Induction Furnace			
1. No. 1, E 352	0.006 ^B	0.0016	0.0032
2. No. 2, E 352	0.008 ^B	0.0013	0.0044
3. No. 3, E 350	0.014 ^B	0.0025	0.0029
4. No. 4, E 350	0.016 ^B	0.0018	0.0024
5. No. 6, E 350	0.032 ^C	0.0032	0.0049
6. No. 7, E 350	0.141 ^D	0.0066	0.0126
7. Stainless steel 13Cr-0.3Mo (NIST 133a, 0.329S + NBS 10g, 0.109S: 0.286S)	0.286 ^E	0.0135	0.0201
Resistance Furnace			
1. No. 1, E 352	0.006 ^B	0.0014	0.0024
2. No. 2, E 352	0.009 ^B	0.0007	0.0020
3. No. 3, E 350	0.014 ^B	0.0014	0.0025
4. No. 4, E 350	0.015 ^B	0.0017	0.0029
5. No. 6, E 350	0.032 ^C	0.0028	0.0041
6. No. 7, E 350	0.140 ^D	0.0074	0.0111
7. Stainless steel 13Cr-0.3Mo (NIST 133a, 0.329S + NBS 10g, 0.109S: 0.286S)	0.288 ^E	0.0123	0.0206

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

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

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

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

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

TABLE 3 Statistical Information—Silicon

Test Specimen	Silicon Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
HClO ₄ Dehydration			
1. Ni-base alloy 75Ni-12Cr-6Al-4Mo-2Cb-0.7Ti	0.029	0.006	0.026
H ₂ SO ₄ Dehydration			
1. Ni-base alloy 75Ni-12Cr-6Al-4Mo-2Cb-0.7Ti	0.030	0.007	0.030
2. Co-base alloy 66Co-28Cr-4W-1.5Ni	1.01	0.03	0.06

SILICON BY THE GRAVIMETRIC METHOD

27. Scope

27.1 This test method covers the determination of silicon in concentrations from 0.05 to 5.00 % in alloys containing not more than 0.1 % boron.

28. Summary of Test Method

28.1 After dissolution of the sample, silicic acid is dehydrated by fuming with sulfuric or perchloric acid. The solution is filtered, and the impure silica is ignited and weighted. The silica is then volatilized with hydrofluoric acid. The residue is ignited and weighed; the loss in weight represents silica.

29. Interferences

29.1 The elements normally present do not interfere. When boron is present in amounts greater than 0.1 %, the sample solution requires special treatment with methyl alcohol (**Warning**—See Practices E 50) prior to acid dehydration. However, since no boron steels were tested, this special treatment was not evaluated.

30. Reagents

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

30.2 Perchloric Acid:

30.2.1 Select a lot of HClO₄ 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 as directed in 30.2.2 through 30.2.7.

30.2.2 Transfer 15 mL of HClO₄ (Note 7) to each of two 400-mL beakers. To one of the beakers transfer an additional 50 mL of HClO₄. Using a pipet, transfer 20 mL of Na₂SiO₃ solution (1 mL = 1.00 mg Si) to each of the beakers. Evaporate the solutions to fumes and heat for 15 to 20 min at such a rate that HClO₄ refluxes on the sides of the beakers. Cool sufficiently, and add 100 mL of water (40 to 50°C).

NOTE 7—The 15-mL addition of HClO₄ came 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.

30.2.3 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 to 5-mL portions of hot HCl (1 + 19) and hot water, for a total of 6 times. Finally wash the papers twice with H₂SO₄(1 + 49). Transfer the papers to platinum crucibles.

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

30.2.5 Add enough H₂SO₄(1 + 1) to moisten the SiO₂, and add 3 to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H₂SO₄ is removed. Ignite for 15 min at 1100 to 1150°C, cool in a desiccator, and weigh.

30.2.6 Calculate the percentage of silicon as follows:

$$\text{Silicon, \%} = [(A - B) - (C - D)] \times 0.4674/E \times 100 \quad (2)$$

where:

A = initial weight of crucible plus impure SiO₂ when 65 mL of HClO₄ was taken, g,

B = final weight of crucible plus impurities when 65 mL of HClO₄ was taken, g,

C = final weight of crucible plus impurities when 15 mL of HClO₄ was taken, g,

D = final weight of crucible plus impurities when 15 mL of HClO₄ was taken, g,

E = nominal weight (80 g) of 50 mL of HClO₄.

30.3 *Sodium Silicate Solution*—Transfer 11.0 g of sodium silicate (Na₂SiO₃·9H₂O) 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 HClO₄.

30.4 *Tartaric Acid Solution* (20.6 g/L)—Dissolve 20.6 g of tartaric acid (C₄H₆O₆) in water, dilute to 1 L, and filter.

30.5 *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.

31. Procedure

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

Silicon, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dehydrating Acid, mL	
			H ₂ SO ₄ (1+4)	HClO ₄
0.05 to 0.10	5.0	5	150	75
0.10 to 1.0	4.0	4	100	60
1.0 to 2.0	3.0	3	100	50
2.0 to 5.0	2.0	2	100	40

Transfer it to a 400-mL beaker or a 300-mL porcelain casserole. Proceed as directed in 31.2 or 31.3.

31.2 Proceed as directed in 31.4 if tungsten is greater than 0.5 %.

31.3 Proceed as directed in 31.2 or 31.5 if tungsten is less than 0.5 %.

31.4 *Sulfuric Acid Dehydration*:

31.4.1 Add amounts of HCl or HNO₃, or mixtures and dilutions of these acids, that are sufficient to dissolve the sample; and then add the H₂SO₄(1 + 4) as specified in 30.1, and cover. Heat until dissolution is complete. Remove and rinse the cover glass; substitute a ribbed cover glass.

31.4.2 Evaporate until salts begin to separate; at this point evaporate the solution rapidly to the first appearance of fumes and fume strongly for 2 to 3 min. Cool sufficiently, and add 100 mL of water (40 to 50°C). Stir to dissolve the salts and heat, if necessary, but do not boil. Proceed immediately as directed in 31.6.

31.5 *Perchloric Acid Dehydration*:

31.5.1 Add amounts of HCl or HNO₃, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample, and cover. Heat until dissolution is complete. Add HNO₃ to provide a total of 35 to 40 mL, followed by HClO₄ as specified in the table in 31.1. Remove and rinse the cover glass; substitute a ribbed cover glass.

31.5.2 Evaporate the solution to fumes and heat for 15 to 20 min at such a rate that the HClO₄ refluxes on the sides of the container. Cool sufficiently and add 100 mL of water (40 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.

31.6 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 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 31.3 was followed, wash the paper twice more with H₂SO₄(1 + 49), but do not collect these washings in the filtrate; discard the washings. Transfer the paper to a platinum crucible and reserve.

31.7 Add 15 mL of HNO₃ to the filtrate, stir, and evaporate as directed either in 31.2 or 31.3, depending upon the dehydrating acid used. Filter immediately, using a low-ash 9-cm 100-porosity filter paper, and wash as directed in 50.4.

31.8 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 to 1150°C to constant weight (at least 30 min). Cool in a desiccator and weigh.

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

32. Calculation

32.1 Calculate the percent of silicon as follows:

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

where:

A = initial weight of crucible and impure SiO₂, g,

B = final weight of crucible and residue, g, and

C = sample used, g.

33. Precision and Bias

33.1 Eleven laboratories cooperated in testing this test method and obtained the data summarized in Table 3. A sample

with silicon concentration near the upper limit of the scope was not available for testing.

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

COBALT BY THE ION-EXCHANGE- POTENTIOMETRIC TITRATION METHOD

34. Scope

34.1 This test method covers the determination of cobalt in concentrations from 2 to 75 %.

35. Summary of Test Method

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

36. Interferences

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

37. Apparatus

37.1 *Ion-Exchange Column*, approximately 25 mm in diameter and 300 mm long, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. A reservoir for the eluants may be added at the top of the column.

37.2 *Apparatus for Potentiometric Titrations*—Instruments for detecting the end points in pH (acid-base), oxidation-reduction, precipitation, and complexation titrations consist of a pair of suitable electrodes, a potentiometer, a buret, and a motor-driven stirrer. Titrations are based on the fact that when two dissimilar electrodes are placed in a solution there is a potential difference between them. This potential difference depends on the composition of the solution and changes as the titrant is added. A high-impedance electronic voltmeter follows the changes accurately. The end point of the titration may be determined by adding the titrant until the potential difference attains a predetermined value or by plotting the potential difference versus the titrant volume, the titrant being added until the end point has been passed.

37.2.1 An elaborate or highly sensitive and accurate potentiometer is not necessary for potentiometric titrations because the absolute cell voltage needs to be known only approximately, and variations of less than 1 MV are not significant. Such instruments should have a range of about 1.5 V and a readability of about 1 MV. Many of the pH meters satisfying the requirements for Apparatus No. 3A are also suitable for potentiometric titrations.

37.2.2 The electrode system must consist of a reference electrode and an indicator electrode. The reference electrode maintains a constant, but not necessarily a known or reproducible potential during the titration. The potential of the indicator electrode does change during the titration; further, the indicator

electrode must be one that will quickly come to equilibrium. In this procedure a platinum indicator electrode and a saturated calomel reference electrode are appropriate.

37.3 *Apparatus No. 3B*, with a platinum and a saturated calomel electrode.

38. Reagents

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

38.2 *Cobalt, Standard Solution* (1 mL = 1.5 mg of Co)—Reagent No. 25B in Practices E 50.

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

Standardization—Calculate the cobalt concentration as follows:

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

38.3 *Ion-Exchange Resin*:⁷

38.3.1 Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a nominal crosslinkage of 8 %, and 200 to 400 nominal mesh size. To remove those beads greater than about 180 μm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a No. 80 (180-μm) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 to 6 min, decant 150 to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

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

⁶ Cobalt sulfate (99.9 % min) 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.

3.0 mL/min. Drain to 10 to 20 mm above the top of the resin bed and then close the lower stopcock.

NOTE 8—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.

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

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

38.4.2 Calculate the cobalt equivalent as follows (Note 9):

$$\text{Cobalt equivalent, mg/mL} = (A \times B)/C \quad (4)$$

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

39. Procedure

39.1 Transfer 0.50-g samples for cobalt concentrations not greater than 25 %; at higher concentrations use samples that represent between 100 and 125 mg of cobalt and weighed to the nearest 0.1 mg. Transfer all of the sample to a 150-mL beaker. Add 20 mL of a mixture of 5 parts of HCl and 1 part of HNO_3 (Note 10). Cover the beaker and digest at 60 to 70°C until the sample is decomposed. Rinse and remove the cover. Place a ribbed cover glass on the beaker and evaporate the solution nearly to dryness, but do not bake. Cool, add 20 mL of HCl (7 + 5), and digest at 60 to 70°C until salts are dissolved (approximately 10 min).

NOTE 10—Other ratios and concentrations of acids, with or without the addition of 1 to 2 mL of HF, are used for the decomposition of special grades of alloys.

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

39.2 Cool to room temperature and transfer the solution to the ion-exchange column. Place a beaker under the column and open the lower stopcock. When the solution reaches a level 10 to 20 mm above the resin bed, rinse the original beaker with 5 to 6 mL of HCl (7 + 5) and transfer the rinsings to the column. Repeat this at 2-min intervals until the beaker has been rinsed

four times. Wash the upper part of the column with HCl (7 + 5) 2 or 3 times and allow the level to drop to 10 to 20 mm above the resin bed each time. Maintain the flow rate at not more than 3.0 mL/min and add HCl (7 + 5) to the column until a total of 175 to 185 mL of solution (sample solution and washings) containing mainly chromium, manganese, and nickel is collected (Note 11). When the solution in the column reaches a level 10 to 20 mm above the resin bed, discard the eluate and then use a 400-mL beaker for the collection of the cobalt eluate.

NOTE 11—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.

39.3 Add HCl (1 + 2) to the column and collect 165 to 175 mL of the solution while maintaining the 3.0-mL/min flow rate. Reserve the solution. If the sample solution did not contain more than 0.200 g of iron, substitute a 250-mL beaker and precondition the column for the next sample as follows: Drain the remaining solution in the column to 10 to 20 mm above the resin bed, pass 35 to 50 mL of HCl (7 + 5) through the column until 10 to 20 mm of the solution remains above the resin bed, then close the lower stopcock. If the sample solution contained more than 0.200 g of iron, or if the column is not to be used again within 3 h, discard the resin and recharge the column as directed in 38.3.

39.4 Add 30 mL of HNO_3 and 15 mL of $HClO_4$ to the solution from 39.3 and evaporate to fumes of $HClO_4$. Cool, add 25 to 35 mL of water, boil for 1 to 2 min, cool, and add 10 mL of ammonium citrate solution.

39.5 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 to 8 mL. Record the buret reading to the nearest 0.01 mL. Add 50 mL of NH_4OH and cool to 5 to 10°C. Transfer the beaker to the potentiometric titration apparatus and maintain the 5 to 10°C temperature during the titration.

39.6 While stirring, add the sample solution to the solution from 39.5, rinse the beaker with water, and add the rinsings to the solution (Note 12). 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 12—For a successful titration, the sample solution must be added to the excess $K_3Fe(CN)_6$ solution.

40. Calculation

40.1 Calculate the percent of cobalt as follows:

$$\text{Cobalt, \%} = [(AB - CD)/E] \times 100 \quad (5)$$

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.

41. Precision and Bias

41.1 Ten laboratories cooperated in testing this test method and obtained the data summarized in Table 4 for Specimens 4 through 8. Although samples covered by this test method with cobalt concentrations near the lower limit of the scope were not available for testing, the precision data obtained for Specimens 1, 2, and 3 using the test method indicated in Table 4 should apply.

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

COBALT BY THE NITROSO-R-SALT PHOTOMETRIC METHOD

42. Scope

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

43. Summary of Test Method

43.1 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. Photometric measurement is made at approximately 520 nm.

44. Concentration Range

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

NOTE 13—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.

TABLE 4 Statistical Information—Cobalt

Test Specimen	Cobalt Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 1, E 352	1.86	0.05	0.12
2. No. 2, E 352	4.82	0.08	0.11
3. No. 3, E 352	8.46	0.03	0.07
4. High-temperature alloy 20Cr-13Ni-5Mo-2W-1Cb	11.27	0.06	0.16
5. Ni-base alloy 57Ni-14Cr (NIST 349, 13.95 Co)	13.88	0.09	0.18
6. High-temperature alloy 21Cr-20Ni-4Mo-3W	19.54	0.08	0.10
7. Co-base alloy 21Ni- 20Cr-4Mo-5W-3Cb (NBS, 167, 42.90 Co)	42.91	0.18	0.15
8. Co-base alloy 28Cr- 6Mo-3Ni	60.10	0.19	0.31

45. Stability of Color

45.1 The color is stable for at least 3 h.

46. Interferences

46.1 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.

47. Reagents

47.1 *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)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 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 mg Co/mL) of the final solution is the exact weight of CoSO_4 taken multiplied by 0.076046.

47.2 *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.

47.3 *Sodium Acetate Solution* (500 g/L)—Dissolve 500 g of sodium acetate trihydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$) in about 600 mL of water, filter, and dilute to 1 L.

47.4 *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.

48. Preparation of Calibration Curve

48.1 *Calibration Solutions*—Using pipets, transfer 2, 5, 10, 15, 20, 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 as directed in 48.3.

48.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed as directed in 48.3.

48.3 *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 to 10 min, add 5 mL of HNO_3 (1 + 2), and mix. Continue the heating for 2 to 4 min. Cool the solution to room temperature, dilute to volume, and mix.

48.4 *Photometry*:

48.4.1 *Multiple-Cell Photometer*—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 photometric readings of the calibration solutions versus the Reference Solution (48.2).

48.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution (48.2) to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 520 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

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

49. Procedure

49.1 *Test Solution:*

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

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

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

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

NOTE 14—Other ratios and concentrations of acids, with or without the addition of 1 to 2 mL of HF, are used for the decomposition of special grades of alloys. If HF is used, the sample should be dissolved in a 150-mL beaker and the solution transferred to the specified volumetric flask.

49.1.3 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 15). Dilute to volume, and mix. Allow the precipitate to settle; filter a portion of the solution through a dry, line (porosity) filter paper, and collect it in a dry, 150-mL beaker after having discarded the first 10 to 20 mL. Using a pipet, transfer 10 mL of the filtrate to a 50-mL borosilicate glass volumetric flask. Proceed as directed in 48.3.

NOTE 15—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.

49.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed as directed in 49.3.

49.3 *Color Development*—Proceed as directed in 48.3.

49.4 *Photometry*—Take the photometric reading of the test solution as directed in 48.4.

50. Calculation

50.1 Convert the net photometric reading of the test solution to milligrams of cobalt by means of the calibration curve. Calculate the percentage of cobalt as follows:

$$\text{Cobalt, \%} = A/(B \times 10) \tag{6}$$

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.

51. Precision and Bias

51.1 *Precision*⁸—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 5 for Specimens 1 and 4. Although samples covered by this test method with cobalt concentration near the extreme limits of the scope were not available for testing, the precision data obtained for other types of alloys, using the test methods indicated in Table 5 should apply.

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

COPPER BY THE NEOCUPROINE PHOTOMETRIC METHOD

52. Scope

52.1 This test method covers the determination of copper in concentrations from 0.010 to 1.50 %.

53. Summary of Test Method

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

54. Concentration Range

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

NOTE 16—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.

55. Stability of Color

55.1 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 photometric readings promptly.

⁸ Supporting data are available from ASTM International Headquarters. Request RR: E03-1028.

TABLE 5 Statistical Information—Cobalt

Test Specimen	Cobalt Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. Ni-base alloy, 36Ni (NIST 126b, 0.032 Co)	0.032	0.005	0.006
2. No. 2, E 353	0.094	0.006	0.013
3. No. 3, E 353	0.173	0.011	0.026
4. Ni-base alloy, 17Cr-15Fe (NIST 161, 0.47 Co)	0.468	0.020	0.028
5. No. 2, E 352	1.87	0.09	0.13
6. No. 3, E 352	4.94	0.08	0.17

56. Interferences

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

57. Reagents

57.1 *Chloroform* (CHCl_3).

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

57.3 *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 $\text{HNO}_3(1 + 1)$. 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.

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

NOTE 17—In addition to absolute ethanol, 95 % ethanol or denatured No.30 or 3A alcohol have been found suitable for preparing this solution.

57.5 *Hydroxylamine Hydrochloride Solution* (100 g/L)—hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 50mL of water. Prepare fresh as needed.

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

58. Preparation of Calibration Curve

58.1 *Calibration Solutions*—Using pipets, transfer 5, 10, 15, 20, 25, and 30 mL of copper solution (1 mL = 0.01 mg Cu) to 150-mL beakers, and dilute to 50 mL. Proceed as directed in 131.3.

58.2 *Reagent Blank Solution*—Transfer 50 mL of water to a 150-mL beaker. Proceed as directed in 58.3.

58.3 *Color Development:*

58.3.1 Add 5 mL of $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution and 10 mL of citric acid solution. Stir for 30 s. Using a pH meter (Note 46), adjust the pH to 5.0 ± 1.0 with NH_4OH (1 + 1). Add 10 mL of neocuproine solution.

NOTE 18—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.

58.3.2 Transfer the solution to a 125-mL conical separatory funnel, rinsing the beaker with 10 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 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 to 5 mL of ethanol, and collect the washings in the volumetric flask. Dilute to volume with ethanol, and mix.

58.4 *Reference Solution*— CHCl_3 .

58.5 *Photometry:*

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

58.5.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 455 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

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

59. Procedure

59.1 *Test Solution:*

59.1.1 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
0.80 to 1.50	0.50	0.1	250	10
1.40 to 3.00	1.00	0.1	1000	10
2.80 to 5.00	0.60	0.1	1000	10
4.80 to 7.50	0.80	0.1	1000	5
7.25 to 10.00	0.60	0.1	1000	5

Transfer it to a 250-mL Erlenmeyer flask.

59.1.1.1 Add amounts of HCl or HNO_3 , or mixtures and dilutions of these acids, which are sufficient to dissolve the sample (Note 19). Heat as required to hasten dissolution. Add HNO_3 to provide an excess of 3 to 4 mL, a sufficient amount of HF to volatilize the silica, and 15 mL of HClO_4 .

NOTE 19—Some alloys are more readily decomposed by a mixture of 5 mL of bromine, 15 mL of HCl, and 1 to 2 drops of HF.

59.1.2 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 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 20) to a volumetric flask that provides for the dilution specified in 59.1.1. Dilute to volume and mix.

NOTE 20—If silver is present in the alloy it must be removed by filtration at this point.

59.1.3 Allow insoluble matter to settle, or dry-filter through a coarse paper and discard the first 15 to 20 mL of the filtrate before taking the aliquot. Using a pipet, transfer a portion as specified in 59.1.1 to a 150-mL beaker, and dilute to 50 mL. Proceed as directed in 59.4.

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

59.3 *Reference Solution*— CHCl_3 .

59.4 *Color Development*—Proceed as directed in 58.3.

59.5 *Photometry*—Take the photometric reading of the test solution as directed in 58.5.

60. Calculation

60.1 Convert the net photometric readings of the test solution and of the reagent blank solution to milligrams of copper by means of the calibration curve. Calculate the percentage of copper as follows:

$$\text{Copper, \%} = (A - B)/(C \times 10) \tag{7}$$

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.

61. Precision and Bias

61.1 *Precision*—Ten laboratories cooperated in testing this test method and obtained the data summarized in Table 6. Although samples only in the lower part of the scope of this test method were available for testing, the precision data obtained for specimens in the remainder of the scope using the test methods indicated should apply.

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

TOTAL ALUMINUM BY THE 8-QUINOLINOL GRAVIMETRIC METHOD

62. Scope

62.1 This test method covers the determination of total aluminum in concentrations from 0.20 to 7.00 %.

TABLE 6 Statistical Information—Copper

Test Specimen	Copper Found, %	Repeatability, (R ₁ , E 173)	Reproducibility, (R ₂ , E 173)
1. Nickel-base alloy, 57Ni-14Cr (NIST 349, 0.006 Cu)	0.006	0.001	0.004
2. Nickel-base alloy, 77Ni-20Cr (NIST 169, 0.015 Cu)	0.014	0.002	0.006
3. Cobalt-base alloy 41Co-20Ni (NIST 168, 0.035 Cu)	0.033	0.005	0.004
4. No. 5, E 352	0.078	0.005	0.010
5. No. 6, E 352	0.118	0.007	0.016
6. No. 6, E 353	0.176	0.019	0.021
7. No. 7, E 353	0.200	0.012	0.018
8. No. 8, E 353	0.221	0.013	0.022
9. No. 9, E 353	0.361	0.015	0.036
10. No. 5, E 351	1.51	0.04	0.05
11. No. 6, E 351	5.53	0.19	0.18

63. Summary of Test Method

63.1 Following dissolution, acid-insoluble aluminum is separated, fused, and recombined. Interfering elements are removed by mercury-cathode, cupferron, and sodium hydroxide separations. Aluminum quinolate is precipitated and weighed.

64. Interferences

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

65. Apparatus

65.1 *Filtering Crucible*, medium-porosity fritted-glass, low form, 30-mL capacity.

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

65.3 *HCl Gas Generator* (Fig. 2)—A simple HCl gas generator constructed from a stoppered wash bottle and glass tubing.

65.4 *Mercury Cathode*—An efficient apparatus for mercury cathode separations is that employing a rotating mercury pool cathode. With this instrument the movement of the cathode causes a fresh surface of mercury to be exposed during electrolysis, thus accelerating the separation. This instrument permits use of a current of 15 A in a 400-mL beaker. The electrolyte may be removed from the cell through a stopcock located just above the level of the mercury or siphoned from it. When 1 % or more of aluminum or titanium is present and these are to be determined, it should be initially ascertained if any of the aluminum or titanium is lost to the cathode.

65.5 *pH Meter*—A number of pH meters are commercially available. Many of these instruments can accept a variety of electrodes and therefore can be used also for potential measurements. Although both line- and battery-operated pH meters are manufactured, the former is recommended for laboratory work because this type of pH meter contains an electronic or transistorized potentiometer which makes the emf balancing operation entirely automatic. Electrometer tube input is used on both the electronic and transistorized pH meters.

65.5.1 The pH meter must have electrode standardization (or asymmetry potential) and manual or automatic temperature compensation controls. The dial must read in pH directly, and permit readings that are accurate to at least ±0.01 pH unit. For higher accuracies it is recommended that a pH meter with an expanded scale be used.

65.5.2 Because there is no accurate method for determining the absolute potential of an individual electrode, two electrodes

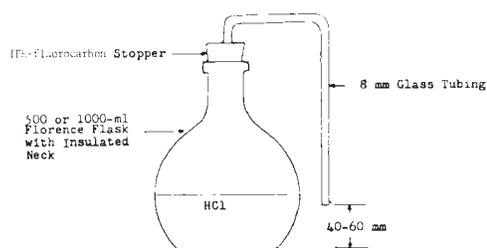


FIG. 2 HCl Gas Generator

are used for pH measurements. These are called the reference and indicator electrodes.

66. Reagents

66.1 *Ammonium Peroxydisulfate Solution* (100 g/L)—Dissolve 20 g of ammonium peroxydisulfate ((NH₄)₂S₂O₈) in water and dilute to 200 mL. Do not use a solution that has stood more than 8 h.

66.2 *Chloroform* (CHCl₃).

66.3 *Cupferron Solution* (60 g/L)—Dissolve 6 g of cupferron in 80 mL of cold water, dilute to 100 mL, and filter. Prepare fresh as needed. (**Warning**—Cupferron is a known carcinogen. Use protective equipment and work in an efficient exhaust hood.)

66.4 *8-Quinolinol Solution* (25 g/L)—Dissolve 25 g of 8-quinolinol in 50 mL of acetic acid, dilute to 300 mL with warm water, filter through a medium paper, and dilute to 1 L. Store in an amber bottle away from direct sunlight. Do not use a solution that has stood more than 1 month.

66.5 *Sodium Hydrogen Sulfate, Fused* (a mixture of Na₃S₂O₇ and NaHSO₄).

66.6 *Sodium Hydroxide Solution* (200 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in water in a platinum dish or in a plastic beaker, and dilute to 500 mL. Store in a polyethylene bottle.

66.7 *Tartaric Acid Solution* (200 g/L)—Dissolve 200 g of tartaric acid in 500 mL of water, filter through a medium paper, and dilute to 1 L.

67. Procedure

67.1 Transfer a 1.000-g sample, weighed to the nearest 0.1 mg, to a 600-mL beaker.

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

67.3 Add 30 mL of HCl and 10 mL of HNO₃ and digest at a low temperature until dissolution is complete. Add 30 mL of HClO₄, heat to fumes, and continue fuming until chromium, if present, is oxidized. If chromium is present, position the gas generator containing boiling HCl (use a fresh portion of HCl for each sample), so that the tube extends into the beaker and the HCl gas is delivered 20 to 30 mm above the surface of the fuming HClO₄. Continue boiling the HCl and fuming the sample solution until there is no evidence of yellow chromyl chloride in the fumes. Remove the generator and continue fuming the solution until the volume is reduced to 10 mL. Alternatively, volatilize the chromium as directed in 84.1.2. Remove from the hot plate and cool. Add 25 mL of water to dissolve the salts. If iron hydrolyzes, indicating that the sample was fumed too long, add 1 to 2 mL of HCl and 5 mL HClO₄ and again take to fumes. Dilute to 75 mL with water and boil to remove chlorine.

67.4 Filter through an 11-cm medium paper into a 400-mL beaker. Scrub and wipe the inside of the beaker with half a sheet of filter paper. Add this paper to the funnel. Wash the original beaker, the paper, and the residue 2 or 3 times with hot HClO₄(2 + 98) and then 3 or 4 times with hot water to ensure removal of HClO₄. Reserve the filtrate.

67.5 Transfer the paper to a platinum crucible, dry it, and then heat at about 600°C until the carbon has been removed. Finally ignite at 1100°C, cool, and add a few drops of H₂SO₄ (1 + 1) and 4 to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until the H₂SO₄ has been removed. Cool, add 2 to 3 g of sodium hydrogen sulfate, fuse, and heat until a clear melt is obtained. Cool the crucible, transfer it to a 250-mL beaker, add 50 mL of water, and then digest until the melt is dissolved. Remove and rinse the crucible with water.

67.6 If the solution is clear, add it to the filtrate reserved in 67.4. If the solution is turbid, filter through an 11-cm fine paper containing paper pulp into the beaker containing the reserved filtrate. Wash the paper 3 to 4 times with hot H₂SO₄ (3 + 97). Discard the paper and residue.

67.7 Evaporate to approximately 100 mL, and cool. Transfer the solution to a mercury cathode cell. Dilute to 150 to 200 mL and electrolyze at 15 A (Note 21) until the iron has been removed (Note 22). Without interrupting the current, transfer the solution from the cell to a 400-mL beaker. Thoroughly rinse the cell and electrodes several times with water and add the rinsings to the solution.

NOTE 21—Contact between the mercury pool and the platinum cathode may be broken intermittently due to stirring the mercury too rapidly. Since this will cause arcing which will result in the dissolution of some mercury in the electrolyte, it should be avoided by adding more mercury to the cell, using less current, or by proper adjustment of the cathode lead wire so that contact will be ensured.

NOTE 22—The completeness of the removal of iron, which usually requires 1 to 3 h, can be determined by the following test: Transfer 1 drop of the electrolyte to a watchglass or spot test plate. Add 1 drop of H₂SO₄ (1 + 1), 1 drop of saturated potassium permanganate (KMnO₄) solution, and 1 drop of sodium thiocyanate (NaSCN) solution (500 g/L). When only a faint pink color is observed, the electrolysis may be considered complete.

67.8 Filter the solution through a 12.5-cm medium paper containing paper pulp (Note 23) into a 600-mL beaker, and wash 3 or 4 times with hot water. To the filtrate add 10 mL of H₂SO₄(1 + 1) and 10 mL of (NH₄)₂S₂O₈ solution. Heat to boiling and evaporate to about 75 mL. Cool in an ice bath to below 10°C.

NOTE 23—This filtration removes any mercurous chloride that may have formed and any metallic mercury that may have been transferred from the cell.

67.9 Transfer the solution to a 250-mL conical separatory funnel, and without delay add 15 mL of cupferron solution. Reserve the beaker. Shake for 30 s and allow the precipitate to settle. Add 20 mL of CHCl₃ and shake for 1 min. Allow the layers to separate. Draw off and discard the CHCl₃ layer. Repeat the extraction [with 20-mL portions of CHCl₃ until the extract is colorless. Transfer the aqueous solution to the reserved 600-mL beaker and evaporate to 35 to 40 mL. Add 25 mL of HNO₃, cover with a ribbed cover glass, evaporate to fumes of H₂SO₄,] and cool. Dilute to 50 mL, heat to boiling, and cool.

67.10 Transfer the solution to a platinum, quartz or high-silica glass, or poly(tetrafluoroethylene) beaker. Police thoroughly (Note 24), rinse the beaker, and add the rinsings to the main solution. Neutralize to litmus with sodium hydroxide (NaOH) solution (Note 25), and add a 10-mL excess. Add 1

mL of H₂O₂, digest near the boiling point for 5 to 7 min and finally boil for 1 to 2 min to coagulate the manganese precipitate. Cool and filter through a 12.5-cm medium paper containing paper pulp previously washed 3 times with hot dilute NaOH solution (20 g/L), into a 600-mL beaker. Wash the paper and precipitate 4 or 5 times with hot water. Immediately add HCl (1 + 1) to the filtrate until acidic to litmus paper, and then add 3 to 4 mL in excess.

NOTE 24—This step is necessary whether or not a precipitate is visible.
NOTE 25—Approximately 70 mL will be required.

67.11 If the aluminum concentration is less than 1.50 %, proceed as directed in 67.12-67.14. If the aluminum concentration is greater than 1.50 %, transfer the solution to a 250-mL volumetric flask, dilute to volume, and mix. Select the proper aliquot in accordance with the following:

Aluminum, %	Aliquot, mL	Weight of Sample in	
		Aliquot, g	
1.50 to 3.50	100	0.400	
3.50 to 7.00	50	0.200	

Using a pipet, transfer it to a 600-mL beaker. Proceed as directed in 67.12-67.14.

67.12 Dilute to approximately 250 mL, and add 25 mL of tartaric acid solution. Using a pH meter, adjust the pH to 8.0 with NH₄OH.

67.13 Add 10 mL of H₂O₂ (Note 26), heat to 55°C, and while stirring add 15 mL of 8-quinolinol solution. Add 5 mL of NH₄OH, and stir continuously for 1 min and then for 5 to 10 s once a min for 9 more min while maintaining the temperature at 50 to 55°C.

NOTE 26—Precipitate aluminum in only one sample at a time. A motor-driven stirrer operating continuously for 10 min may be used.

67.14 Allow the solution to cool to room temperature. Filter with suction, using a weighed, medium-porosity, fritted-glass crucible. Police the beaker, rinse with NH₄OH (1 + 100), and wash the precipitate 4 times with warm NH₄OH (1 + 100). Dry for 1.5 h at 135°C, cool, and weigh as aluminum quinolate.

68. Calculation

68.1 Calculate the percent of total aluminum as follows:

$$\text{Total aluminum, \%} = [(A - B) \times 0.0587] / C \times 100 \quad (8)$$

where:

- A = aluminum quinolate found, g,
- B = correction for blank, g, and
- C = sample in final aliquot, g.

69. Precision and Bias

69.1 *Precision*—Eight laboratories cooperated in testing this test method using Test Specimens 3 and 6, nine using Test Specimens 4 and 5, with one laboratory reporting a second pair of values in each instance; the data are summarized in Table 7. Although samples covered by this test method with aluminum concentrations at the upper limit and at the lower limit of the scope were not available for testing, the precision data obtained using the test methods indicated in Table 7 should apply.

69.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be

TABLE 7 Statistical Information—Aluminum

Test Specimen	Aluminum Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 1, E 353	0.232	0.036	0.041
2. No. 2, E 353	1.16	0.06	0.10
3. Nickel-base alloy 57Ni-14Cr (NIST 349, 1.23 Al)	1.21	0.02	0.08
4. No. 4, E 350	1.44	0.07	0.16
5. Nickel-base alloy 19Cr-19Co-4Mo-3Ti	2.88	0.06	0.12
6. Nickel-base alloy 13Cr-4.5Mo-2.2Cb	5.84	0.16	0.26

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

NICKEL BY THE DIMETHYLGLYOXIME GRAVIMETRIC METHOD

70. Scope

70.1 This test method covers the determination of nickel in concentrations from 0.1 to 84.0 %.

71. Summary of Test Method

71.1 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.

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

72. Interferences

72.1 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.

73. Apparatus

73.1 *Anion-Exchange Column*, approximately 25 mm in diameter and 300 mm long, tapered at one end, and provided with a stopcock to control the flow rate and a second, lower stopcock to stop the flow. A reservoir for the eluants may be added at the top of the column.

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

73.3 *pH Meter*—See section 65.5.

74. Reagents

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

74.2 Anion Exchange Resin:

74.2.1 Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a crosslinkage of 8 % and a 200 to 400 nominal mesh size.⁹ To remove those beads greater than 180 μm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a No. 80 (180- μm) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Wash the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 to 6 min, decant 150 to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

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

74.3 *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.

75. Procedure

75.1 Double Precipitation:

75.1.1 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 5.0	1.0	0.5
5.0 to 10.0	0.5	0.2
10.0 to 20.0	0.25	0.1
20.0 to 48.0	1.0	0.5
48.0 to 84.0	0.5	0.2

Transfer it to a 600-mL beaker.

75.1.2 Add 60 mL of HCl (1 + 1) and 10 mL of HNO_3 . Heat to dissolve the sample and boil to expel oxides and 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.

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

75.1.4 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 $\text{pH } 6.3 \pm 0.1$.

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

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

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

75.1.8 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.

75.1.9 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 75.3-75.7.

75.2 Anion-Exchange Separation:

75.2.1 Proceed as directed in 75.1.1.

75.2.2 Proceed as directed in 75.1.2, but dilute with only 50 mL of water.

75.2.3 Filter the solution obtained in 75.2.2 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.

75.2.4 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.

75.2.5 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 10 to 20 mm from the top of the resin bed.

75.2.6 Place a clean 600-mL beaker under the ion-exchange column and open the bottom stopcock. Transfer the solution from 75.2.4 to the column. Allow the sample to drain to 5 to 10 mm from the top of the resin bed. Rinse the 250-mL beaker with a 5-mL portion of HCl (3 + 1) and transfer the rinsing to the column. When it has drained to 5 to 10 mm above the resin bed, add a second 5-mL rinse portion from the 250-mL beaker. Repeat this operation 3 more times, and allow the level to drop

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

to 5 to 10 mm above the resin bed before adding the next. Add sufficient HCl (3 + 1) at the top of the column to collect a total of 200 mL in the 600-mL beaker. Close the lower stopcock and reserve the solution.

75.2.7 Precondition the column for the next sample as follows: Open the lower stopcock. Drain any remaining solution in the column to 5 to 10 mm from the top of the resin bed. Add HCl (1 + 19) in 50-mL increments until iron has been eluted and the eluate is visibly free of color (approximately 300 mL). Drain the solution to 5 to 10 mm from the top of the resin bed and close the lower stopcock. If the column is not to be used immediately, cover and store. If another sample solution is to be put through the column, proceed as directed in 75.2.5.

75.2.8 Heat the solution reserved in 75.2.6 to boiling and evaporate to 60 mL to remove excess HCl. If the sample contains less than 20 % nickel, cool and dilute to 200 mL. If the sample contains more than 20 % nickel, cool and transfer to a 200-mL volumetric flask. Add 20 mL of HCl, dilute to volume, and mix. Using a pipet, transfer a 20-mL aliquot to a 600-mL beaker, and dilute to 200 mL with water.

75.3 Add 10 mL of ammonium citrate solution and 10 mL of HCl. Using a pH meter, adjust the pH to at least 7.5 with NH₄OH. Remove and rinse the electrodes with water, collecting the rinsings in the original beaker.

75.4 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.

75.5 Using a pH meter, adjust the pH to 7.4 ± 0.1 with NH₄OH. Remove and rinse the electrode with water. Heat at 50 to 70°C for 30 min and allow to stand for at least 4 h at 20 to 25°C.

75.6 With the aid of suction, filter using a weighed (Note 27) fritted glass crucible, wash the beaker and precipitate 6 times with cold water.

NOTE 27—Heat the crucible at 150°C and cool in a desiccator before weighing.

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

76. Calculation

76.1 Calculate the percent of nickel as follows:

$$\text{Nickel, \%} = [(A - B) \times 0.2032] / C \times 100 \quad (9)$$

where:

A = weight of crucible and precipitate, g,

B = weight of crucible, g, and

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

77. Precision and Bias

77.1 *Precision*—Ten laboratories cooperated in the testing of this test method and obtained the data summarized in Table 8. Although a sample covered by this test method near the lower end of the scope was not tested, the data obtained for other types of alloys using the test methods indicated in Table 8 should apply.

TABLE 8 Statistical Information—Nickel

Test Specimen	Nickel Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. No. 1, E 352	0.135	0.012	0.015
2. No. 2, E 353	1.81	0.09	0.09
3. Nickel-chrome steel 16 Cr-4 Ni-3 Cu (NIST 345, 4.24 Ni)	4.22	0.06	0.06
4. Cobalt alloy 41 Co-20 Ni-20 Cr-4 Mo-4W (NIST 168, 20.25 Ni)	20.26	0.23	0.23
5. Nickel alloy 77 Ni-20 Cr (NBS 169, 77.26 Ni)	77.13	0.56	0.56

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

TIN BY THE SOLVENT EXTRACTION-ATOMIC ABSORPTION METHOD

78. Scope

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

79. Summary of Test Method

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

80. Concentration Range

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

81. Interferences

81.1 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.

82. Apparatus

82.1 *Atomic Absorption Spectrophotometer*, capable of resolving the 2863 Å line, equipped with a tin hollow-cathode lamp or tin electrodeless discharge lamp whose radiant energy is modulated, with a detector system tuned to the same frequency and a premix nitrous oxide-acetylene burner. The performance of the instrument must be such that the upper limit of the concentration range (40 µg/mL) produces an absorbance of 0.15 or higher, and a calibration curve whose deviation from linearity is within the limits specified in 84.4.

83. Reagents

83.1 *Ascorbic Acid*.

83.2 *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.

83.3 *Methyl Isobutyl Ketone (MIBK)*.

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

83.5 *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.

83.6 *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.

84. Preparation of Calibration Curve

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

NOTE 28—Volumetric flasks with ground glass stoppers must be used.

84.2 *Extraction:*

84.2.1 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.

84.2.2 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 29—Prepare the test solution and have it ready to aspirate immediately after aspirating the calibration solutions.

84.3 *Photometry:*

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

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

NOTE 30—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 84.3.1.

84.3.3 Aspirate the solution with the highest concentration (40 µg Sn/mL) from the series prepared in 84.1 a sufficient number of times to establish that the absorbance is not drifting.

NOTE 31—Make certain that the capillary end does not enter the aqueous (bottom) layer at any time.

NOTE 32—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.

84.3.4 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 84.3.3 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 84.3.1 through 84.3.4.

84.3.5 Proceed immediately as directed in 85.3.

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

$$\text{Deviation from linearity} = (A - B)/C \quad (10)$$

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.

85. Procedure

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

85.2 *Test Solution:*

85.2.1 Select and weigh a sample (Note 33) 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 400-mL poly(tetrafluoroethylene) beaker.

NOTE 33—Select a sample that will pass through a No. 20 (850-µm) sieve.

85.2.2 Add 100 mL of HCl, 20 drops of 30 % H₂O₂, and 5 drops of HF. Cover the beaker with a poly(tetrafluoroethylene) cover and heat at a low temperature (approximately 90°C). At 20-min intervals, remove the cover with platinum-tipped tongs and cautiously add an additional 20 drops of 30 % H₂O₂. Repeat this step until dissolution is complete.

NOTE 34—If silicon is above 0.5 %, use 10 to 12 drops of HF. If dissolution is very slow, add an additional 50 mL of HCl and heat at approximately 90°C overnight.

85.2.3 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 of HCl (1 + 1), and again evaporate to 15 mL. Rinse the sides of the beaker with about 5 mL of water and cool.

NOTE 35—If niobium, tantalum, tungsten, or certain other elements are present in sufficiently high concentration, they will precipitate. Extract such samples as directed with minimal delay.

85.2.4 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.

85.2.5 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.

85.2.6 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.

85.3 *Photometry*—Aspirate the top (MIBK) phase of the test solution and the reagent blank solution (Note 31) and record the absorbance values. Take three readings of each solution (Note 32). Measure the absorbance of the calibration solution with the highest concentration of tin to check for drift as in 84.3.4 and 84.3.5.

86. Calculation

86.1 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 percent of tin as follows:

$$T_{\text{in}}, \% = [(D - E)/(F \times 1000)] \quad (11)$$

where:

D = tin per mL of the final test solution, μg ,

E = tin per mL of the final reagent blank solution, μg and

F = sample used, g.

87. Precision and Bias¹⁰

87.1 *Precision*—Eleven laboratories cooperated in testing this test method and obtained the precision listed for No. 1, 2, 4, and 6 in Table 9. This test method differs only slightly from the test method for tin, Test Methods E 350, in that the reagents

¹⁰ Supporting data are available from ASTM International Headquarters. Request RR: E03-1022.

TABLE 9 Statistical Information—Tin

Test Specimen	Tin Found, %	Repeat-ability (R_1 , E 173)	Repro-ducibility (R_2 , E 173)
1. Cobalt-alloy (49 Co-balance Fe), 0.001 Sn (not certified)	0.0017	0.0002	0.0004
2. Nickel-base alloy (74 Ni-15 Cr), 0.002 Sn (not certified)	0.0021	0.0005	0.0006
3. No. 1, E 350	0.0034	0.0009	0.0014
4. Nickel-base alloy (74 Ni-15 Cr), 0.008 Sn (not certified)	0.0076	0.0013	0.0017
5. No. 2, E 350	0.0079	0.0009	0.0014
6. Nickel-base alloy (74 Ni-15 Cr), 0.017 Sn (not certified)	0.015	0.002	0.003
7. No. 4, E 350	0.031	0.003	0.004
8. No. 6, E 350	0.097	0.011	0.011

used for sample dissolution were slightly modified. The fact that the precision obtained for No. 2, 4, and 6 of Table 9, corresponds closely to that obtained for samples of similar tin content in Test Methods E 350, suggests that the precision of the two test methods is the same.

87.2 *Bias*—No information on the accuracy of this test method is available. The accuracy of a test method may be judged, however, by comparing accepted reference values with the arithmetic average obtained by interlaboratory testing. The values listed for these samples, while not certified, were obtained by other test methods and are believed to be substantially correct.

MOLYBDENUM BY THE PHOTOMETRIC METHOD

88. Scope

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

89. Summary of Test Method

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

90. Concentration Range

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

NOTE 36—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.

91. Stability of Color

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

92. Interferences

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

93. Reagents

93.1 *Butyl Acetate*:

NOTE 37—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.

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

93.3 *Iron*¹¹—Purity: 99.8 % minimum, molybdenum 0.001 % maximum.

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

¹¹ Johnson-Matthey JMC 847 sponge iron has been found suitable for this purpose.

93.5 *Iron Solution B* (1 mL = 0.84 mg Fe)—Add 12 mL of Iron Solution A to 175 mL of H₂SO₄(1 + 1), and dilute to 1 L.

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

93.7 *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.

93.8 *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.

93.9 *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.

93.10 *Stannous Chloride Solution* (350 g/L)—Transfer 350 g of stannous chloride dihydrate (SnCl₂·2H₂O) and 200 g of tartaric acid to a 1-L beaker, add 400 mL of HCl (1 + 1), and heat at 60 to 70°C until dissolution is complete. Cool, and dilute to 1 L. Add several pieces of tin, and store in an air-tight bottle.

NOTE 38—This solution is used for color development in 94.3, 95.3, 96.3, and 97.3. When an absorption cell is used sequentially for a number of photometric measurements, a white film of an insoluble tin compound may adhere to the inside of the cell and must be removed before further measurements are made.

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

94.1 Calibration Solutions:

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

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

94.1.3 Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 94.3.

94.2 *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 94.1.2, 94.1.3, and 94.3.

94.3 *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 SnCl₂ 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 H₂SO₄(1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl₂ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel, containing a dry filter paper, to fill an absorption cell.

NOTE 39—This funnel should be cleaned thoroughly after each filtration to avoid development of a pink color that would contaminate the filtrate.

94.4 *Reference Solution*—Butyl acetate.

94.5 Photometry:

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

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

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

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

95.1 Calibration Solutions:

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

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

95.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 95.3.

95.2 *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 95.1.2, 95.1.3, and 95.3.

95.3 *Color Development*—Using a pipet, transfer 50 mL to a 250-mL separatory funnel. Add in order, mixing for 15 s after each addition, 15 mL of NaSCN solution, 15 mL of SnCl₂ solution, and 50 mL of butyl acetate measured with a pipet. Stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Add to the funnel 50 mL of H₂SO₄(1 + 6), 5 mL of NaSCN solution, and 5 mL of SnCl₂ solution. Replace the stopper and shake vigorously for 2 min. Allow the phases to separate, remove the stopper, drain off, and discard the aqueous phase. Drain enough of the butyl acetate layer through a funnel containing a dry filter paper to fill an absorption cell. (See Note 39.)

95.4 *Reference Solution*—Butyl acetate.

95.5 Photometry:

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

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

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

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

96.1 Calibration Solutions:

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

96.1.2 Increase the temperature and evaporate to HClO_4 fumes. Cool, add 50 mL of water and 70 mL of $\text{H}_2\text{SO}_4(1 + 1)$. Heat to boiling and cool in a water bath.

96.1.3 Transfer to a 500-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 96.3.

96.2 *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 96.1.2, 96.1.3, and 96.3.

96.3 *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 $\text{H}_2\text{SO}_4(1 + 6)$, 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 39.)

96.4 *Reference Solution*—Butyl acetate.

96.5 Photometry:

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

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

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

97. Procedure

97.1 Test Solution:

97.1.1 Transfer 0.3-g sample, weighed to the nearest 1 mg to a 250-mL Erlenmeyer flask. If the alloy contains tungsten, add 30 mL of dissolving acid. Add HCl, or HNO_3 , or mixtures

and dilutions of these acids, or bromine and HCl in a ratio of 1:3 (plus a few drops of HF), and heat until dissolution is complete.

97.1.2 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 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 $\text{H}_2\text{SO}_4(1 + 1)$, 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 97.1.3. Wash the paper with five 5-mL portions of $\text{H}_2\text{SO}_4(1 + 99)$ collecting these in the same volumetric flask. Proceed as directed in 97.3. If the solution is clear, proceed to 97.1.3.

97.1.3 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 97.3.

97.2 *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 97.1.2, 97.1.3, and 97.3, using the same dilution and aliquots used for the test solution.

97.3 *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 $\text{H}_2\text{SO}_4(1 + 6)$, 5 mL of NaSCN solution, and 5 mL of SnCl_2 solution. Replace the stopper and shake vigorously 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 39.)

97.4 *Reference Solution*—Butyl acetate.

97.5 *Photometry*—Take the photometric reading of the test solution and of the reagent blank solution as directed in 97.5.

98. Calculation

98.1 Convert the net photometric reading of the test solution to milligrams of molybdenum in the final solution by means of

the appropriate calibration curve. Calculate the percent of molybdenum as follows:

$$\text{Molybdenum, \%} = \frac{A}{B \times 10} \quad (12)$$

where:

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

B = sample, g, represented in 25, 50, or 100 mL, as appropriate, of butyl acetate and the aliquot used (see aliquot guide 97.1.3).

99. Precision and Bias

99.1 *Precision*¹²—No data are presently available to determine the precision of this test method. However, the difference between this test method and molybdenum Test Methods E 350, E 351, E 352, and E 353 are minor and will not affect the precision of the results (see Table 10). This fact suggests that the precision for these test methods is the same.

99.2 *Bias*—No data are presently available to determine the bias of this test method.

CHROMIUM BY THE ATOMIC ABSORPTION METHOD

100. Scope

100.1 This test method covers the determination of chromium in concentrations from 0.018 to 1.00 %.

101. Summary of Test Method

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

102. Concentration Range

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

103. Interferences

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

104. Apparatus

104.1 *Atomic Absorption Spectrophotometer*, capable of resolving the 3579-Å line, equipped with a chromium hollow-cathode lamp, and a laminar flow nitrous oxide burner. The performance of the instrument must be such that it meets the limits defined in 106.3. If your instrument does not meet this criteria, you cannot expect to obtain the precision and accuracy stated in this test method.

105. Reagents

105.1 *Chromium Standard Solution* (1 mL = 0.1 mg Cr)—Transfer 2.8290 g of potassium dichromate (K₂Cr₂O₇) (NBS 136 or equivalent) to an 800-mL borosilicate beaker, add 500 mL of water, and mix. When dissolution is complete, add 5 mL of H₂SO₄ and, while stirring, add 10 mL of H₂O₂ (30 %). Heat at near boiling for 5 min to remove excess H₂O₂. 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.

105.2 *Iron*,¹³ *Low Chromium*—Cr < 0.0001 %.

105.3 *Potassium Carbonate Solution* (50 g/L)—Dissolve 50 g of potassium carbonate (K₂CO₃) in water and dilute to 1 L. Store the solution in a polyethylene bottle.

106. Preparation of Calibration Curves

106.1 *Calibration Solutions for Concentrations 0.005 to 0.10 %*—To each of seven 250-mL borosilicate beakers, transfer 1.0 g of low-chromium iron weighed to the nearest 1 mg. Add to each beaker 20 mL of HCl and 10 mL of HNO₃ 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 K₂CO₃ solution to each of 7 flasks. Using pipets, transfer 1, 3, 5, 7, 10, and 15 mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium concentration. Dilute to volume and mix.

106.2 *Calibration Solution for Concentrations 0.10 to 1.00 %*—Transfer 2 g of low-chromium iron weighed to the nearest 1 mg to a 250-mL borosilicate beaker. Add 20 mL of HCl and 10 mL of HNO₃. 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 K₂CO₃ solution. Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Transfer 10-mL aliquots to each of seven 100-mL volumetric flasks and add 9 mL of HCl to each flask. Using pipets, transfer 1, 3, 5, 7, 10, and 15 mL of chromium standard solution to each flask respectively. Designate the seventh flask as zero chromium concentration. Dilute to volume and mix.

106.3 *Photometry*:

106.3.1 With the chromium hollow-cathode lamp in position, energized and stabilized, adjust the wavelength to maximize the energy response of the 3579-Å line. The wavelength

¹² Supporting data are available from ASTM International Headquarters. Request RR: E03-1023.

TABLE 10 Statistical Information—Molybdenum

Test Specimen	Molybdenum Found, %	Repeatability R ₁ , F 173	Reproducibility R ₂ , E 173
1. No. 1, E 350	0.012	0.002	0.006
2. No. 3, E 353	0.432	0.010	0.017
3. No. 4, E 353	1.34	0.032	0.092

¹³ Johnson-Matthey sponge iron or Spex iron has been found suitable for this purpose.

setting in the vicinity of 4289 Å may be used provided that the instrument meets the performance requirements.

106.3.2 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 106.1, 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.

106.3.3 Aspirate the chromium solutions used in 106.3.2 to assure that the absorbance reading is repeatable. Record 6 readings, and calculate the standard deviation, s , of the readings as follows:

$$s = (A - B) \times 0.40 \quad (13)$$

where:

A = highest of six values found, and
 B = lowest of the six values found.¹⁴

106.3.4 Using water as a reference solution, and beginning with the solution to which no addition of chromium was made in 106.1 and 106.2, 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 106.3.3 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 106.3.1-106.3.4.

106.3.5 Proceed immediately as directed in Section 106.4.

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

$$\text{Deviation from linearity} = (C - D)/E \quad (14)$$

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 adjustments of instrument or hollow cathode lamp, and repeat the calibration. The absorbance value for C must be 0.200 or higher.

106.5 *Calibration for Concentrations from 0.10 to 1.00 %*—Proceed as directed in 106.4.

107. Procedure

107.1 Test Solution:

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

Chromium, %	Sample Weight, g	Tolerance in Sample Weight, mg	Dilution After Dis- solution, mL	Aliquot Required, mL	HCl to be added to Ali- quot, mL	Final Dilution, mL
0.005–0.10	1	0.10	100	0	0	100

¹⁴ The value 0.40, which is used to estimate the standard deviation from the range of six values, was published by Dixon, W.J. and Massey, F. J., "Introduction to Statistical Analysis," McGraw-Hill, 1957, Table 8b, (1), p. 404.

0.10–1.00 1 0.10 100 10 9 100

Transfer it to a 250-mL borosilicate beaker.

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

107.1.3 Transfer the paper and contents to a platinum crucible. Dry on a hot plate and transfer to a muffle furnace that is less than 400°C. Gradually heat to 600°C and hold at this temperature for 1 h. Cool, add 0.5 g of K₂CO₃ and carefully fuse over a free flame until a clear melt is obtained (see Note 40). 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 40—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.

107.1.4 Transfer this solution to the filtrate from 107.1.2 and evaporate just to dryness. Add 10 mL HCl and warm to dissolve salts. Transfer quantitatively to a 100-mL volumetric flask, dilute to volume, and mix. For samples with expected chromium concentrations less than 0.10 %, proceed as directed in 107.3. For samples with expected chromium concentration greater than 0.10 %, transfer by pipet 10 mL to a 100-mL volumetric flask, add 9 mL of HCl, dilute to volume, and mix.

107.2 Prepare for each concentration range a reagent blank by treating the same amount of all reagents as directed in 107.1.1-107.1.4, including the low-chromium iron. Use reagents from the same lots for blank and test solutions.

107.3 *Photometry*—Using water as a reference solution, aspirate and record the absorbance of the calibration, test, and reagent blank solutions. After each group of 4 or fewer test solutions and reagent blank solutions has been aspirated, apply the test using the standard solution as directed in 106.3.4, 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 106.3.3, 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.

108. Calculation

108.1 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 percent chromium as follows:

$$\text{Chromium, \%} = \frac{(A - B) \times C}{W \times 10} \quad (15)$$

where:

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

109. Precision and Bias¹⁵

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

109.2 *Bias*—The accuracy can be inferred from the data in Table 11 by comparing the certified values for chromium with the average value obtained by using this test method.

CHROMIUM BY THE PEROXYDISULFATE OXIDATION—TITRATION METHOD

110. Scope

110.1 This test method covers the determination of chromium in concentrations from 0.10 to 33.00 %.

111. Summary of Test Method

111.1 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 41—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.

112. Interferences

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

112.2 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 K₂Cr₂O₇ is chosen as the back-titrant. The limits are: nickel 1.300 g, copper 0.260 g, 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:

$$(2.6A + 0.05B + 0.01C) D \quad (16)$$

where:

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

When the value exceeds 1.300, the end point must be determined potentiometrically if K₂Cr₂O₇ is the back-titrant.

113. Apparatus

113.1 *Apparatus for Potentiometric Titrations*—See Section 37.2.

114. Reagents

114.1 *Ammonium Peroxydisulfate Solution*—Dissolve 15 g of ammonium peroxydisulfate [(NH₄)₂S₂O₈] in water and dilute to 100 mL. Do not use solutions that have stood for more than 24 h.

114.2 *Ferrous Ammonium Sulfate, Standard Solutions* (0.05 N and 0.10 N)—Reagent No. 5 (Practices E 50) but use 20 and 40 g of Fe(NH₄)₂(SO₄)₂·6H₂O, respectively, instead of the specified weight. Standardize the solution as directed in 115.1, 115.2, or 115.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h.

114.2.1 Dissolve 20 and 40g of (Fe(NH₄)₂(SO₄)₂·6H₂O), respectively, in 500 mL of cold H₂SO₄ (5 + 95) and dilute each to 1 L with H₂SO₄ (5 + 95). Saturating the solution with CO₂ will decrease the rate of oxidation of the ferrous ion.

114.2.2 *Standardization*—Standardize the solution as directed in 115.1, 115.2, or 115.3 depending upon the titration procedure to be employed. Use only if the solution has been standardized or restandardized within 24 h. 114.3.

114.3 *Potassium Dichromate, Standard Solution* (0.05 N and 0.10 N)—Dissolve 2.4518 and 4.9036 g of National Institute of Standards and Technology standard K₂Cr₂O₇ or equivalent primary standard grade K₂Cr₂O₇ in water, transfer each weight to a 1-L volumetric flask, dilute each to volume, and mix. These are primary standard solutions.

114.4 *Potassium Permanganate Solution* (25 g/L)—Dissolve 25 g of reagent grade KMnO₄ in 200 mL of water, dilute to 1 L, and mix.

114.5 *Potassium Permanganate, Standard Solution* (0.05 N and 0.10 N)—Reagent No. 13 (Practices E 50) but use 1.6 and 3.2 g of KMnO₄, respectively, instead of the specified weight. Standardize as directed in 34.2 of Practices E 50 but use 0.1500 g of sodium oxalate, (NBS 40 h) or equivalent primary standard grade.

114.5.1 Dissolve 1.6 and 3.2 g of potassium permanganate (KMnO₄) 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.

114.5.2 *Standardization*—Dry a portion of the National Institute of Standards and Technology standard sample of sodium oxalate or equivalent primary standard grade at 105°C. Transfer 0.1500 g of the sodium oxalate to a 600-mL beaker. Add 250 mL of H₂SO₄ (5 + 95), previously boiled for 10 to 15 min and then cooled to 27 ± 3°C, and stir until the oxalate has

¹⁵ Supporting data are available from ASTM International Headquarters. Request RR: E03-1030.

TABLE 11 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R ₁ , E 173)	Reproducibility (R ₂ , E 173)
1. 40 Ni 0.2 Si 0.5 Mn 0.02 C Steel	0.072	0.007	0.009
2. No. 1, E 352	0.149	0.028	0.028
3. 18 Ni 9 Co 5 Mo 0.5 Ti Steel	0.961	0.036	0.093

dissolved. Add 39 to 40 mL of the KMnO_4 solution, at a rate of 25 to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s). If the pink color does not fade begin again, adding a few milliliters less of the KMnO_4 solution. Heat to 55 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 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 - 0.05 mL.

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

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

114.7.1 *Method A (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.

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

114.8 *1,10 Phenanthroline Ferrous Complex Indicator Solution* (0.025 M)—Dissolve 6.95 g of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in 500 mL of water and dilute to 1 L. Dissolve 1.485 g of 1,10-phenanthroline monohydrate in 100 mL of the ferrous sulfate solution ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

115. Standardization of Ferrous Ammonium Sulfate Solution

115.1 *Against Potassium Permanganate Solution:*

115.1.1 Transfer 180 mL of water, 12 mL of H_2SO_4 (1 + 1), and 5 mL of H_3PO_4 into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 or 0.10 N $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ with either 0.05 or 0.10 N KMnO_4 solution (179.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 1 to 2 drops of 1,10 phenanthroline indicator solution. Using a 25-mL buret, titrate the ferrous ions with 0.05 N KMnO_4 standard solution (179.5) 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.

115.1.2 Calculate the normality of the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution as follows:

$$\text{Normality} = AB/C \quad (17)$$

where:

A = normality of KMnO_4 solution (114.5),

B = KMnO_4 solution, mL, and

C = $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution, mL.

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

115.2.1 Transfer 180 mL of water, 12 mL of H_2SO_4 (1 + 1), and 5 mL of H_3PO_4 into a 500-mL Erlenmeyer flask. Add 20 mL of 0.05 or 0.10 N $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (179.2) from a 25-mL buret and record the volume to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using a 25-mL buret, titrate the ferrous ions with either 0.05 or 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution, while swirling the flask. As the end point is

approached, add the $\text{K}_2\text{Cr}_2\text{O}_7$ titrant dropwise. Continue until a blue color appears and persists for at least 30 s. Record the buret reading to the nearest 0.01 mL. Refill the burets, add the same volume of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution, and again titrate with either 0.05 or 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution to the blue end point. Subtract this volume of $\text{K}_2\text{Cr}_2\text{O}_7$ solution from the volume recorded for the first titration and record the difference as the indicator blank.

115.2.2 Calculate the normality of the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution as follows:

$$\text{Normality} = (0.05 \text{ or } 0.10 (A - B))/C \quad (18)$$

where:

A = 0.05 or 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution used in the first titration, mL,

B = mL equivalent to the indicator blank, and

C = $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution used in the first titration, mL.

115.3 *Against Potassium Dichromate Using Potentiometric End Point:*

115.3.1 Using a 25-mL buret, transfer 20 mL of 0.05 or 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution into a 600-mL beaker. Reserve the remaining 0.05 or 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ 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 $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ until the dichromate ion yellow color disappears and then a slight excess. Record the volume of the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution to the nearest 0.01 mL. Back-titrate with the remaining 0.05 or 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ 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 was 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 $\text{K}_2\text{Cr}_2\text{O}_7$ Back Titrant, mL	Voltage, mV	Δ Voltage, mV	Difference Before and After, max
20.80	555		
20.90	570	50	50
21.00	620	100	20
21.10	720	80	
21.20	800		
21.30	835		
21.40	854		

Maximum voltage change occurred between 21.00 and 21.10 mL of $\text{K}_2\text{Cr}_2\text{O}_7$ 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 and 20 mV, respectively. Their sum equals 70 and the ratio of the first to the sum equals 50/70. Thus 50/70 multiplied by 0.1 mL must be added to the smaller volume between the two increments where the maximum change in voltage occurred. The end point is 21.07 mL.

115.3.2 Calculate the normality of the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution as follows:

$$\text{Normality} = 0.05 \text{ or } 0.10 A/B \quad (19)$$

where:

A = 0.05 or 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution, mL, and

B = $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution, mL.

116. Procedure

116.1 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	20.05
3.30 to 8.00	0.25	0.1	0.05
8.00 to 14.00 ^A	0.50	0.1	0.10
13.00 to 20.00 ^A	0.40	0.1	0.10
18.00 to 30.00 ^A	0.20	0.1	0.10
28.00 to 33.00 ^A	0.15	0.1	0.10

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

Transfer it to a 600-mL beaker.

116.2 Add 80 mL of $\text{H}_2\text{SO}_4(1+5)$ and 5 mL of H_3PO_4 . Cover the beaker with a ribbed cover glass and heat at 85 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. Proceed as directed in 116.4.

116.3 If the alloy does not dissolve in the acids specified in 116.2, add amounts of HCl or HNO_3 , or mixtures and dilutions of these acids, or bromine and HCl in a ratio of 1 to 3 plus a few drops of HF, which are sufficient to dissolve the sample. When dissolution is complete, add 80 mL of $\text{H}_2\text{SO}_4(1+5)$, 5 mL of H_3PO_4 , and evaporate to light fumes. Rinse the cover walls of the beaker. Again evaporate to fumes and fume for 1 min. Cool, add 100 mL of water, and heat at 85 to 100°C until salts are dissolved.

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

116.5 Transfer the paper and residue to a platinum crucible, char the paper, and ignite at 850 to 900°C for 15 min. Cool, add sufficient $\text{H}_2\text{SO}_4(1+1)$ to moisten the residue, and then 3 to 5 mL of HF. Evaporate to dryness and heat at a gradually increasing rate until H_2SO_4 is removed. Fuse the residue with a minimum amount of either fused sodium hydrogen sulfate (sodium pyrosulfate— $\text{Na}_2\text{S}_2\text{O}_7$) or potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$). Cool the crucible, place in a 250-mL beaker, and dissolve the melt in 20 mL of $\text{H}_2\text{SO}_4(1+10)$. Remove the crucible, rinse with water, transfer the solution to the reserved filtrate (116.4), and dilute to 200 mL.

116.6 Add 5 mL of AgNO_3 solution and 20 mL of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution. If a beaker is used, cover it with a ribbed cover glass. Boil the solution 8 to 10 min, maintaining the volume at 200 mL by additions of hot water. If the color due to permanganate ions does not develop, or develops but does not persist, add 2 drops of KMnO_4 solution (179.4), 5 mL more of AgNO_3 solution, 20 mL more of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution, and boil for an additional 8 to 10 min. Add hot water to maintain the volume at 200 mL during this operation and the operations that follow in 116.7.

116.7 Reduce the permanganate ions as follows: Add 5 mL of HCl (1 + 3) and continue boiling for 10 min after the disappearance of permanganate color. If the permanganate ions have not been completely reduced or if a precipitate of 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 116.9. If vanadium is absent and the criteria of 116.2 are met, proceed as directed in 116.9. If vanadium is absent and the criteria of 116.2 are not met, or if potentiometric titration is preferred and vanadium is absent, proceed as directed in 116.10.

116.8 *Titration With Potassium Permanganate*—While swirling the flask, add 1 to 2 drops of 1,10 phenanthroline indicator solution and then add sufficient $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution to effect a change in color from clear green to pink. Add 1 to 2 mL more and record the buret reading to the nearest 0.01 mL. Using a 25-mL buret, back-titrate the excess ferrous ions with 0.05 N 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.

116.9 *Titration with Potassium Dichromate to the Diphenylamine Sulfonate End Point*—While swirling the flask, add $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution from a 25-mL buret until the disappearance of the yellow color. Then add 1 to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Add 2 drops of diphenylamine sulfonate indicator solution. Using another 25-mL buret, back-titrate the excess ferrous ions with 0.05 N $\text{K}_2\text{Cr}_2\text{O}_7$ standard solution. Add the $\text{K}_2\text{Cr}_2\text{O}_7$ 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.

116.10 *Titration with Potassium Dichromate and Potentiometric End Point Detection*—Stir the sample solution in the 600-mL beaker with a magnetic stirrer and insert the saturated calomel reference and platinum indicator electrodes. With the electrodes connected to the potentiometer apparatus, add from a 25-mL buret the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution while stirring until the yellow color disappears. Then add 1 to 2 mL in excess and record the buret reading to the nearest 0.01 mL. Using another 25-mL buret add 0.05 N $\text{K}_2\text{Cr}_2\text{O}_7$ standard solution in 0.1-mL increments recording the voltage after equilibrium for each increment. Inspect the data for the maximum voltage change between increments of standard dichromate solution (see 115.3). 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 115.3.

117. Calculation

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

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (20)$$

where:

- A = $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution, mL,
- B = normality of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution,
- C = KMnO_4 solution used, mL,
- D = normality of the KMnO_4 solution, and
- E = sample taken, g.

117.2 If $\text{K}_2\text{Cr}_2\text{O}_7$ was used, calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = [(AB - CD) \times 1.733]/E \quad (21)$$

where:

- A = $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution, mL,
- B = normality of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution,
- C = $\text{K}_2\text{Cr}_2\text{O}_7$ solution, mL,
- D = normality of $\text{K}_2\text{Cr}_2\text{O}_7$ solution, and
- E = sample taken, g.

118. Precision and Bias ¹⁶

118.1 *Precision*—Nine laboratories cooperated in testing this test method and obtained the data summarized in Table 12. Although samples at the lower and midrange of the scope were not tested, the precision data for other types of alloys using the test methods indicated in Table 12 should apply.

118.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be judged, however, by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing (see Table 12).

MOLYBDENUM BY THE ION EXCHANGE— 8-HYDROXYQUINOLINE GRAVIMETRIC METHOD

119. Scope

119.1 This test method covers the determination of molybdenum in concentrations from 1.5 to 30 %.

¹⁶ Supporting data are available from ASTM International Headquarters. Request RR:E03-1036.

TABLE 12 Statistical Information—Chromium

Test Specimen	Chromium Found, %	Repeatability (R_1 , E 173)	Reproducibility (R_2 , E 173)
1. No. 2, E 350	0.481	0.015	0.053
2. No. 2, E 351	1.96	0.10	0.16
3. No. 3, E 352	3.68	0.16	0.48
4. High-Temperature Alloy Waspalloy (NIST 349, 19.50Cr)	19.46	0.25	0.49
5. High-Temperature Alloy 41Co, 20Ni, 20Cr (NIST 168, 20.33Cr)	20.26	0.35	0.57

120. Summary of Test Method

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

121. Interferences

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

122. Apparatus

122.1 *Ion Exchange Column, Polystyrene*,¹⁷ approximately 400 mm long and 25 mm in inside diameter, the bottom tapered to a 2-mm bore outlet, fitted with a hosecock or stopcock to control the liquid flow. All parts of the apparatus must be constructed of HF-resistant plastic, such as polytetrafluoroethylene, polyethylene, or poly(vinyl chloride) (Note 42).

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

123. Reagents

123.1 *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.

123.2 *Ammonium Fluoride* (NH_4F).

123.3 *Ammonium Oxalate* ($\text{NH}_4\text{OCOCOONH}_4\text{H}_2\text{O}$).

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

123.5 *Eluent Solutions*—**Warning**—See Note 43.

NOTE 43—**Warning:** Hydrofluoric Acid causes serious burns which may not be immediately painful; read the paragraph about HF in the Safety Precautions section of Practices E 50.

123.5.1 *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.

123.5.2 *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.

123.5.3 *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.

123.5.4 *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.)

123.5.5 *Ammonium Fluoride/Ammonium Chloride Solution*—To 600 mL of ammonium chloride solution (240

¹⁷ Columns available from Ledoux & Co., Inc., Teaneck, NJ have been found satisfactory.

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

123.6 *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.

123.7 *Ion-Exchange Resin:*

123.7.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and of 200 to 400 nominal U.S. mesh size.¹⁸ To remove those beads greater than about 180 μm in diameter, as well as the very small diameter beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow at least 30 min for the beads to undergo maximum swelling. Place a No. 80 (180- μm) screen, 150 mm in diameter, over a 2-L beaker. Prepare a thin slurry of the resin and pour it into the screen. Wash the fine beads through the screen using a small stream of water. Discard the beads retained on the screen periodically to avoid undue clogging of the openings. When the bulk of the resin has settled in the 2-L beaker, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19) and stir vigorously. Allow the resin to settle for 4 to 6 min, decant 150 to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

123.7.2 Prepare the column as follows: Place a 10 to 20-mm layer of poly (vinyl chloride) plastic fiber¹⁹ in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 150 to 175 mm. Place a 20-mm layer of poly (vinyl chloride) plastic fiber on the top of the resin surface to protect it from being carried into suspension when the solutions are added. Add 100 to 125 mL of HCl (3 + 1) to the column. When the solution level is 5 to 10 mm above the top of the resin bed add 100 mL of HCl (1 + 9) to the column. Repeat this cycle twice more and finally wash the resin bed with 200 mL HCl (1 + 3) turning off the stopcock when the solution level is 10 to 20 mm above the top of the resin bed.

123.8 *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.

123.9 *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.

124. Procedure

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

124.2 Over a steambath or other low-temperature arrangement evaporate the solution to dryness. Cool, wash down the sides of the beaker with HCl (1 + 1) and again evaporate to dryness over low heat. Cool, add 5 mL HF and 25 mL water. Warm over low heat until all salts are dissolved (Note 44). Cool to room temperature and dilute to 100 mL with water.

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

124.3 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.

124.4 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 45).

NOTE 45—If insoluble molybdenum compounds are suspected or known to be present, halt the flow from the column when the washing of the paper is complete. Cautiously transfer the paper to a platinum crucible and ignite at 500°C (no higher) in a muffle furnace. Cool in a desiccator, add 1 g anhydrous sodium carbonate powder (Na_2CO_3) and fuse over a burner. Cool, add 20 mL water, and heat to dissolve the melt. Carefully acidify with dropwise additions of HCl (1 + 4) until effervescence ceases plus 10 drops excess. Evaporate to dryness, cool, add 20 mL HF/HCl/water (4 + 1 + 95), heat to dissolve, cool, and transfer this solution to the column. Resume the 2-mL/min flow from the column.

124.5 Continue to add HF/HCl/water (4 + 1 + 95) until 650 mL have been collected in the 800-mL plastic beaker (Note 46). Drain the solution to the top of the resin bed. Cautiously discard this solution.

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

¹⁸ AG1-X8, 200 to 400 mesh, chloride form, available from Bio-Rad Laboratories, Richmond, CA, has been found satisfactory.

¹⁹ Dynel plastic wool available from Union Carbide Corp., Chemical Division, Textile Fibers Dept., Needham Heights, MA, has been found satisfactory.

124.6 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 the solution to the top of the resin bed. Cautiously discard this solution (Note 47).

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

124.7 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 the solution to the top of the resin bed. Proceed with this eluent solution as described in 136.11.

124.8 Place an 800-mL plastic beaker under the column and elute 300 mL of HF/NH₄Cl/water (4 + 60 + 36) at a rate of 2 mL/min. Drain the solution to the top of the resin bed. Cautiously discard this solution (Note 48).

NOTE 48—This solution contains all the niobium.

124.9 Place an 800-mL plastic beaker under the column and elute 350 mL of NH₄F/NH₄Cl solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 49).

NOTE 49—This solution contains all the tantalum.

124.10 Place an 800-mL plastic beaker under the column and elute 100 mL of water, then 100 mL of HCl (1 + 3), stopping the flow when the liquid level is 10 to 20 mm above the resin bed. Cautiously discard the solution. The column is now ready to be stored for future use or to be preconditioned for another sample (124.3).

124.11 To the eluent containing the molybdenum (from 124.7) cautiously add 15 mL of H₂SO₄(1 + 1) and evaporate to light fumes on a sandbath or other carefully controlled heat source. (**Warning**—See Note 50.) Cool and cautiously rinse into a 400-mL borosilicate glass beaker. Heat to low volume (about 10 mL), cool, add 2 mL of HNO₃, and evaporate to strong fumes of SO₃.

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

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

124.13 Dilute to 100 mL. Heat to boiling and while hot, cautiously add NaOH solution (100 g/L) until litmus paper moistened with the solution just turns blue, then add 10 mL excess. Boil for 1 min. If a precipitate is present, filter through high-porosity, surface-hardened filter paper and wash the paper thoroughly with warm NaOH solution (10 g/L). Discard the paper. If no precipitate is present, proceed directly to 124.14.

124.14 If the molybdenum content of the solution or filtrate obtained in 124.13 is known to be less than 125 mg proceed to 124.15. If the molybdenum content of the solution or filtrate obtained in 124.13 is known to be greater than 125 mg, transfer the solution to a 250-mL volumetric flask, cool to room temperature, dilute to volume, and mix. Transfer a 100-mL aliquot by pipet to a 400-mL borosilicate beaker (**Precaution**—Note 51).

NOTE 51—**Precaution:** Minimize contact time of caustic solutions in volumetric glassware; wash glassware thoroughly immediately after use.

124.15 Adjust the volume of the solution in the 400-mL beaker to approximately 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).

124.16 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.

124.17 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 volume of about 100 mL.

124.18 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.

125. Calculation

125.1 Calculate the percent of molybdenum as follows:

$$\text{Molybdenum, \%} = [(A - B) \times C \times 23.05]/D \quad (22)$$

where:

A = weight of crucible plus precipitate, g,

B = weight of crucible, g,

C = aliquot factor (direct: *C* = 1, aliquot: *C* = 2.5), and

D = sample weight, g.

126. Precision and Bias

126.1 *Precision*—Seven laboratories cooperated in testing this test method and obtained the data summarized in Table 13. The unavailability of appropriate test specimens at the upper limit of the scope necessitated the inclusion of Test Material 5 which is a different class of material. While the testing range exceeds the upper limit of the scope, the data for Test Material 5 suggests the precision at the upper limit of the scope is adequate.

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

TABLE 13 Statistical Information—Molybdenum Ion Exchange—8-Hydroxyquinoline Gravimetric Method

Test Material	Molybdenum Found, %	Repeatability, (<i>R</i> ₁ , E 173 ⁴)	Reproducibility, (<i>R</i> ₂ , E 173 ⁴)
1. No. 1, E 351	1.48	0.070	0.086
2. Co-base alloy 43Co-21Ni-20Cr-5W-3Nb-2Fe-2Mn (NIST 167, 3.90 Mo-prov.)	3.92	0.219	0.250
3. No. 3, E 352	8.85	0.180	0.188
4. Ni-base alloy 16Cr-5Fe-4W-Bal. Ni (AMS 5388, 17 Mo—not certified)	17.49	0.285	0.641
5. Ferromolybdenum Balance Fe (FeMo-2, 53.20 Mo)	52.70	1.21	2.34

⁴This test method was performed in accordance with the 1980 version of Practice E 173.

IRON BY THE SILVER REDUCTION TITRIMETRIC METHOD

127. Scope

127.1 This test method covers the determination of iron in concentrations from 1.0 to 50.0 %.

128. Summary of Test Method

128.1 The sample is dissolved in HCl and HNO₃ and fumed in HClO₄. Iron is precipitated with NH₄OH in the presence of ammonium peroxydisulfate. The precipitate is dissolved in HCl. The resulting solution is adjusted to dilute acidity and passed through a silver reductor. After addition of a mixture of H₃PO₄ and H₂SO₄ and sodium diphenylaminesulfonate indicator the sample is titrated with standard potassium dichromate solution.

129. Interferences

129.1 The elements normally present do not interfere if their concentrations are less than the maximum amounts shown in 1.1.

130. Apparatus

130.1 Silver Reductor Column:

130.1.1 *Preparation*—Use a glass column (2-cm diameter and 25-cm length) fitted with a stopcock and a reservoir cup (approximately 100-mL capacity). Lightly insert a glass wool plug above the stopper. Fill the column with a slurry of silver powder in HCl (1 + 11) and drain the acid solution to within 1 cm of the top of the column to produce a silver metal column of 17-cm length. Wash the column with 150 mL of HCl (1 + 11), allowing the acid solution to drain at a rate of about 30 mL/min. Store the column with 1 to 2 cm of HCl (1 + 11) above the top of the metal.

130.1.2 *Regeneration*—When a dark grey area extends down 10 cm from the top of the metal column, the column must be regenerated as follows. Pass 150 mL of H₂SO₄(1 + 99) through the column at a rate of about 30 mL/min. Leave 1 cm of solution above the metal. Lower two zinc rods (15 cm long) attached to cotton strings until they contact the silver metal and let stand overnight. Pass 50 mL of H₂SO₄(1 + 1) through the column. Remove the zinc rods. Pass 150 mL of HCl (1 + 11) through the column at a rate of 30 mL/min. The column is now ready for reuse. Store the column with 1 to 2 cm of HCl (1 + 11) above the top of the metal.

NOTE 52—If the flow from the column slows significantly in use or if the liquid layer falls below the metal, the metal and glass wool must be removed and the column repacked. For this reason some laboratories may find it convenient to maintain two silver reductor columns.

131. Reagents

131.1 *Ammonium Peroxydisulfate*, [(NH₄)₂S₂O₈].

131.2 *Potassium Dichromate, Standard Solution* (0.10 N)—Dissolve 4.9032 g of National Bureau of Standards standard potassium dichromate in water, transfer to a 1-L volumetric flask, dilute to volume, and mix.

131.3 *Silver Powder*:

131.3.1 Use high-purity (99.9 % minimum purity) silver powder, 40 to 60 mesh.

131.3.2 *Alternate*: Dissolve 100 g of silver nitrate (AgNO₃) in 400 mL of water in a 600-mL beaker. Add 10 mL of HNO₃. Place two zinc rods (15 cm in length) crosswise in the solution and let stand overnight. Remove the rods, washing them into the solution. Decant the supernatant solution and discard it. Add 400 mL H₂SO₄(1 + 99) to the precipitated silver metal, stir well, allow to settle, and discard the supernatant solution. Repeat the decantation until the supernatant solution is clear. The precipitated silver may be transferred to the glass column in this form, then washed with HCl (1 + 11), as described in 130.1.1.

131.4 *Sodium Diphenylaminesulfonate Indicator Solution* (2 g/L)—Dissolve 0.20 g of sodium diphenylaminesulfonate in 100 mL of water. Store in a dark glass bottle.

131.5 *Sulfuric Acid—Phosphoric Acid Mixture*—Add 150 mL of H₃PO₄ to 400 mL of water, stirring well. Cool in a water bath and cautiously add 150 mL of H₂SO₄ while stirring well. Cool to room temperature and dilute to 1 L while cautiously cooling and stirring. Cool again to room temperature.

131.6 *Zinc Metal Rods* (approximately 8 mm in diameter and 150 mm in length), 99.9 % purity.

132. Procedure

132.1 Select a sample weight which is expected to contain 60 to 100 mg of iron (but not exceeding 3.0 g). Weigh the sample to the nearest 0.2 mg and transfer it to a 400-mL beaker. Add 25 mL of HCl and 25 mL of HNO₃ and heat to dissolve. Add 4 drops of HF to remove SiO₂. Cool and cautiously add 20 mL HClO₄. Heat to dense white fumes. Continue heating for 5 min to fully oxidize chromium.

132.2 Cool and dilute to 200 mL with water. Add NH₄OH slowly, while stirring, until the precipitate redissolves slowly, then add 25 mL additional NH₄OH and 2 g of ammonium peroxydisulfate. Boil carefully for 2 min and filter through a high-porosity filter paper, wash 5 times with NH₄OH (1 + 50). Discard the filtrate.

132.3 Place the original beaker under the funnel and dissolve the precipitate in 50 mL hot HCl (1 + 3). Wash the paper alternately with hot water and with hot HCl (1 + 3) until it is free of yellow iron color. Discard the paper.

NOTE 53—Several drops of hydrogen peroxide (H₂O₂), 30 %, added to the hot HCl (1 + 3) in the funnel will aid in dissolving the precipitate if a large amount of manganese is present.

132.4 Dilute the solution to 150 mL. Add NH₄OH cautiously, while stirring, until the precipitate redissolves slowly, then add 25 mL additional NH₄OH and 2 g ammonium peroxydisulfate. Boil carefully for 2 min and filter through a high-porosity filter paper,²⁰ wash 5 times with NH₄OH (1 + 50). Discard the filtrate.

132.5 Place the original beaker under the funnel and dissolve the precipitate in 50 mL hot HCl (1 + 3). Wash the paper alternately with hot water and with hot HCl (1 + 3) until it is free of yellow iron color. Discard the paper.

132.6 Boil the solution to reduce the volume to approximately 10 mL. Cool, dilute to 100 mL with water. Place a

²⁰ Whatman No. 541 has been found acceptable.

600-mL beaker under the silver reductor column. Pass the solution through the column at a rate of approximately 35 mL/min. Rinse the 400-mL beaker 3 times with HCl (1 + 11) and add the rinsings to the column. Drain the solution to within 1 cm of the top of the silver metal, then add 150 mL of HCl (1 + 11) to the column, collecting all the eluent at approximately 35 mL/min in the 600-mL beaker. Retain a 1-cm layer of HCl (1 + 11) above the silver.

132.7 Add 25 mL of the sulfuric acid-phosphoric acid mixture to the 600-mL beaker, then add 5 to 6 drops of sodium diphenylaminesulfonate indicator solution. Titrate immediately with potassium dichromate standard solution (0.10 N) to a permanent purple end point.

133. Calculation

133.1 Calculate the percent of iron as follows:

$$\text{Iron, \%} = [(0.55847) \times (A)/(B)] \quad (23)$$

where:

- A = K₂Cr₂O₇ standard solution (0.1000 N), mL, and
- B = sample taken, g.

134. Precision and Bias

134.1 *Precision*—Six laboratories cooperated in testing this test method and obtained data summarized in Table 14. The precision data demonstrates that this test method is applicable between 0.5 to 53 % iron well within the stated concentration range, in the scope.

134.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be judged by the agreement between the certified reference values and the corresponding arithmetic average obtained by inter-laboratory testing (see Table 14).

NIOBIUM BY THE ION EXCHANGE—CUPFERRON GRAVIMETRIC METHOD

135. Scope

135.1 This test method covers the determination of niobium (columbium) in concentrations from 0.5 to 6.0 %.

136. Summary of Test Method

136.1 Niobium is separated from interfering elements on an anion-exchange resin column using a sequence of HF+HCl

eluent solutions. The isolated niobium is precipitated with cupferron, ignited to the oxide, and weighed as Nb₂O₅.

137. Interferences

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

138. Apparatus

138.1 *Ion Exchange Column, Polystyrene*,²¹ approximately 400 mm long and 25 mm in inside diameter, the bottom tapered to a 2-mm bore outlet, fitted with a hosecock or stopcock to control the liquid flow. All parts of the apparatus must be constructed of HF-resistant plastic, such as polytetrafluoroethylene, polyethylene, or poly(vinyl chloride) (see 138.2).

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

139. Reagents

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

139.2 *Ammonium Fluoride (NH₄F)*.

139.3 *Boric Acid (N₃BO₃)*.

139.4 *Cupferron Solution*—Dissolve 30 g of cupferron in 400 mL of water. Dilute to 500 mL and filter through a medium-porosity filter paper. Store in a refrigerator. Prepare fresh weekly.

NOTE 54—**Warning:** Cupferron is a known carcinogen. Use protective equipment and work in an efficient exhaust hood.

139.5 *Eluent Solutions:*

NOTE 55—**Warning:** Hydrofluoric acid causes serious burns which may not be immediately painful; see the Safety Precautions section of Practices E 50.

139.5.1 *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.

139.5.2 *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.

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

139.5.4 *Hydrofluoric Acid/Ammonium Chloride/Water (4 + 60 + 36)*—To 600 mL of ammonium chloride solution (240 g/L) in a 1-L polyethylene graduated cylinder, add 40 mL HF; dilute to 1 L and mix. Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH₄Cl on a weight/volume basis.)

139.5.5 *Ammonium Fluoride/Ammonium Chloride Solution*—To 600 mL of ammonium chloride solution (240

TABLE 14 Statistical Information—Iron by the Silver Reduction Titrimetric Method

Sample	Certified, %	Iron Found %	Repeatability, (R ₁ , E 173 ^A)	Reproducibility, (R ₂ , E 173 ^A)
NIST 169 Ni Base	0.54	0.54	0.0179	0.0186
NIST 162a Cu-Ni	2.19	2.19	0.0317	0.0331
NIST 864 Inconel 600	9.6	9.62	0.0289	0.0688
NIST 161 Ni Base	15.01	15.00	0.1152	0.1260
NIST 348 A286	53.3	53.25	0.1653	0.2952

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

²¹ Columns available from Ledoux & Co., Inc., Teaneck, NJ have been found satisfactory.

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

139.6 Ion-Exchange Resin:

139.6.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and of 200 to 400 nominal U.S. mesh size.²² To remove those beads greater than about 180 μm in diameter, as well as the very small diameter beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow at least 30 min NH_4Cl for the beads to undergo maximum swelling. Place a No. 80 (180- μm) screen, 150 mm in diameter, over a 2-L beaker. Prepare a thin slurry of the resin and pour it into the screen. Wash the fine beads through the screen using a small stream of water. Discard the beads retained on the screen periodically to avoid undue clogging of the openings. When the bulk of the resin has settled in the 2-L beaker, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19) and stir vigorously. Allow the resin to settle for 4 to 6 min, decant 150 to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more, and reserve the coarser resin for the column preparation.

139.6.2 Prepare the column as follows: Place a 10 to 20-mm layer of plastic fiber²³ in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately 150 to 175 mm. Place a 20-mm layer of plastic fiber on the top of the resin surface to protect it from being carried into suspension when the solutions are added. Add 100 to 125 mL of HCl (3 + 1) to the column. When the solution level is 5 to 10 mm above the top of the resin bed add 100 mL of HCl (1 + 9) to the column. Repeat this cycle twice more and finally wash the resin bed with 200 mL HCl (1 + 3) turning off the stopcock when the solution level is 10 to 20 mm above the top of the resin bed.

140. Procedure

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

140.2 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 and add 5 mL of HF and 25 mL of water. Warm over low heat until all salts are dissolved (Note 56). Cool to room temperature and dilute to 100 mL with water.

NOTE 56—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

140.3 Drain the solution in the ion exchange column and pass 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.

140.4 Place an 800-mL plastic beaker under the column. Place a small plastic funnel holding a high-porosity hard-surfaced 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 57).

NOTE 57—If insoluble niobium 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 1000°C in a muffle furnace. Cool in a desiccator, add 1 g anhydrous sodium carbonate powder (Na_2CO_3) and fuse over a burner with a platinum lid. 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.

140.5 Continue to add HF/HCl/water (4 + 1 + 95) until 650 mL have been collected in the 800-mL plastic beaker (Note 58). Drain the solution to the top of the resin bed. Cautiously discard this solution.

NOTE 58—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper, and manganese.

140.6 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 the solution to the top of the resin bed. Cautiously discard this solution (Note 59).

NOTE 59—This solution contains all the tungsten, titanium, zirconium, and hafnium.

140.7 Place an 800-mL polytetrafluoroethylene beaker under the column and elute 500 mL of HF/HCl/water (20 + 25 + 55) at a rate of 2 mL/min. Drain the solution to the top of the resin bed. Cautiously discard this solution (Note 60).

NOTE 60—This solution contains all the molybdenum.

140.8 Place an 800-mL plastic beaker under the column and elute the niobium with 300 mL of HF/ NH_4Cl /water (4 + 60 + 36) at a rate of 2 mL/min. Drain the solution to the top of the resin bed. Proceed with this eluent as described in 6.11.

²² AG1-X8, 200 to 400 mesh, chloride form, which is available from Bio-Rad Laboratories, Richmond, CA, has been found satisfactory.

²³ SEF modacrylic fiber available from Monsanto Chemical Co., P.O. Box 2204, Decatur, AL 35609-2204, has been found satisfactory.

140.9 Place an 800-mL plastic beaker under the column and elute 350 mL of NH₄F/NH₄Cl solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 61).

NOTE 61—This solution contains all the tantalum.

140.10 Place an 800-mL plastic beaker under the column and elute 100 mL of water, then 100 mL of HCl (1 + 3), stopping the flow when the liquid level is 10 to 20 mm above the resin bed. Cautiously discard the solution. The column is now ready to be stored for future use or to be preconditioned for another sample (see 140.3).

140.11 Weigh 15 g of boric acid into a 250-mL beaker, add 150 mL HCl (1 + 1), and heat to boiling. When dissolved, add the hot solution cautiously, with stirring, to the eluent containing the niobium (from 140.8).

140.12 Cool the solution in an icebath to approximately 5°C. Add with stirring 15 mL of cold Cupferron solution for each 10 mg of niobium expected to be present in the sample. Filter the precipitate using low-porosity filter paper and a vacuum filtration apparatus. Police the beaker well and rinse with cold HCl (1 + 19). Wash the paper with cold HCl (1 + 19).

140.13 Transfer the paper to a 600-mL borosilicate glass beaker. Add 100 mL of HNO₃, then 60 mL of H₂SO₄(1 + 1), then 10 mL of HClO₄. Boil to reduce volume to approximately 50 mL, then heat strongly until organic material has been destroyed and heavy fumes of HClO₄ are evolved. Cool to room temperature, add 2 drops HF, and heat to strong fumes of HClO₄. Fume for 1 min.

140.14 Cool to room temperature. Dilute to 250 mL with water and cool in an ice bath. Add, with stirring, 15 mL of cold cupferron solution for each 10 mg of niobium expected to be present in the sample. Filter the precipitate using low-porosity filter paper and a vacuum filtration apparatus. Police the beaker well and rinse with cold HCl (1 + 19). Wash the paper with cold HCl (1 + 19).

140.15 Transfer the paper to a large tared platinum or porcelain crucible. Press a small filter paper down over the filter and precipitate and dry under a heat lamp in a hood for approximately 2 h.

140.16 Char in a muffle furnace in a hood at 550°C, then raise the temperature to 1000°C and ignite for 1 h. Cool in a desiccator and weigh as Nb₂O₅.

141. Calculation

141.1 Calculate the percentage of niobium as follows:

$$\text{Niobium, \%} = [(A - B) \times 69.904]/C \quad (24)$$

where:

- A = weight of crucible plus oxide, g,
- B = weight of crucible, g, and
- C = sample weight, g.

142. Precision and Bias²⁴

142.1 *Precision*—Six laboratories participated in the testing of this test method, providing seven sets of data. The obtained precision is summarized in Table 15.

142.2 *Bias*—The bias of this test method may be judged by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing, such as the data listed in Table 15.

**TANTALUM BY THE ION EXCHANGE—
PYROGALLOL SPECTROPHOTOMETRIC
METHOD**

143. Scope

143.1 This test method covers the determination of tantalum in concentrations from 0.03 to 1.0 %.

144. Summary of Test Method

144.1 Tantalum is separated from interfering elements on an anion-exchange resin column using a sequence of HF + HCl eluent solutions. The isolated tantalum is further purified with a cupferron separation. The ignited and fused residue is reacted with pyrogallol in the presence of ammonium oxalate and the optical density of the solution is measured at 415 nm.

145. Interferences

145.1 All interfering elements which are normally present are removed by the anion exchange separation and the cupferron precipitation.

²⁴ Supporting data are available from ASTM International Headquarters. Request RR:E01-1014.

TABLE 15 Statistical Information—Niobium

Test Material	Niobium Found, %	Repeat-ability (R ₁ , E 173)	Repro-ducibility (R ₂ , E 173)	Number of Labora-tories ^A
1. Nickel-base alloy (53Ni, 19Cr, 18Fe, 3Mo, 1Ti) (5.48 Nb, estimated)	5.47	0.14	0.15	7
2. BCS 351 (53Ni, 18Cr, 18Fe, 3Mo, 1Ti) (5.20 Nb, certified)	5.20	0.36	0.36	7
3. BAM 328-1 (42Co, 21Cr, 20Ni, 4Mo, 4W, 2Fe, 1Mn, 1Si) (3.61 ± 0.22 Nb, certified)	3.72	0.08	0.28	7
4. NIST SRM 168 (41Co, 20Cr, 20Ni, 4Mo, 4W, 3Fe, 2Mn, 1Si) (2.95 Nb, certified)	2.98	0.11	0.25	7
5. NIST SRM 1203 (76Ni, 12Cr, 4Al, 3Mo, 1Ti, 1Si) (1.00Nb, certified)	1.00	0.09	0.31	7
6. NIST SRM 123 (70Fe, 18Cr, 11Ni) (0.433Nb, certified)	0.46	0.08	0.15	6

^ANumber of independent data sets.

146. Apparatus

146.1 *Ion Exchange Column, Polystyrene*,²⁵ approximately 400 mm long and 25 mm in inside diameter, the bottom tapered to a 2-mm bore outlet, fitted with a hosecock or stopcock to control the liquid flow. All parts of the apparatus must be constructed of HF-resistant plastic, such as polytetrafluoroethylene, polyethylene, or poly(vinyl chloride) (Note 62).

NOTE 62—The ion exchange column system must be carefully assembled and checked to avoid possible leakage of solutions containing HF.

147. Reagents

147.1 *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.

147.2 *Ammonium Fluoride* (NH_4F).

147.3 *Ammonium Oxalate Solution* (40 g/L)—Dissolve 40 g of ammonium oxalate ($\text{NH}_4\text{OCOCOOH}_4$) in 800 mL of warm water, dilute to 1 L, and mix.

147.4 *Boric Acid* (H_3BO_3).

147.5 *Cupferron Solution* (60 g/L)—Dissolve 30 g cupferron in 400 mL of water. Dilute to 500 mL and filter through a medium-porosity filter paper. Store in a refrigerator. Prepare fresh weekly (see Note 63).

NOTE 63—**Warning:** Cupferron is a known carcinogen. Use protective equipment and work in an efficient exhaust hood.

147.6 *Eluent Solutions: Warning*—Hydrofluoric acid causes serious burns which may not be immediately painful; see the paragraph about HF in the Safety Precautions section of Practices E 50.

147.6.1 *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 HF-resistant plastic bottle.

147.6.2 *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.

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

147.6.4 *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.)

147.6.5 *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 a 1 L and mix. With narrow-range pH paper, verify that the pH is between 147.6 and 147.8. If it is above this range, adjust the solution with drop-wise additions of HF; if it is

below this range, adjust the solution with dropwise additions of NH_4OH . Store in an HF-resistant plastic bottle. (This solution is 14.4 % in NH_4Cl and 4.1 % in NH_4F on a weight/volume basis.)

147.7 *Potassium Pyrosulfate* ($\text{K}_2\text{S}_2\text{O}_7$)

147.8 *Pyrogallol Solution*—Dissolve 4.5 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 35 mL of HCl. Add 150 mL of hot water and 50 g of pyrogallol. Stir until dissolved, dilute to 250 mL with water and filter through low-porosity filter paper. Prepare fresh on day of use.

147.9 *Tantalum Standard Solution* (1 mL = 0.1 mg Ta)—Weigh 0.1000 g of high purity tantalum metal to a 400-mL poly(tetrafluoroethylene) beaker. Add 20 mL HF, then, cautiously dropwise HNO_3 while warming gently, until dissolved. Cool to room temperature, transfer to a 1-L plastic volumetric flask; dilute to the mark and mix. Store in a plastic bottle.

147.10 *Zirconium Carrier Solution* (1 mL = 5 mg Zr)—Weigh 0.27 g of zirconium oxide (ZrO_2) (purity:99.9 % min) into a 250-mL borosilicate glass beaker. Add 30 mL of $\text{H}_2\text{SO}_4(1+1)$ and heat to fumes. Fume for several minutes. Cool to room temperature. If not completely dissolved, cautiously add 1 mL of HCl and heat again to fumes; repeat until dissolved. Cool to room temperature and cautiously dilute to 40 mL with water. A more rapid alternate procedure is to weigh 1.7663 g of zirconium oxychloride-8 hydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) (purity:99.9 % min) into a 250-mL beaker, add 15 mL HCl to dissolve, transfer to a 100-mL volumetric flask and dilute to the mark and mix.

147.11 *Ion-Exchange Resin:*

147.11.1 Use an anion-exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a cross-linkage of 8 % and of 200 to 400 nominal U.S. mesh size.²⁶ To remove those beads greater than about 1800 μm in diameter, as well as the very small diameter beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow at least 30 min for the beads to undergo maximum swelling. Place a No. 80 (180- μm) screen, 150 mm in diameter, over a 2-L beaker.

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

147.11.2 Prepare the column as follows: Place a 10- to 20-mm layer of poly(vinyl chloride) plastic fiber²⁷ in the bottom of the column, and add a sufficient amount of the prepared resin to fill the column to a height of approximately

²⁵ Columns available from Ledoux & Co., Inc., Teaneck, NJ have been found satisfactory.

²⁶ AG1-X8, 200–400 mesh, chloride form, which is available from Bio-Rad Laboratories, Richmond, CA has been found satisfactory.

²⁷ SEF modacrylic fiber available from Monsanto Chemical Co., P.O. Box 2204, Decatur, AL 35609-2204 has been found satisfactory.

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

148. Preparation of Calibration Curve

148.1 Calibration Solutions:

148.1.1 Prepare six 600-mL borosilicate glass beakers, each containing 250 mL of H₂SO₄(1+8). Using pipets, transfer 1.00, 2.00, 5.00, 10.00, 15.00, and 20.00 mL of tantalum standard solution to the respective beakers. Add 2 mL of zirconium carrier solution, stir, and cool in an icebath.

148.1.2 Add, with stirring, 15 mL of cold cupferron solution. Filter the precipitate using low-porosity filter paper and a vacuum filtration apparatus. Police the beaker well and rinse with cold HCl (1+19). Wash the paper with cold HCl (1+19).

148.1.3 Transfer the papers to 50-mL platinum or porcelain crucibles. Dry for 1 h under a heat lamp in a hood. Char in a muffle furnace in a hood at 550°C. Raise the temperature to 650°C and ignite for 2 h. Cool in a desiccator.

148.1.4 Add 2.0 g of potassium pyrosulfate and fuse over a burner, swirling the crucible to ensure that all residue dissolves. Cool, transfer the crucibles to 150-mL beakers, add 50 mL of ammonium oxalate solution and heat to dissolve the fused salt. Rinse the crucibles into the beakers with ammonium oxalate solution. Cool solutions to room temperature.

148.2 *Reagent Blank Solution*—Prepare a 600-mL borosilicate glass beaker containing 250 mL of H₂SO₄(1+8). Add 2 mL of zirconium carrier solution, stir, cool in an icebath and treat as in 148.1.2-148.1.4.

148.3 Color Development:

148.3.1 Transfer 20.00 mL of pyrogallol solution by means of a pipet to each of six, 100-mL volumetric flasks. Transfer the solutions from 148.1 and 148.2 into the respective flasks, rinsing the beakers with ammonium oxalate solution into the flasks. Dilute each flask to the mark with ammonium oxalate solution and mix.

148.4 Photometry:

148.4.1 *Multiple-Cell Photometer*—Measure the cell correction using water in the absorption cells with a 1-cm light path and using a light band centered at 415 nm. Wait 15 min for full color development after final dilution, then using the test cell, take absorbance readings of the reagent blank solution and of the calibration solutions versus water in the reference cell. Readings shall be taken within 1 h of full color development.

148.4.2 *Single-Cell Photometer*—Wait 15 min for full color development after final dilution, then with water in the absorption cell, with a 1-cm light path, adjust the photometer to the initial setting, using a light band centered at 415 nm. While maintaining this adjustment, take the absorbance readings of the reagent blank solution and of the calibration solutions. Readings should be taken within 1 h of full color development.

148.5 *Calibration Curve*—Subtract the cell-corrected reagent blank absorbance reading from each of the cell-corrected

calibration solution absorbance readings. Plot these net absorbance readings against milligrams of tantalum per 100 mL of solution.

149. Procedure

149.1 Transfer 1 g of sample weighed to the nearest 0.1 mg of a 200-mL polytetrafluoroethylene beaker marked at the 100 mL level of the outside. Add 10 mL of HF and cover with a polytetrafluoroethylene watchglass. Warm the solution with low heat and cautiously add HNO₃ in 1-mL increments allowing the reaction to subside between additions. High chromium samples may also require cautious dropwise additions of HCl. When dissolution is complete, cool the beaker, remove the cover with platinum-tipped tongs and cautiously rinse it into the solution with water.

149.2 Over a steambath or other low temperature arrangement evaporate the solution to dryness. Cool, wash down the sides of the beaker with HCl (1+1) and again evaporate to dryness over low heat. Cool, add 5 mL HF and 25 mL water. Warm over low heat until all salts are dissolved (Note 64). Cool to room temperature and dilute to 100 mL with water.

NOTE 64—It may be necessary to add additional water and to stir cautiously with a polytetrafluoroethylene stirring rod to completely dissolve all salts.

149.3 Drain the solution in the ion exchange column by passing 100 mL of HF/HCl water (4+1+9) 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.

149.4 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 65).

NOTE 65—If insoluble tantalum 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 1000°C in a muffle furnace. Cool in a desiccator, add 1 g anhydrous sodium carbonate powder (Na₂CO₃) and fuse over a burner. Cool, add 20 mL water and heat to dissolve the melt. Carefully acidify with dropwise additions of HCl (1+4) until effervescence ceases plus 10 drops excess. Evaporate to dryness, cool, add 20 mL HF/HCl/water (4+1+95), heat to dissolve, cool, and transfer this solution to the column. Resume the 2 mL/min flow from the column.

149.5 Continue to add HF/HCl/water (4+1+95) until 650 mL have been collected in the 800 mL plastic beaker (Note 66). Drain solution to the top of the resin bed. Cautiously discard this solution.

NOTE 66—This solution contains all the iron, chromium, nickel, cobalt, aluminum, copper, and manganese.

149.6 Place an 800-mL plastic beaker under the column and dilute 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 67).

NOTE 67—This solution contains all the tungsten, titanium, zirconium and hafnium.

149.7 Place an 800-mL polytetrafluoroethylene beaker under the column and elute 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. Cautiously discard this solution (Note 68).

NOTE 68—This solution contains all the molybdenum.

149.8 Place an 800-mL plastic beaker under the column and elute 300 mL of HF/NH₄Cl/water (4+60+36) at a rate of 2 mL/min. Drain solution to the top of the resin bed. Cautiously discard this solution (Note 69).

NOTE 69—This solution contains all the niobium.

149.9 Place an 800-mL plastic beaker under the column and elute the tantalum with 350 mL of NH₄F/NH₄Cl solution at a rate of 2 mL/min. Drain solution to the top of the resin bed. Proceed with this eluent solution as described in 149.11. Take 350 mL of NH₄F/NH₄Cl solution and proceed with it as a blank, as described in 149.11.

149.10 Place an 800-mL plastic beaker under the column and elute 100 mL of water, then 100 mL of HCl (1 + 3); stopping the flow when the liquid level is 10 to 20 mm above the resin bed. Cautiously discard the solution. The column is now ready to be stored for future use or to be preconditioned for another sample (see section 7.3).

149.11 Weight 8 g of boric acid into a 250-mL beaker, add 150 mL HCl (1+1) and heat to boiling. When dissolved, add the hot solution cautiously, with stirring, to the eluent containing the tantalum (see 7.9). If the test sample is estimated to contain less than 2 mg of tantalum, add 2 mL of zirconium carrier solution and proceed to 149.12. If the test sample is estimated to contain between 2 and 15 mg of tantalum, transfer the sample to a 500-mL plastic volumetric flask, dilute to the mark and mix. Transfer by means of a pipet 50.00 mL of this solution to an 800-mL plastic beaker, add 2 mL of zirconium solution and dilute to 500 mL. Proceed as described in 149.12.

149.12 Cool the solution in an icebath to approximately 5°C. Add, with stirring, 15 mL of cold cupferron solution. Filter the precipitate using low-porosity filter paper and a vacuum filtration apparatus. Police the beaker well and rinse with cold HCl (1+19). Wash the paper with cold HCl (1+19).

149.13 Transfer the paper to a 50-mL platinum crucible. Dry for 1 h under a heat lamp in a hood. Char in a muffle

furnace in a hood at 550°C. Raise the temperature to 650°C and ignite for 2 h. Cool in a desiccator.

149.14 Add 2.0 g of potassium pyrosulfate and fuse over a burner, swirling the crucible to ensure that all the residue dissolves. Cool, transfer the crucible to a 150-mL beaker, add 50 mL of ammonium oxalate solution and heat to dissolve the fused salt. Rinse crucible into the beaker with ammonium oxalate solution. Cool solution to room temperature.

149.15 Transfer 20.00 mL of pyrogallol solution by means of a pipet into a 100-mL volumetric flask. Add the sample extract and rinse the beaker with ammonium oxalate solution into the flask. Dilute to the mark with ammonium oxalate solution and mix.

149.16 *Reagent Blank Solution*—Treat the blank described in 149.9 exactly the same as described in 149.11-149.15.

149.17 *Photometry*—Wait 15 min for full color development after the final dilution, then measure the absorbance of the reagent blank and test solutions versus water in cell-blank corrected 1-cm cuvettes as directed in 148.4.

150. Calculation

150.1 Subtract the cell-corrected reagent blank (149.16) absorbance from the cell-corrected test solution absorbance and convert this net absorbance to milligrams of tantalum using the calibration curve. Calculate the percentage of tantalum as follows:

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

where:

- A = tantalum found in 100 mL of the final test solution, mg,
- B = aliquot factor (direct = 1.0; aliquot = 10.0), and
- C = sample weight, g.

151. Precision and Bias ²⁸

151.1 *Precision*—Six laboratories participated in the testing of this method, providing seven sets of data. The obtained precision is summarized in Table 16.

151.2 *Bias*—The bias of this test method may be judged by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing, such as the data listed in Table 16.

²⁸ Supporting data are available from ASTM International Headquarters. Request RR:E01-1014.

TABLE 16 Statistical Information—Tantalum

Test Material	Tantalum Found, %	Repeatability (R_1 , E 173 – 92)	Reproducibility (R_2 , E 173 – 92)	Number of Laboratories ^A
1. NIST SRM 168 (41Co, 20Cr, 20Ni, 4Mo, 4W, 3Fe, 2Mn, 1Si) (0.95Ta, certified)	0.94	0.18	0.21	7
2. NIST 1203 (76Ni, 12Cr, 4Al, 3Mo, 1Ti, 1Si) (0.34Ta, certified)	0.35	0.10	0.10	7
3. BAM 328-1 (42Co, 21Cr, 20Ni, 4Mo, 4W, 2Fe, 1Mn, 1Si) (0.18Ta, certified)	0.17	0.04	0.08	7
4. NIST SRM 123 (70Fe, 18Cr, 11Ni) (0.027Ta, certified)	0.028	0.007	0.009	5
5. Nickel-base alloy (53Ni, 19Cr, 18Fe, 3Mo, 1Ti) (0.012Ta, estimated)	0.010	0.006	0.008	4

^ANumber of independent data sets.

152. Keywords

152.1 aluminum; chromium; cobalt; cobalt-base alloys; copper; high temperature alloys; iron; manganese; molybdenum; nickel; nickel-base alloys; niobium; silicon; sulfur; tantalum; tin

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