Designation: E1473 – 22

Standard Test Methods for Chemical Analysis of Nickel, Cobalt, and High-Temperature Alloys[1]

This standard is issued under the fixed designation E1473; 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	Composition 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:

1.3 Other test methods applicable to the analysis of nickel alloys that may be used in lieu of or in addition to this method are E1019, E1834, E1835, E1917, E1938, E2465, E2594, E2823.

1.4 Some of the composition 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 *Units*—The values stated in SI units are regarded as standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific caution and hazard statements are given in Section 7 and in 13.4, 15.1.1, 15.1.2, 21.2, 22.3, 57.3, 84.2, 114.5, 115.14, 130.4, 130.5, 138.5, and 138.6.

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

[1] These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.08 on Ni and Co and High Temperature Alloys.

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2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1997)[3]

E350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron

E351 Test Methods for Chemical Analysis of Cast Iron—All Types

E352 Test Methods for Chemical Analysis of Tool Steels and Other Similar Medium- and High-Alloy Steels

E353 Test Methods for Chemical Analysis of Stainless, Heat-Resisting, Maraging, and Other Similar Chromium-Nickel-Iron Alloys

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

E1019 Test Methods for Determination of Carbon, Sulfur, Nitrogen, and Oxygen in Steel, Iron, Nickel, and Cobalt Alloys by Various Combustion and Inert Gas Fusion Techniques

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1834 Test Method for Analysis of Nickel Alloys by Graphite Furnace Atomic Absorption Spectrometry

E1835 Test Method for Analysis of Nickel Alloys by Flame Atomic Absorption Spectrometry

E1917 Test Method for Determination of Phosphorus in Nickel, Ferronickel, and Nickel Alloys by Phosphovanadomolybdate Spectrophotometry

E1938 Test Method for Determination of Titanium in Nickel Alloys by Diantipyrylmethane Spectrophotometry

E2465 Test Method for Analysis of Ni-Base Alloys by Wavelength Dispersive X-Ray Fluorescence Spectrometry

E2594 Test Method for Analysis of Nickel Alloys by Inductively Coupled Plasma Atomic Emission Spectrometry (Performance-Based)

E2823 Test Method for Analysis of Nickel Alloys by Inductively Coupled Plasma Mass Spectrometry (Performance-Based)

2.2 *Other Documents:*[4]

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

3. Terminology

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

4. Significance and Use

4.1 These test methods for the chemical analysis of metals and alloys are primarily intended as referee methods to test such materials for compliance with compositional specifications, particularly those under the jurisdiction of Committee B02 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 E882.

5. Apparatus, Reagents, and Instrumental Practice

5.1 *Apparatus*—Specialized apparatus requirements are listed in the "Apparatus" section in each test method.

5.1.1 In the methods specifying spectrophotometric testing, the cells utilized to contain the reference material and sample solutions in spectrophotometers are referred to as "absorption cells." Please note that the radiant energy passed through the cells can be measured as absorbance or transmittance. These methods refer to absorbance measurements. Refer to Practices E60 for details.

5.2 *Reagents:*

5.2.1 *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 sections.

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

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

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

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

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

[5] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC, www.acs.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, http://www.usp.org.

6. Interlaboratory Studies and Rounding Calculated Values

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

6.2 Rounding of test results obtained using this Test Method shall be performed in accordance with Practice E29, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

7. Hazards and Sampling

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

7.2 *Sampling*—For procedures to sample the material, refer to Practices E55 and E88.

MANGANESE BY THE METAPERIODATE SPECTROPHOTOMETRIC METHOD

8. Scope

8.1 This test method covers the determination of manganese 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 in amounts greater than 0.5 %, is kept in solution with H_3PO_4. Solutions of the samples are fumed with $HClO_4$ so that the effect of periodate is limited to the oxidation of manganese. Spectrophotometric measurements are made at 545 nm.

10. Concentration Range

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

NOTE 1—This 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 $HClO_4$ treatment, which is used in the procedure, yields solutions which can be highly colored due to the presence of hexavalent chromium 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 spectrophotometers are used: Select a filter with maximum transmittance between 545 nm and 565 nm. The filter must transmit not more than 5 % of its maximum at a wavelength shorter than 530 nm. The band width of the filter should be less than 30 nm when measured at 50 % of its maximum transmittance. Similar restrictions apply with respect to the wavelength region employed when other "wide-band" instruments are used.

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 HNO_3 by heating. Cool, dilute to volume, and mix. Using a pipet, transfer 20 mL to a 500-mL volumetric flask, dilute to volume, and mix.

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

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

13.4 *Water, Pretreated with Metaperiodate*—Add 20 mL of KIO_4 solution to 1 L of water, mix, heat at not less than 90 °C for 20 min to 30 min, and cool. Use this water to dilute solutions to volume that have been treated with KIO_4 solution to oxidize manganese, and thus avoid reduction of permanganate ions by any reducing agents in the untreated water. (**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 KIO_4 solution, and heat the solutions at not less than 90 °C for 20 min to 30 min (Note 2). Cool, dilute to volume with pretreated water, and mix.

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

14.4 *Spectrophotometry:*

14.4.1 *Multiple-Cell Spectrophotometer*—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 545 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions (14.1) versus the reference solution (14.2).

14.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (14.2) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at 545 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions (14.1).

14.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against the milligrams of manganese per 50 mL of solution.

15. Procedure

15.1 *Test Solutions*—Select and weigh a sample as follows.

Manganese, %	Sample Mass, g	Tolerance in Sample Mass, 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*—(**Warning—**See Practices E50 for details pertaining to the special hazards associated with the use of $HClO_4$.)

15.1.1.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO_3 as needed to hasten dissolution, and then add 3 mL to 4 mL in excess. When dissolution is complete, cool, then add 10 mL of $HClO_4$, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, and digest if necessary to dissolve the salts. Cool and transfer the solution to a 100-mL volumetric flask. Proceed to 15.1.3.

15.1.1.2 For samples whose dissolution is hastened by HF, add 8 mL to 10 mL of HCl (1 + 1), and heat. Add HNO_3 and a few drops of HF as needed to hasten dissolution, and then add 3 mL to 4 mL of HNO_3. When dissolution is complete, cool, then add 10 mL of $HClO_4$, evaporate to fumes to oxidize chromium, if present, and to expel HCl. Continue fuming until salts begin to separate. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to either a 100-mL or 500-mL volumetric flask as indicated in 15.1. Proceed to 15.1.3.

15.1.2 *For Samples Containing More Than 0.5 % Tungsten*—(**Warning—**See Practices E50 for details pertaining to the special hazards associated with the use of $HClO_4$.)

15.1.2.1 To dissolve samples that do not require HF, add 8 mL to 10 mL of H_3PO_4, 10 mL of $HClO_4$, 5 mL to 6 mL of H_2SO_4, and 3 mL to 4 mL of HNO_3. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 min to 12 min or until the chromium is oxidized and the HCl is expelled but avoid heating to fumes of SO_3. Cool, add 50 mL of water, and digest if necessary to dissolve the salts. Transfer the solution to either a 100-mL or 500-mL volumetric flask as directed in 15.1. Proceed to 15.1.3.

15.1.2.2 For samples whose dissolution is hastened by HF, add 8 mL to 10 mL of H_3PO_4, 10 mL of $HClO_4$, 5 mL to 6 mL of H_2SO_4, 3 mL to 4 mL of HNO_3, and a few drops of HF. Heat moderately until the sample is decomposed, and then heat to copious white fumes for 10 min to 12 min or until the chromium is oxidized and the HCl is expelled, but avoid heating to fumes of SO_3. Cool, add 50 mL of water, digest if necessary to dissolve the salts, cool, and transfer the solution to a 100-mL 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 mL 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 HNO_3-H_3PO_4 mixture, and heat the solution at not less than 90 °C for 20 min to 30 min (Note 2). Cool, dilute to volume (with untreated water), and mix.

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 *Spectrophotometry*—Establish the cell corrections with the reagent blank Reference solution to be used as a reference solution for background color solutions. Take the spectrophotometric absorbance 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 spectrophotometric absorbance 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:

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

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 mass 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*—The accuracy of this test method has been deemed satisfactory based upon the data for the certified reference materials in Table 1. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

SILICON BY THE GRAVIMETRIC METHOD

18. Scope

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

19. Summary of Test Method

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

20. Interferences

20.1 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. However, since no boron steels were tested, this special treatment was not evaluated and is not described in this test method.

21. Reagents

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

21.2 *$HClO_4$*—(**Warning—**See Practices E50 for details pertaining to the special hazards associated with the use of $HClO_4$.)

TABLE 1 Statistical Information—Manganese – Metaperiodate Spectrophotometric Method

Test Specimen	Manganese Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Nickel alloy, 77Ni-20Cr (NIST 169, 0.073 % Mn, certified)	0.074	0.002	0.008
2. High-temperature alloy, 68Ni-14Cr-7Al-6Mo (NIST 1205, 0.29 % Mn, not certified)	0.289	0.007	0.026
3. Cobalt alloy, 41Co-20Ni-20Cr-4Mo-4W (NIST 168, 1.50 % Mn, not certified)	1.49	0.03	0.08
4. Stainless steel 18Cr-9Ni (NIST 101e, 1.77 % Mn, certified)	1.79	0.07	0.07

21.2.1 Select a lot of $HClO_4$ that contains not more than 0.0002 % silicon for the analysis of samples containing silicon in the range from 0.02 % to 0.10 % and not more than 0.0004 % silicon for samples containing more than 0.10 % by determining duplicate values for silicon as directed in 21.2.2 – 21.2.6.

21.2.2 Transfer 15 mL of $HClO_4$ (Note 3) to each of two 400-mL beakers. To one of the beakers transfer an additional 50 mL of $HClO_4$. Using a pipet, transfer 20 mL of sodium silicate solution (1 mL = 1.00 mg Si) to each of the beakers. Evaporate the solutions to fumes and heat for 15 min to 20 min at such a rate that $HClO_4$ refluxes on the sides of the beakers. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C).

NOTE 3—The 15-mL addition of $HClO_4$ can be from the same lot as the one to be tested. Once a lot has been established as having less than 0.0002 % silicon, it should preferably be used for the 15-mL addition in all subsequent tests of other lots of $HClO_4$.

21.2.3 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. Rinse the papers and precipitates alternately with 3-mL to 5-mL portions of hot HCl (1 + 19) and hot water, for a total of six times. Finally, rinse the papers twice with H_2SO_4 (1 + 49). Transfer the papers to platinum crucibles.

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

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

21.2.6 Calculate the percentage of silicon as follows:

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

where:

A = initial mass of crucible plus impure SiO_2 when 65 mL of $HClO_4$ was taken, g,
B = final mass of crucible plus impurities when 65 mL of $HClO_4$ was taken, g,
C = final mass of crucible plus impure SiO_2 when 15 mL of $HClO_4$ was taken, g,
D = final mass of crucible plus impurities when 15 mL of $HClO_4$ was taken, g, and
E = nominal mass (80 g) of 50 mL of $HClO_4$.

21.3 *Sodium Silicate Solution* (1.00 mg/mL Si)—Transfer 11.0 g of sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) to a 400-mL beaker. Add 150 mL of water and dissolve the salt. Filter through a medium paper, collecting the filtrate in a 1-L volumetric flask, dilute to volume, and mix. Store in a polyethylene bottle. Use this solution to determine the suitability of the $HClO_4$.

21.4 *Tartaric Acid Solution* (20.6 g/L)—Dissolve 20.6 g of tartaric acid ($C_4H_6O_6$) in water, dilute to 1 L, and filter.

21.5 *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 absorb silicon.

22. Procedure

22.1 Select and weigh a sample as follows.

Silicon, %	Sample Mass, g	Tolerance in Sample Mass, mg	Dehydrating Acid, mL H_2SO_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

22.1.1 Transfer the sample to a 400-mL beaker or a 300-mL porcelain casserole. Proceed as directed in 22.2 or 22.3.

22.2 *H_2SO_4 Dehydration, if tungsten is greater than 0.5 %.*

22.2.1 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, that are sufficient to dissolve the sample; and then add the H_2SO_4 (1 + 4) as specified in 21.1, and cover. Heat until dissolution is complete. Remove and rinse the cover glass; substitute a ribbed cover glass.

22.2.2 Evaporate until salts begin to separate; at this point evaporate the solution rapidly to the first appearance of fumes and fume strongly for 2 min to 3 min. Cool sufficiently, and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat, if necessary, but do not boil. Proceed immediately as directed in 22.4.

22.3 *$HClO_4$ Dehydration, if tungsten is less than 0.5 % or use 22.2.* (**Warning—**See Practices E50 for details pertaining to the special hazards associated with the use of $HClO_4$.)

22.3.1 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample, and cover. Heat until dissolution is complete. Add HNO_3 to provide a total of 35 mL to 40 mL, followed by $HClO_4$ as specified in the table in 22.1. Remove and rinse the cover glass; substitute a ribbed cover glass.

22.3.2 Evaporate the solution to fumes and heat for 15 min to 20 min at such a rate that the $HClO_4$ refluxes on the sides of the container. Cool sufficiently and add 100 mL of water (40 °C to 50 °C). Stir to dissolve the salts and heat to boiling. If the sample solution contains more than 100 mg of chromium, add, while stirring, 1 mL of tartaric acid solution for each 25 mg of chromium.

22.4 Add paper pulp and filter immediately, on a low-ash 11-cm medium-porosity filter paper. Collect the filtrate in a 600-mL beaker. Transfer the precipitate to the paper and scrub the container thoroughly with a rubber-tipped rod. Rinse the paper and precipitate alternately with 3-mL to 5-mL portions of hot HCl (1 + 19) and hot water until iron salts are removed but for not more than a total of ten rinsings. If 22.3 was followed, rinse the paper twice more with H_2SO_4 (1 + 49), but do not collect these rinsings in the filtrate; discard the rinsings. Transfer the paper to a platinum crucible and reserve.

22.5 Add 15 mL of HNO_3 to the filtrate, stir, and evaporate as directed either in 22.2 or 22.3, depending upon the dehydrating acid used. Filter immediately, using a low-ash 9-cm 100-porosity filter paper, and rinse as directed in 22.4.

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

22.7 Add enough H_2SO_4 (1 + 1) to moisten the impure silica (SiO_2), and add 3 mL to 5 mL of HF. Evaporate to dryness and then heat at a gradually increasing rate until H_2SO_4 is removed. Ignite at 1100 °C to 1150 °C for 15 min, cool in a desiccator, and weigh. If the sample contains more than 0.5 % tungsten, ignite at 750 °C instead of 1100 °C to 1150 °C after volatilization of SiO_2.

23. Calculation

23.1 Calculate the percent of silicon as follows:

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

where:

A = initial mass of crucible and impure SiO_2, g,
B = final mass of crucible and residue, g, and
C = sample used, g.

24. Precision and Bias

24.1 *Precision*—Eleven laboratories cooperated in testing this test method and obtained the data summarized in Table 2. A sample with silicon content near the upper limit of the scope was not available for testing.

24.2 *Bias*—No information on the bias of this test method is known because at the time of the interlaboratory study, suitable reference materials were not available. The user of this method is encouraged to employ accepted reference materials, if available, to determine the presence or absence of bias.

COBALT BY THE ION-EXCHANGE-POTENTIOMETRIC TITRATION METHOD

25. Scope

25.1 This test method covers the determination of cobalt from 2 % to 75 %.

26. Summary of Test Method

26.1 Cobalt is separated from interfering elements by selective elution from an anion-exchange column using HCl. The

TABLE 2 Statistical Information—Silicon – Gravimetric Method

Test Specimen	Silicon Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
$HClO_4$ Dehydration			
1. Ni-base alloy 75Ni-12Cr-6Al-4Mo-2Cb-0.7Ti	0.029	0.006	0.026
H_2SO_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

cobalt is oxidized to the trivalent state with ferricyanide, and the excess ferricyanide is titrated potentiometrically with cobalt solution.

27. Interferences

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

28. Apparatus

28.1 *Ion-Exchange Column,* approximately 25 mm in diameter and 300 mm in length, tapered at one end, and provided with a stopcock to control the flow rate, and a second, lower stopcock to stop the flow. A Jones Reductor (Fig. 1), may be adapted to this method. It consists of a column 19 mm in diameter and 250 mm in length, of 0.853-mm to 0.599-mm (20-mesh to 30-mesh) amalgamated zinc. To amalgamate the zinc, shake 800 g of zinc (as free of iron as possible) with 400 mL of $HgCl_2$ solution (25 g/L) in a 1-L flask for 2 min. Rinse several times with H_2SO_4 (2 + 98), and then thoroughly with water. The reductor, when idle, should always be kept filled with distilled water to above the top of the zinc. A reservoir for the eluants may be added at the top of the column.

28.2 *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 follow the principle 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.

28.2.1 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 pH meters are also suitable for potentiometric titrations.

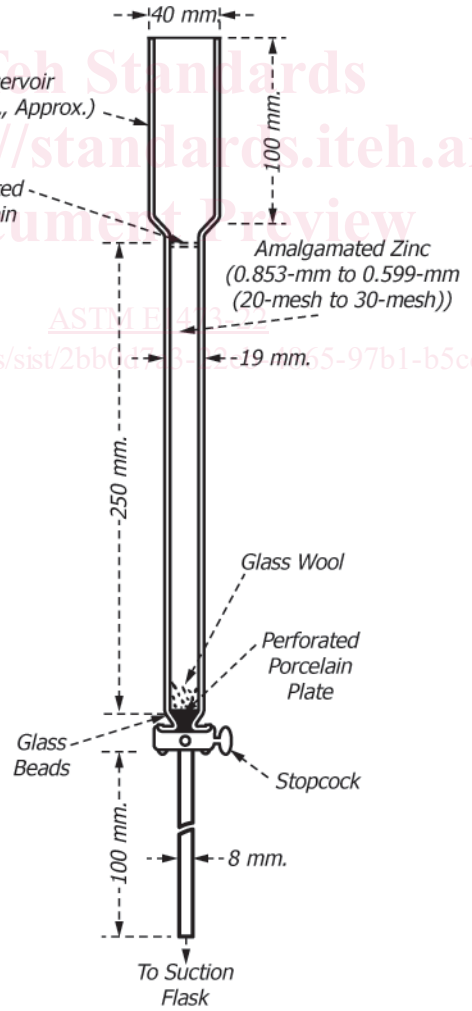

FIG. 1 Jones Reductor

28.2.2 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.

28.3 Platinum and saturated calomel electrodes.

29. Reagents

29.1 *Ammonium Citrate Solution* (200 g/L).

29.2 *Bromine.*

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

29.3.1 Dry a weighing bottle in an oven at 130 °C for 1 h, cool in a desiccator, and weigh. Transfer 3.945 g of cobalt sulfate ($CoSO_4$)[6] that has been heated at 550 °C for 1 h to the weighing bottle. Dry the bottle and contents at 130 °C for 1 h, cool in desiccator, stopper the bottle, and weigh. The difference in mass is the amount of $CoSO_4$ taken. Transfer the weighed $CoSO_4$ to a 400-mL beaker, rinse the weighing bottle with water, and transfer the rinsings to the beaker. Add 150 mL of water and 20 mL of HNO_3, and heat to dissolve the salts. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

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

Cobalt, mg/mL = mass of $CoSO_4$, g, × 0.38026

29.4 *Ion-Exchange Resin:*[7]

29.4.1 Use an anion exchange resin of the alkyl quaternary ammonium type (chloride form) consisting of spherical beads having a nominal cross-linkage of 8 %, and 0.075-mm to 0.037-mm (200-nominal to 400-nominal mesh) size. To remove those beads greater than about 180 µm in diameter as well as the excessively fine beads, treat the resin as follows: Transfer a supply of the resin to a beaker, cover with water, and allow sufficient time (at least 30 min) for the beads to undergo maximum swelling. Place a 180-µm (No. 80) screen, 150 mm in diameter over a 2-L beaker. Prepare a thin slurry of the resin and pour it onto the screen. Rinse the fine beads through the screen, using a small stream of water. Discard the beads retained on the screen, periodically, if necessary, to avoid undue clogging of the openings. When the bulk of the collected resin has settled, decant the water and transfer approximately 100 mL of resin to a 400-mL beaker. Add 200 mL of HCl (1 + 19), stir vigorously, allow the resin to settle for 4 min to 6 min, decant 150 mL to 175 mL of the suspension, and discard. Repeat the treatment with HCl (1 + 19) twice more and reserve the coarser resin for the column preparation.

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

NOTE 4—The maximum limits of 0.125 g of cobalt and a 0.500 g sample (30.1) in the sample solution consider the exchange capacity of the resin, the physical dimensions of the column, and the volume of eluants.

29.5 *Mercuric Chloride Solution,* $HgCl_2$ (25g/L).

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

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

29.6.2 Calculate the cobalt equivalent as follows (29.6.2.1):

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

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.

29.6.2.1 Duplicate or triplicate values should be obtained for the cobalt equivalent. The values obtained should check within 1 g/Kg to 2 g/Kg.

30. Procedure

30.1 Proceed as directed in 30.2 – 30.7, using 0.50 g samples for cobalt compositions not greater than 25%; at higher compositions, use samples that represent between 100 mg and 125 mg of cobalt weighed to the nearest 0.1 mg.

30.2 Transfer a 0.50-g sample to a 150-mL beaker. Add 20 mL of a mixture of five parts of HCl and one part of HNO_3 (30.2.1). Cover the beaker and digest at 60 °C to 70 °C until the sample is decomposed. Rinse and remove the cover. Place a ribbed cover glass on the beaker and evaporate the solution nearly to dryness, but do not bake. Cool, add 20 mL of HCl (7 + 5), and digest at 60 °C to 70 °C until salts are dissolved (approximately 10 min).

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

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

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

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

30.3 Cool to room temperature and transfer the solution to the ion-exchange column. Place a beaker under the column and open the lower stopcock. When the solution reaches a level 10 mm to 20 mm above the resin bed, rinse the original beaker with 5 mL to 6 mL of HCl (7 + 5) and transfer the rinsings to the column. Repeat this at 2-min intervals until the beaker has been rinsed four times. Rinse the upper part of the column with HCl (7 + 5) two times or three times and allow the level to drop to 10 mm to 20 mm above the resin bed each time. Maintain the flow rate at not more than 3.0 mL/min and add HCl (7 + 5) to the column until a total of 175 mL to 185 mL of solution (sample solution and rinsings) containing mainly chromium, manganese and nickel is collected (30.3.1). When the solution in the column reaches a level 10 mm to 20 mm above the resin bed, discard the eluate and then use a 400-mL beaker for the collection of the cobalt eluate.

30.3.1 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.

30.4 Add HCl (1 + 2) to the column and collect 165 mL to 175 mL of the solution while maintaining the 3.0-mL/min flow rate. Reserve the solution. If the sample solution did not contain more than 0.200 g of iron, substitute a 250-mL beaker and precondition the column for the next sample as follows: Drain the remaining solution in the column to 10 mm to 20 mm above the resin bed, pass 35 mL to 50 mL of HCl (7 + 5) through the column until 10 mm to 20 mm of the solution remains above the resin bed, then close the lower stopcock. If the sample solution contained more than 0.200 g of iron, or if the column is not to be used again within 3 h, discard the resin and recharge the column as directed in 29.4.

30.5 Add 30 mL of HNO_3 and 15 mL of $HClO_4$ to the solution from 30.4 and evaporate to fumes of $HClO_4$. Cool, add 25 mL to 35 mL of water, boil for 1 min to 2 min, cool, and add 10 mL of ammonium citrate solution.

30.6 Using a 50-mL buret, transfer to a 400-mL beaker a sufficient volume of $K_3Fe(CN)_6$ solution to oxidize the cobalt and to provide an excess of about 5 mL to 8 mL. Record the buret reading to the nearest 0.01 mL. Add 50 mL of NH_4OH and cool to 5 °C to 10 °C. Transfer the beaker to the potentiometric titration apparatus and maintain the 5 °C to 10 °C temperature during the titration.

30.7 While stirring, add the sample solution to the solution from 30.6, rinse the beaker with water, and add the rinsings to the solution. For a successful titration, the sample solution must be added to the excess $K_3Fe(CN)_6$ solution. 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 one-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.

31. Calculation

31.1 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.

32. Precision and Bias

32.1 *Precision*—Ten laboratories cooperated in testing this test method and obtained the data summarized in Table 3 for Specimens 4 through 8. Although samples covered by this test method with cobalt contents 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 3 should apply.

32.2 *Bias*—The accuracy of this test method has been deemed satisfactory based upon the data for the certified reference materials in Table 3. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

COBALT BY THE NITROSO-R-SALT SPECTROPHOTOMETRIC METHOD

33. Scope

33.1 This test method covers the determination of cobalt from 0.10 % to 5.0 %.

TABLE 3 Statistical Information—Cobalt – Ion-Exchange Potentiometric Titration Method

Test Specimen	Cobalt Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. No. 1, E352 (High alloy steel, 4Mo-6W-4Cr-2V)	1.86	0.05	0.12
2. No. 2, E352 (Tool steel, 18W-4Cr-1V)	4.82	0.08	0.11
3. No. 3, E352 (High alloy steel, 8Co-9Mo-2W-4Cr-2V, NIST 153a, 8.47 % Co)	8.46	0.03	0.07
4. High-temperature alloy 20Cr-13Ni-5Mo-2W-1Nb	11.27	0.06	0.16
5. Ni-base alloy 57Ni-14Cr (NIST 349, 13.95 % Co, certified)	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-3Nb (NIST, 167, 42.90 % Co, not certified)	42.91	0.18	0.15
8. Co-base alloy 28Cr-6Mo-3Ni	60.10	0.19	0.31

34. Summary of Test Method

34.1 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 HNO_3 stabilizes the cobalt complex and destroys certain interfering complexes. Spectrophotometric measurement is made at 520 nm.

35. Concentration Range

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

NOTE 5—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.

36. Stability of Color

36.1 The color is stable for at least 3 h.

37. Interferences

37.1 Nickel, manganese, and copper form complexes with nitroso-R-salt that deplete the reagent and inhibit the formation of the colored cobalt complex. Enough 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 HNO_3.

38. Reagents

38.1 *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 ($CoSO_4$)[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 mass 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 mass of $CoSO_4$ taken multiplied by 0.076046.

38.2 *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 one week.

38.3 *Sodium Acetate Solution* (500 g/L)—Dissolve 500 g of sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$) in about 600 mL of water, filter and dilute to 1 L.

38.4 *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.

39. Preparation of Calibration Curve

39.1 *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 39.3.

39.2 *Reference Solution*—Transfer 10 mL of water to a 50-mL volumetric flask. Proceed as directed in 39.3.

39.3 *Color Development*—Add 5 mL of sodium acetate solution and mix. Using a pipet, add 10 mL of nitroso-R-salt solution and mix. Place the flask in a boiling water bath. After 6 min to 10 min, add 5 mL of HNO_3 (1 + 2), and mix. Continue the heating for 2 min to 4 min. Cool the solution to room temperature, dilute to volume, and mix.

39.4 *Spectrophotometry:*

39.4.1 *Multiple-Cell Spectrophotometer*—Measure the cell correction with water using absorption cells with a 1-cm light path and using a light band centered at 520 nm. Using the test cell, take the spectrophotometric absorbance readings of the calibration solutions versus the Reference Solution (39.2).

39.4.2 *Single-Cell Spectrophotometer*—Transfer a suitable portion of the reference solution (39.2) to an absorption cell with a 1-cm light path and adjust the spectrophotometer to the initial setting, using a light band centered at 520 nm. While maintaining this adjustment, take the spectrophotometric absorbance readings of the calibration solutions.

39.5 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against the milligrams of cobalt per 50 mL of solution.

40. Procedure

40.1 *Test Solution:*

40.1.1 Select and weigh a sample as follows:

Cobalt, %	Sample Mass, g	Tolerance in Sample Mass, 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

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

40.2 Add 5 mL of a mixture of one volume of HNO_3 and 3 volumes of HCl. Heat gently until the sample is dissolved. Boil the solution until brown fumes have been expelled. Add 50 mL to 55 mL of water and cool.

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

40.3 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 6). Dilute to volume and mix. Allow the precipitate to settle; filter a portion of the solution through a dry, fine-porosity filter paper, and collect it in a dry, 150-mL beaker after having discarded the first 10 mL to 20 mL. Using a pipet, transfer 10 mL of the filtrate to a 50-mL borosilicate glass volumetric flask. Proceed as directed in 39.3.

NOTE 6—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.

40.4 *Spectrophotometry*—Take the spectrophotometric absorbance reading of the test solution as directed in 39.4.

41. Calculation

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

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

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.

42. Precision and Bias

42.1 *Precision*[8]—Eight laboratories cooperated in testing this test method and obtained the data summarized in Table 4 for Specimens 1 and 4. Although samples covered by this test method with cobalt content 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 4 should apply.

42.2 *Bias*—The accuracy of this test method has been deemed satisfactory based upon the data for the certified reference materials in Table 4. Users are encouraged to use these or similar reference materials to verify that the test method is performing accurately in their laboratories.

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E03-1028. Contact ASTM Customer Service at service@astm.org.

TABLE 4 Statistical Information—Cobalt – Nitroso-R-Salt Spectrophotometric Method

Test Specimen	Cobalt Found, %	Repeatability (R_1, Practice E173)	Reproducibility (R_2, Practice E173)
1. Ni-base alloy, 36Ni (NIST 126b, 0.032 % Co, certified)	0.032	0.005	0.006
2. No. 2, E353 (Stainless steel, 17Cr-9Ni-0.2Se, NIST 339, 0.096 % Co)	0.094	0.006	0.013
3. No. 3, E353 (Stainless steel, 18Cr-9Ni, NIST 101e, 0.18 % Co)	0.173	0.011	0.026
4. Ni-base alloy, 17Cr-15Fe (NIST 161, 0.47 % Co, certified)	0.468	0.020	0.028
5. No. 2, E352 (High alloy steel, 4Mo-6W-4Cr-2V)	1.87	0.09	0.13
6. No. 3, E352 (High speed tool steel, 8Mo-2W-5Cr-1V, NIST 438, 4.9 % Co)	4.94	0.08	0.17

COPPER BY THE NEOCUPROINE SPECTROPHOTOMETRIC METHOD

43. Scope

43.1 This test method covers the determination of copper from 0.010 % to 1.50 %.

44. Summary of Test Method

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

45. Concentration Range

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

NOTE 7—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.

46. Stability of Color

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

47. Interferences

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

48. Reagents

48.1 *Benzoic Acid* (C_6H_5COOH).

48.2 *Bromine.*

48.3 *Chloroform* ($CHCl_3$).

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

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

48.6 *2,9-Dimethyl-1,10-Phenanthroline (Neocuproine) Solution (1 g/L)*—Dissolve 0.1 g of neocuproine in 100 mL of absolute ethanol.

NOTE 8—In addition to absolute ethanol, 95 % ethanol or denatured ethanol have been found suitable for preparing this solution.

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

49. Preparation of Calibration Curve

49.1 *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 49.3.

49.2 *Reagent Blank Solution*—Transfer 50 mL of water to a 150-mL beaker. Proceed as directed in 49.3.

49.3 *Color Development:*

49.3.1 Add 5 mL of $NH_2OH·HCl$ solution and 10 mL of citric acid solution. Stir for 30 s. Using a pH meter (Note 9), adjust the pH to 5.0 ± 1.0 with NH_4OH (1 + 1). Add 10 mL of neocuproine solution.

NOTE 9—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.

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

49.4 *Reference Solution*—$CHCl_3$.

49.5 *Spectrophotometry:*

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

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

49.6 *Calibration Curve*—Follow the instrument manufacturer's instructions for generating the calibration curve. Plot the net spectrophotometric absorbance readings of the calibration solutions against the milligrams of copper per 50 mL of solution.

50. Procedure

50.1 *Test Solution:*

50.1.1 Select a sample as follows.

Copper, %	Sample Mass, g	Tolerance in Sample Mass, 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

50.1.2 Some alloys are more readily decomposed by a mixture of 5 mL of bromine, 15 mL of HCl, and one drop to two drops of HF.

50.2 Transfer it to a 250-mL Erlenmeyer flask.

50.3 Add amounts of HCl or HNO_3, or mixtures and dilutions of these acids, which are sufficient to dissolve the sample (50.1.2). Heat as required to hasten dissolution. Add HNO_3 to provide an excess of 3 mL to 4 mL, enough HF to volatilize the silica, and 15 mL of $HClO_4$.

50.4 Heat to fumes, and continue fuming until chromium, if present, is oxidized and the white $HClO_4$ vapors are present only in the neck of the flask. Add, with care, 1.0 mL to 1.5 mL of HCl allowing it to drain down the side of the flask. If there is evidence of the volatilization of chromyl chloride, make repeated additions of HCl, followed by fuming after each addition, until most of the chromium has been removed. Continue fuming the solution until the volume has been reduced to about 10 mL. Cool, add 7 mL of water and digest if necessary to dissolve the salts. Cool to room temperature, add 1 mL of HCl, and transfer the solution (50.4.1) to a volumetric flask that provides for the dilution specified in 50.1.1. Dilute to volume and mix.

50.4.1 If silver is present in the alloy, it must be removed by filtration at this point.

50.5 Allow insoluble matter to settle, or dry filter through a coarse paper and discard the first 15 mL to 20 mL of the filtrate before taking the aliquot. Using a pipet, transfer a portion as specified in 50.1.1 to a 150-mL beaker, and dilute to 50 mL. Proceed as directed in 49.3.

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

50.7 *Spectrophotometry*—Take the spectrophotometric absorbance reading of the test solution as directed in 49.5.

51. Calculation

51.1 Convert the net spectrophotometric absorbance 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:

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

where:

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