



Designation: E 34 – 94 (Reapproved 1998)

Standard Test Methods for Chemical Analysis of Aluminum and Aluminum-Base Alloys¹

This standard is issued under the fixed designation E 34; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the chemical analysis of aluminum and aluminum-base alloys having compositions within the following limits:

Beryllium, ppm	0.3 to 100
Bismuth, %	0.02 to 1.0
Boron, %	0.005 to 0.060
Cadmium, %	0.001 to 0.50
Chromium, %	0.01 to 1.0
Copper, %	0.01 to 20.0
Gallium, %	0.001 to 0.05
Iron, %	0.01 to 3.0
Lead, %	0.01 to 1.0
Lithium, %	0.001 to 4.0
Magnesium, %	0.002 to 12.0
Manganese, %	0.005 to 2.0
Nickel, %	0.01 to 4.0
Silicon, %	0.05 to 20.0
Tin, %	0.03 to 1.0
Titanium, %	0.002 to 0.30
Vanadium, %	0.002 to 0.16
Zinc, %	0.003 to 12.0
Zirconium, %	0.01 to 0.30

1.2 The analytical procedures appear in the following order:

	Sections
Beryllium by Argon Plasma Optical Emission Spectroscopy	283 to 292
Beryllium by the Morin (Fluorometric) Test Method	8-19
Bismuth by the Thiourea (Photometric) Method	1a
Bismuth and Lead by the Atomic Absorption Test Method	188 to 198
Boron by the Carmine (Photometric) Test Method	30 to 38
Cadmium by the Atomic Absorption Test Method	167 to 177
Chromium:	
Diphenylcarbazide (Photometric) Test Method	39 to 47
Persulfate Oxidation (Titrimetric) Test Method	1b
Chromium by the Atomic Absorption Test Method	199 to 209
Copper and Lead by the Electrolytic (Gravimetric) Test Method	1c
Copper and Zinc by the Atomic Absorption Test Method	210 to 220
Copper by the Electrolytic (Gravimetric) Test Method	303 to 311

Copper by the Neocuproine (Photometric) Test Method	Sections 1a
Gallium by the Ion Exchange-Atomic Absorption Test Method	312 to 323
Iron by the 1,10-Phenanthroline (Photometric) Method	73 to 81
Iron and Manganese by the Atomic Absorption Test Method	221 to 231
Lithium by the Atomic Absorption Test Method	324 to 334
Magnesium:	
Pyrophosphate (Gravimetric) Method	1b
Ethylenediamine Tetraacetate (Titrimetric) Test Method	88 to 93
Magnesium by the Atomic Absorption Test Method	232 to 242
Manganese by the Periodate (Photometric) Test Method	293 to 302
Nickel:	
Dimethylglyoxime (Photometric) Test Method	1a
Dimethylglyoxime (Gravimetric) Test Method	1b
Nickel by the Atomic Absorption Test Method	243 to 253
Silicon:	
Molybdisilicic Acid (Photometric) Test Method	118 to 127
Sodium Hydroxide-Perchloric Acid (Gravimetric) Method	128 to 133
Tin by the Iodate (Titrimetric) Test Method	134 to 140
Titanium by the Chromotropic Acid (Photometric) Test Method	141 to 150
Titanium by the Diantipyrilmethane Photometric Test Method	254 to 263
Vanadium by an Extraction-Photometric Test Method using <i>N</i> -Benzoyl- <i>N</i> -Phenylhydroxylamine	264 to 273
Zinc:	
Ammonium Mercuric Thiocyanate or the Zinc Oxide (Gravimetric) Test Method	1b
Ethylenediamine Tetraacetate (Titrimetric) Test Method	1d
Ion Exchange-EDTA Titrimetric Test Method	274 to 282
Zirconium by the Arsenazo III (Photometric) Method	178 to 187

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety problems, 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 throughout these test methods.*

2. Referenced Documents

2.1 ASTM Standards:

E 29 Practice for Using Significant Digits in Test Data to

¹ These test methods are under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and are the direct responsibility of Subcommittee E01.04 on Aluminum and Magnesium.

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^{1a} Discontinued as of Feb. 25, 1983.

^{1b} Discontinued as of May 29, 1981.

^{1c} Discontinued as of Oct. 25, 1985.

^{1d} Discontinued as of March 25, 1983.

- Determine Conformance with Specifications²
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals³
- E 55 Practice for Sampling Wrought Nonferrous Metals and Alloys for Determination of Chemical Composition³
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals³
- E 88 Practice for Sampling Nonferrous Metals and Alloys in Cast Form for Determination of Chemical Composition³
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals³
- E 716 Practices for Sampling Aluminum and Aluminum Alloys for Spectrochemical Analysis⁴
- E 1024 Guide for Chemical Analysis of Metals and Metal Bearing Ores by Flame Atomic Absorption Spectrophotometry⁴

3. Significance and Use

3.1 These test methods for the chemical analysis of metals and alloys are primarily intended to test such materials for compliance with compositional specifications. 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.

4. Apparatus, Reagents, and Photometric Practice

4.1 Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions, and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in Practices E 50, except that photometers shall conform to the requirements prescribed in Practice E 60.

4.2 Photometric practice prescribed in these test methods shall conform to Practice E 60.

5. Precautions

5.1 For precautions to be observed in the use of certain reagents in these test methods, reference shall be made to Practices E 50.

6. Sampling

6.1 Wrought products shall be sampled in accordance with Practice E 55. Cast products shall be sampled in accordance with Practice E 88.

6.2 Chill cast disks produced for analysis by spectrochemical methods (see Practices E 716) shall be considered cast products. The principles of Practice E 88 shall apply.

6.2.1 Prepare such disks for chemical analysis by drilling or milling through the entire thickness of an unmachined disk (Note 1). Use a minimum of two positions approximately opposite each other and combine the drillings or millings.⁵

NOTE 1—The use of a machined disk may result in the exclusion of an element-rich portion of the sample. This practice should be avoided wherever possible, especially for analyses affecting product acceptance.

6.2.2 The outer edges of the holes shall be approximately 0.48 cm ($\frac{3}{16}$ in.) from the edge of the disk. Drills shall be not less than 0.95 cm ($\frac{3}{8}$ in.) in diameter and not larger than 1.27 cm ($\frac{1}{2}$ in.) in diameter.⁴

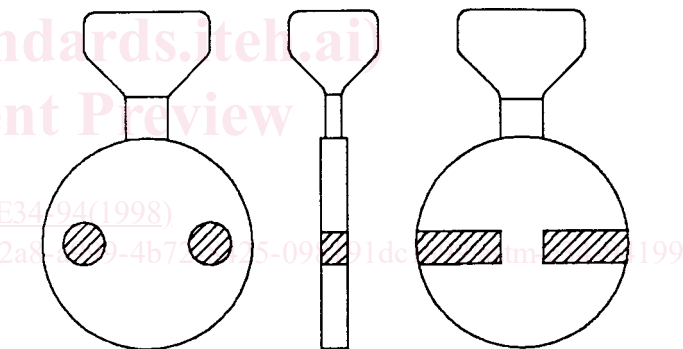
6.2.3 Mill disks at similar points to a distance of 40 % of the sample diameter. Use a 0.95-cm ($\frac{3}{8}$ in.) milling cutter.⁴

6.2.4 Sample book mold disks (Type A, Practices E 716) at approximately the 9 o'clock and the 3 o'clock positions when the sprue is at the 12 o'clock position. Center pour (Type B, Practices E 716) and vacuum cast disks may be sampled around the entire circumference. Fig. 1 illustrates the areas suitable for sampling Type A and Type B disks. Vacuum cast disks are sampled in the same manner as Type B disks.⁴

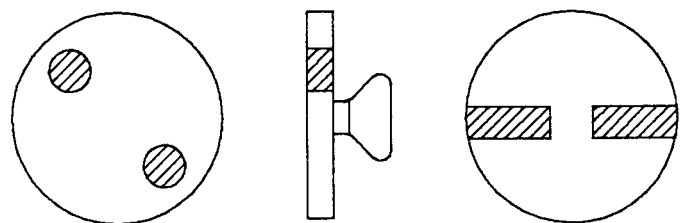
6.2.5 Drilling or milling techniques ideally should produce uniformly small chips. Break large continuous pieces into smaller pieces 0.64 cm ($\frac{1}{4}$ in.) to 0.95 cm ($\frac{3}{8}$ in.) long. Drilling or milling techniques should minimize production of fine, dust-like material.⁴

7. Rounding Calculated Values

7.1 Calculated values shall be rounded to the desired number of places in accordance with the rounding method given in 3.4 and 3.5 of Practice E 29.



Type A Mold



Type B Mold

NOTE 1—Shaded areas are suitable for sampling.
FIG. 1 Type A and Type B Disks

² Annual Book of ASTM Standards, Vol 14.02.

³ Annual Book of ASTM Standards, Vol 03.05.

⁴ Annual Book of ASTM Standards, Vol 03.06.

⁵ Olson, H. A., and Macy, D. W., "Metallurgical Approach to Evaluating Chemical Sample Disks," *Light Metals*, Vol 2, 1978, pp. 301-311.



BERYLLIUM BY THE MORIN (FLUOROMETRIC) TEST METHOD

8. Scope

8.1 This test method covers the determination of beryllium in concentrations from 1 to 100 ppm.

9. Summary of Test Method

9.1 In an alkaline solution, beryllium and morin form a compound which produces a yellow-green fluorescence at approximately 520 nm when excited by light at approximately 430 nm.

10. Concentration Range

10.1 The recommended concentration range is from 0.05 to 0.5 μg of beryllium in 25 mL of solution.

11. Stability of Fluorescence

11.1 The fluorescence is stable for at least 1 h if the test solutions are kept at constant temperature.

12. Interferences

12.1 Silicon must be removed by dehydration or volatilization. Beryllium is separated from interfering ions by an acetylacetone extraction. Fluoride and pyrophosphate interfere in the extraction.

13. Apparatus

- 13.1 *Bottles*, plastic, 500-mL capacity.
- 13.2 *Constant-Temperature Bath*, 20 or 25°C.
- 13.3 *Fluorescence-Measuring Instrument*—A suitable filter fluorometer or spectrofluorometer with primary excitation at approximately 430 nm and a means of isolating and measuring the secondary fluorescent emission at approximately 520 nm.

14. Reagents

- 14.1 *Acetylacetone* (2,4-pentanedione), practical.
- 14.2 *Aluminum Sulfate Solution* (49 g/L)—Dissolve 4.9 g of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) in 70 mL of water, add 1 mL of HClO_4 , transfer to a 100-mL volumetric flask, dilute to volume, and mix.
- 14.3 *Ammonium Nitrate Wash Solution* (10 g/L)—Dissolve 5 g of ammonium nitrate (NH_4NO_3) in water and dilute to 500 mL.
- 14.4 *Beryllium, Standard Solution A* (1 mL = 100 μg Be)—Dissolve 1.964 g of beryllium sulfate ($\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$) in water, add 10 mL of HClO_4 , transfer to a 1-L volumetric flask, dilute to volume, and mix. Standardize as follows: transfer a 100-mL aliquot of this solution to a 250-mL beaker, add NH_4OH (1+1) until a permanent turbidity forms, and then add 10 mL in excess. Allow to stand for 2 to 3 h or overnight. Filter using a low-ash, medium paper and wash well with NH_4NO_3 wash solution. Transfer the precipitate and paper to a weighed, covered platinum crucible and char. Finally ignite to constant weight at 1000°C and weigh as beryllium oxide (BeO).
- 14.5 *Beryllium, Standard Solution B* (1 mL = 0.10 μg Be)—Transfer a 10-mL aliquot of Beryllium Solution A to a 100-mL volumetric flask. Add 1 mL of HClO_4 , dilute to volume, and

mix. Transfer a 10-mL aliquot of this solution to a 1-L volumetric flask. Add 10 mL of HClO_4 , dilute to volume, and mix.

14.6 *Chloroform* (CHCl_3).

14.7 *Diethylenetriaminepentaacetic Acid (DTPA), Recrystallized* (Note 2)—Add 100 g of DTPA to 800 mL of boiling water and heat to boiling. Add 8 to 10 g of high-quality decolorizing carbon and mix thoroughly. Filter with suction through a hardened retentive paper. Transfer the clear filtrate to a 1-L beaker and stir vigorously to induce crystallization throughout the solution. Cool thoroughly in a water bath. Filter with suction using a hardened paper and remove as much water as possible. Dry the salts at 110°C.

NOTE 2—It is essential that the DTPA salts be recrystallized since commercial DTPA contains impurities that absorb ultraviolet and visible light. These impurities produce bright blue fluorescence under ultraviolet light, and react under certain conditions to produce a bright yellow fluorescence.

14.8 *Disodium Ethylenediaminetetraacetate (EDTA) Solution* (100 g/L)—Dissolve 100 g of EDTA in water and dilute to 1 L.

14.9 *EDTA Wash Solution*—Add 5 mL of H_2SO_4 and 10 mL of the EDTA solution to 300 mL of water. Add 2 drops of phenol red indicator solution and NH_4OH until the solution turns red. Cool and dilute to 500 mL.

14.10 *Morin Solution* (0.075 g/L)—Dissolve 0.0075 g of anhydrous morin (3,5,7,2',4'-penta-hydroxyflavone), reagent grade, in 40 mL of ethanol. Transfer to a 100-mL volumetric flask with water, dilute to volume, and mix.

14.11 *Phenol Red Indicator Solution* (1 g/L)—Dissolve 0.1 g of phenol red in 50 mL of methanol and dilute to 100 mL with water.

14.12 *Piperidine Buffer Solution*—Dissolve 15 g of the recrystallized DTPA in 200 mL of water. Add 75 mL of redistilled piperidine and cool. Add 20 g of anhydrous sodium sulfite (Na_2SO_3) and dilute to 500 mL. Store in a plastic bottle. This solution slowly decomposes and should be discarded after 6 months.

14.13 *Potassium Iodide-Starch Paper*.

14.14 *Quinine Sulfate Solution* (0.1 g/L)—Dissolve 0.1 g of quinine sulfate in 300 mL of water. Add 10 mL of HClO_4 and dilute to 1 L.

14.15 *Sodium Hydroxide-Sodium Perchlorate-DTPA-Triethanolamine (TEA) Solution*—Dissolve 60 g of sodium hydroxide (NaOH) and 320 g of anhydrous sodium perchlorate (NaClO_4) in 250 mL of water. Filter through a double 7-cm glass-fiber filter. Add 10 mL of TEA solution (20 volume %) to 13.0 g of the recrystallized DTPA and dissolve in 50 mL of water and about 20 mL of the NaOH-NaClO_4 solution. When dissolution is complete, add the remainder of the NaOH-NaClO_4 solution and dilute to 500 mL. Store in a plastic bottle. Acidify a small portion of the solution and test for oxidizing agents with the potassium iodide-starch paper. If the presence of an oxidizing agent is indicated, add sodium sulfite (Na_2SO_3) in small portions until the oxidizing agent is destroyed.

14.16 *Sodium Hydroxide Solution* (40 g/L)—Dissolve 20 g of NaOH in water and dilute to 500 mL. Store in a plastic bottle.

15. Hazards

15.1 Beryllium and its compounds are extremely toxic and care must be exercised in the handling of these compounds. Hot perchloric acid and organic compounds present the possibility of an explosion if not handled carefully.

16. Preparation of Calibration Curve

16.1 *Calibration Solutions*—Transfer 0.5, 1.0, 3.0, 5.0, 7.0, and 9.0 mL of Beryllium Solution B (1 mL = 0.10 µg Be) to six 25-mL volumetric flasks. Proceed as directed in 16.3.

16.2 *Reference Solution*—Transfer 5 mL of water to a 25-mL volumetric flask and proceed as directed in 16.3.

16.3 Fluorescence Development:

16.3.1 Add 1 mL of $\text{Al}_2(\text{SO}_4)_3$ solution, 3 mL of NaOH-NaClO₄-DTPA-TEA solution, and 3 drops of quinine sulfate solution.

16.3.2 Add HClO₄ dropwise until the solution fluoresces under an ultraviolet light, then add 1 drop in excess. Swirl the contents of the flask so that any beryllium that may have been deposited as the hydroxide on the wall of the flask is redissolved.

16.3.3 Add NaOH solution dropwise until the fluorescence is destroyed and then add 2 drops in excess. Rinse down the neck of the flask with water.

16.3.4 Add 5 mL of piperidine buffer solution and mix.

16.3.5 Add 1.00 mL of morin solution, dilute to volume, and mix. Place the flask in the constant-temperature bath for 20 min.

16.4 Fluorometry:

16.4.1 Following the manufacturer's operating instructions, adjust the fluorometer so that the calibration solution is excited by light at approximately 430 nm, and its fluorescence is detected at approximately 520 nm.

16.4.2 Transfer a suitable portion of the reference solution to the cuvette and adjust the fluorometer to the initial setting. While maintaining this adjustment, take the fluorometric readings of the calibration solutions.

16.5 *Calibration Curve*—Plot the fluorometric readings of the calibration solutions against micrograms of beryllium per 25 mL of solution.

17. Procedure

17.1 Test Solution:

17.1.1 Transfer 1.00 g of the sample, weighed to the nearest 1 mg, to a 250-mL beaker. Add 25 mL of water and 10 mL of HCl. Warm the solution, if necessary, to hasten dissolution. When dissolution is complete, boil for a few minutes.

17.1.2 Add 5 mL of HNO₃ and 20 mL of HClO₄ and evaporate to the appearance of HClO₄ fumes. Reduce the heat to avoid bumping and continue fuming for 10 min. Cool to room temperature. Add 100 mL of water and heat to dissolve the salts. Filter through a medium paper into a 500-mL volumetric flask. Wash the paper and precipitate with 10 mL of H₂SO₄(1+4) followed by several washings with hot water. Cool to room temperature, dilute to volume, and mix.

17.1.3 Transfer an aliquot containing an amount of beryllium that is in the linear portion of the calibration curve, but not containing more than 70 mg of aluminum, to a 150-mL beaker. Add 10 mL of EDTA solution and adjust the volume to

approximately 40 mL. Add 2 drops of phenol red indicator solution and NH₄OH until the solution turns red. Add 5 drops of HClO₄, cover the beaker with a watch glass, and boil for 5 min (Note 3). Cool to room temperature.

NOTE 3—The aluminum-EDTA complex is slow in forming and, therefore, requires the 5-min boiling period. If the complex is not formed, an emulsion will result in the extraction procedure causing erroneous results. Ten millilitres of EDTA solution will chelate approximately 70 mg of .

17.1.4 Transfer the solution to a 125-mL separatory funnel. A standard containing an amount of beryllium that is in the linear portion of the calibration curve must be carried through the extraction for calibration purposes. Add 10 drops of acetylacetone, stopper the funnel, and mix by shaking. Add NH₄OH dropwise until the solution turns red and add 5 drops in excess. Add 10 mL of CHCl₃ and shake vigorously for 2 min; allow the phases to separate. Transfer the CHCl₃ (lower) layer to a clean 125-mL separatory funnel and reserve. Repeat the extraction from the aqueous layer with 4 drops of acetylacetone and 10 mL of CHCl₃ and add the CHCl₃ layer to the reserved one. Add 20 mL of EDTA wash solution to the reserved CHCl₃ extracts, shake for 30 s, and allow the phases to separate. Drain the CHCl₃ layer into a 100-mL beaker. Add 2 drops of acetylacetone and 10 mL of CHCl₃ to the EDTA wash solution layer, shake for 30 s, and add the CHCl₃ extracts to those in the 100-mL beaker.

17.1.5 Add 3 mL of HNO₃ and 5 mL of HClO₄. Cover the beaker with a watchglass and volatilize the CHCl₃ at a temperature just sufficient to boil the CHCl₃. When volatilization of the CHCl₃ is complete, increase the heat and allow the solution to boil until HClO₄ fumes appear. This refluxing action will dissolve materials adhering to the walls of the beaker. Cool, remove the watchglass after rinsing with water, and evaporate the solution to a volume of 0.5 mL. Do not bake or allow the beaker to go dry during the evaporation. Cool, add a few drops of water, warm to dissolve salts, and cool again. Transfer the solution to a 25-mL volumetric flask, keeping the volume in the flask to approximately 10 mL.

17.2 *Reference Solution*—Carry a reagent blank through the entire procedure, using the same amounts of all reagents, for use as a reference solution.

17.3 *Fluorescence Development*—Proceed as directed in 16.3.

NOTE 4—If the solution fluoresces after the addition of the reagents in 16.3.1, neutralize the excess acid with NaOH solution (50 %) dropwise until the fluorescence disappears. This neutralization step will keep the solution within the 25-mL volume.

17.4 *Fluorometry*—Take the fluorometric readings of the standard beryllium and test solutions as directed in 16.4.

NOTE 5—If the beryllium standard differs significantly from the calibration curve, the test solution and the beryllium standard must be rerun.

18. Calculation

18.1 Convert the fluorometric reading of the test solution to micrograms of beryllium by means of the calibration curve. Calculate the parts per million of beryllium as follows:

$$\text{Beryllium, ppm} = A/B \quad (1)$$

where:

- A = beryllium found in 25 mL of the final solution, μg , and
B = sample represented in 25 mL of the final solution, g.

19. Precision

19.1 Due to the limited number of laboratories participating in the cooperative testing of this test method, a precision statement conforming to the requirements of Practice E 173 cannot be furnished. However, in a cooperative program conducted by three laboratories, the between-laboratory range was from 8.4 to 8.5 ppm beryllium on a sample averaging 8.5 ppm, and from 13.5 to 14.2 ppm on a sample averaging 13.8 ppm.

BISMUTH BY THE THIOUREA (PHOTOMETRIC) TEST METHOD

(This test method, which consisted of Sections 20 through 29 of this standard, was discontinued in 1983.)

BORON BY THE CARMINE (PHOTOMETRIC) TEST METHOD

30. Scope

30.1 This test method covers the determination of boron in concentrations from 0.005 to 0.060 %.

31. Summary of Test Method

31.1 Boron, in the form of boric acid, reacts with carmine in concentrated sulfuric acid to produce a violet color. Photometric measurement is made at approximately 585 nm, at which wavelength the blue boron complex absorbs strongly while the absorption due to the reagent is very slight.

32. Concentration Range

32.1 The recommended concentration range is from 0.002 to 0.025 mg of boron per 22 mL of solution, using a cell depth of 1 cm.

NOTE 6—Use of a cell having other dimensions may alter the recommended concentration range.

33. Stability of Color

33.1 Color development is slow. It is practically complete after 45 min, however, and thereafter the rate of increase of absorbance is negligible. The effect of the slight photosensitivity of the complex is minimized by protecting the solutions against strong light during the color development.

34. Interferences

34.1 The elements ordinarily present in aluminum and aluminum-base alloys do not interfere. Vanadium, if present in amounts greater than 0.3 %, will interfere.

35. Reagents

35.1 *Boron, Standard Solution* (1 mL = 0.05 mg B)—Dissolve 0.2857 g of boric acid (H_3BO_3) crystals in warm (not over 40°C) water. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

35.2 *Bromine Water (Saturated)*.

35.3 *Carmine Solution* (0.92 g/L)—Transfer 0.46 g of carmine to a dry 1-L stoppered plastic bottle. Add 500 mL of H_2SO_4 , and a plastic-coated magnetic stirring bar. Stopper the bottle and stir on a magnetic stirrer until the carmine is completely dissolved. Store in a dark place.

35.4 *Sodium Carbonate* (Na_2CO_3), anhydrous.

36. Preparation of Calibration Curve

36.1 *Calibration Solutions*—Transfer 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, and 12.0 mL of boron solution (1 mL = 0.05 mg B) to seven 50-mL volumetric flasks (Note 7). Add 10 mL of H_2SO_4 (1+1), dilute to 40 mL, mix, and cool to room temperature. Dilute to volume, and mix again. Proceed as directed in 36.3.

NOTE 7—All glassware must be rinsed with warm H_2SO_4 , then with water, and air-dried. It must not be contaminated with grease or soap.

36.2 *Reference Solution*—Transfer 10 mL of H_2SO_4 (1+1) to a 50-mL volumetric flask, dilute to 40 mL, mix, and cool to room temperature. Dilute to volume and mix again. Proceed as directed in 36.3.

36.3 *Color Development*—Transfer 2-mL aliquots of the reference solution and of each of the calibration solutions to dry 50-mL glass-stoppered Erlenmeyer flasks. Add 10.0 mL of H_2SO_4 , mix, and cool to room temperature. Add 10.0 mL of carmine solution, stopper, mix, and allow to stand away from strong light for at least 45 min.

36.4 *Photometry*—Transfer a suitable portion of the reference solution to a dry absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 585 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

36.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of boron per 22 mL of solution.

37. Procedure

37.1 Test Solution:

37.1.1 Transfer 1.0 g of the sample, weighed to the nearest 1 mg, to a 250-mL Erlenmeyer flask. Add 15 mL of bromine water followed by 10 mL of HCl. If effervescence becomes so rapid as to obscure the surface of the solution, cool until the reaction moderates. If reaction becomes very slow, heat the solution moderately. When dissolution is complete, heat just below boiling to remove any excess bromine.

37.1.2 Filter the solution using a 7-cm, low-ash, coarse paper into a 50-mL volumetric flask. Wash the Erlenmeyer flask and paper 3 or 4 times with hot water, being careful to keep the volume of the filtrate below 40 mL, and reserve the filtrate.

37.1.3 Cover any residue on the filter paper with 0.25 g of anhydrous Na_2CO_3 and transfer the paper to a small platinum crucible. Dry and char at a low heat over a Meker burner, gradually raising the temperature until the paper is completely oxidized and the melt fuses. Continue to heat the melt until it is clear (about 10 min). Cool to room temperature. Dissolve the melt with about 5 mL of hot water and add H_2SO_4 (1+1) dropwise until the effervescence ceases. Add the solution to the reserved filtrate in the 50-mL volumetric flask, cool, dilute to volume, and mix.

37.2 *Reference Solution*—Carry a reagent blank through the entire procedure using the same amounts of all reagents, for use as a reference solution.

37.3 *Color Development*—Transfer a 2-mL aliquot of the solution to a dry 50-mL glass-stoppered Erlenmeyer flask and proceed as directed in 36.3.

37.4 *Photometry*—Take the photometric reading of the test



solution as directed in 36.4.

38. Calculation

38.1 Convert the photometric reading of the test solution to milligrams of boron by means of the calibration curve. Calculate the percentage of boron as follows:

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

where:

A = boron found in 22 mL of the final solution, mg, and

B = sample represented in 22 mL of the final solution, g.

CHROMIUM BY THE DIPHENYLCARBAZIDE (PHOTOMETRIC) TEST METHOD

39. Scope

39.1 This test method covers the determination of chromium in concentrations from 0.01 to 0.30 %.

40. Summary of Test Method

40.1 After dissolution of the sample in acids, chromium is oxidized to the hexavalent state in fuming perchloric acid. Hexavalent chromium forms a soluble red-violet complex with diphenyl-carbazide. Photometric measurement is made at approximately 540 nm.

41. Concentration Range

41.1 The recommended concentration range is from 0.004 to 0.08 mg of chromium per 100 mL of solution, using a cell depth of 2 cm (see Note 6).

42. Stability of Color

42.1 The color of the chromium diphenylcarbazide complex develops almost immediately but starts to fade within a short period of time. Photometric measurement must be made within 5 min after adding the diphenylcarbazide.

43. Interferences

43.1 The elements ordinarily present in aluminum and aluminum-base alloys do not interfere if their concentrations are under the maximum limits shown in 1.1. Oxidizing agents cause rapid fading of the chromium diphenylcarbazide complex.

44. Reagents

44.1 *Aluminum or Aluminum-Base Alloy, Low-Chromium*—Aluminum or aluminum-base alloy containing less than 0.005 % chromium.

44.2 *Chromium, Standard Solution* (1 mL = 0.08 mg Cr)—Prepare as directed for Reagent No. 10, using 0.2263 g instead of the specified weight.

44.3 *Diphenylcarbazide Solution* (10 g/L)—Dissolve 0.20 g of diphenylcarbazide in 20 mL of methanol. This solution decomposes within a few hours and must be prepared fresh as needed.

44.4 *Sodium Chloride Solution* (2 g/L)—Dissolve 2 g of sodium chloride (NaCl) in water and dilute to 1 L.

45. Preparation of Calibration Curve

45.1 Calibration Solutions:

45.1.1 Transfer 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 mL of chromium solution (1 mL = 0.08 mg Cr) to six 300-mL Erlenmeyer flasks and dilute to 20 mL with water. Add 0.500 g of low-chromium aluminum, 7 mL of HClO₄, and 10 mL of H₂SO₄.

45.1.2 Allow to react without applying heat. When the

reaction is complete, wash down the sides of the flask with a minimum of water, and add 5 mL of HNO₃ and 2 mL of HF. Heat to complete the dissolution of any metal sponge and silicon, and continue heating to copious white fumes (Note 8). Cool somewhat, add 30 mL of water, and heat to dissolve the soluble salts. Add 5 mL of NaCl solution (Note 9) and boil for 5 min to remove any chlorine formed by the presence of oxidized manganese. Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 45.3.

NOTE 8—In order to oxidize the chromium completely to chromate, it is necessary to heat the solution through the stage where copious white fumes of HClO₄ are evolving and refluxing. This operation may be carried out over a free flame; avoid heating to dryness.

NOTE 9—In some cases, manganese is precipitated as manganese dioxide (MnO₂) after fuming. The NaCl solution is added to dissolve any MnO₂ that might be present.

45.2 *Reference Solution*—Transfer 0.500 g of low-chromium aluminum to a 300-mL Erlenmeyer flask. Add 20 mL of water, 7 mL of HClO₄, and 10 mL of H₂SO₄. Proceed as directed in 45.1.2 and 45.3.

45.3 *Color Development*—Transfer a 5-mL aliquot to a 100-mL volumetric flask. Dilute to about 90 mL, add 1 mL of diphenylcarbazide solution, dilute to volume, and mix.

45.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 540 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

45.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of chromium per 100 mL of solution.

46. Procedure

46.1 *Test Solution*—Transfer 0.500 g of the sample, weighed to the nearest 1 mg, to a 300-mL Erlenmeyer flask. Add in the following order (**Precaution:** see Note 10), 20 mL of water, 7 mL of HClO₄, and 10 mL of H₂SO₄. Proceed as directed in 45.1.2.

NOTE 10—**Precaution:** The order of adding the reagents used in decomposing the sample must be strictly adhered to. Under no circumstances should HClO₄ be added directly to the metallic aluminum. See the Safety Precautions Section of Practices E 50 for a discussion of the hazards involved in the use of HClO₄.

46.2 *Reference Solution*—Carry a reagent blank through the entire procedure, using the same amount of all reagents, for use as a reference solution.

46.3 *Color Development*—Proceed as directed in 45.3

46.4 *Photometry*—Take the photometric reading of the test solution as directed in 45.4.

47. Calculation

47.1 Convert the photometric reading of the test solution to milligrams of chromium by means of the calibration curve. Calculate the percentage of chromium as follows:

$$\text{Chromium, \%} = A/(B \times 10)$$

where:



- A = chromium found in 100 mL of the final solution, mg, and
B = sample represented in 100 mL of the final solution, g.

CHROMIUM BY THE PERSULFATE OXIDATION (TITRIMETRIC) TEST METHOD

(This test method, which consisted of Sections 48 through 53 of this standard, was discontinued in 1981.)

COPPER BY THE NEOCUPROINE (PHOTOMETRIC) TEST METHOD

(This test method, which consisted of Sections 54 through 63 of this standard, was discontinued in 1983.)

COPPER AND LEAD BY THE ELECTROLYTIC (GRAVIMETRIC) TEST METHOD

(This test method, which consisted of Sections 64 through 72 of this standard, was discontinued in 1985.)

IRON BY THE 1,10-PHENANTHROLINE (PHOTOMETRIC) TEST METHOD

73. Scope

73.1 This test method covers the determination of iron in concentrations from 0.01 to 3.0 %.

74. Summary of Test Method

74.1 Ferrous iron, in a solution having a pH of about 5, forms an orange-red complex with 1,10-phenanthroline. Photometric measurement is made at approximately 510 nm.

75. Concentration Range

75.1 The recommended concentration range is from 0.02 to 0.20 mg of iron per 100 mL of solution, using a cell depth of 2 cm (see Note 6).

76. Stability of Color

76.1 The color develops within 5 min and is stable for at least 2 h.

77. Interferences

77.1 The elements ordinarily present in aluminum and aluminum-base alloys do not interfere. Zinc and nickel form complexes and consume 1,10-phenanthroline; however, enough reagent is added to complex the maximum amounts of nickel and zinc to be encountered, in addition to the iron.

78. Reagents

78.1 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Dissolve 10 g of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in water and dilute to 100 mL.

78.2 *Iron, Standard Solution A* (1 mL = 0.10 mg Fe)—Dissolve 0.1000 g of iron metal (purity 99.8 % min) in 50 mL of water, 25 mL of HCl, and 1 mL of HNO_3 . Heat gently to dissolve the iron and expel brown fumes. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

78.3 *Iron, Standard Solution B* (1 mL = 0.02 mg Fe)—Transfer a 100-mL aliquot of Iron Solution A to a 500-mL volumetric flask, add 10 mL of HCl, dilute to volume, and mix.

78.4 *1,10-Phenanthroline Solution* (2 g/L)—Dissolve 0.4 g of 1,10-phenanthroline monohydrate in methanol and dilute to 200 mL with methanol.

78.5 *Sodium Acetate-Acetic Acid Buffer Solution*—Dissolve

272 g of sodium acetate trihydrate in 500 mL of water. Add 240 mL of glacial acetic acid, cool, and dilute to 1 L.

78.6 *Sodium Hydroxide Solution* (200 g/L)—Dissolve 200 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Store in a plastic bottle.

78.7 *Test Lead*—Finely granulated lead containing less than 0.001 % iron.

79. Preparation of Calibration Curve

79.1 *Calibration Solutions*—Transfer 1.0, 2.0, 4.0, 7.0, and 10.0 mL of Iron Solution B (1 mL = 0.02 mg Fe) to five 100-mL volumetric flasks. Dilute to 60 mL and proceed as directed in 79.3.

79.2 *Reference Solution*—Transfer 60 mL of water to a 100-mL volumetric flask and proceed as directed in 79.3.

79.3 *Color Development*—Add successively, mixing after each addition: 4 mL of $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution, 10 mL of sodium acetate-acid buffer solution, and 10 mL of 1,10-phenanthroline solution. Dilute to volume and mix. Allow to stand for 5 min.

79.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 510 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

79.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of iron per 100 mL of solution.

80. Procedure

80.1 Test Solution:

80.1.1 Remove adventitious iron as follows: immerse the entire sample in HCl (1+9) for 5 to 10 s, decant the acid, wash with water, then with acetone, and dry. Transfer 0.50 g of the sample, weighed to the nearest 1 mg, to a 250-mL nickel beaker. Cover with a watchglass and dissolve by adding, in small increments, 15 mL of NaOH solution. When the reaction subsides, wash down the cover and sides of the beaker, and boil gently until the silicon is completely dissolved. Cool, transfer to a 250-mL glass beaker containing 25 mL of HCl (1+1), and wash and polish the nickel beaker.

80.1.2 Place the beaker containing the solution on a hot plate and boil until the salts are dissolved. Remove from the hot plate, and add a few drops of H_2O_2 . Allow to react without further heating until any metallic sponge is dissolved. Boil gently until the H_2O_2 is decomposed and chlorine removed. Cool, transfer to a 250-mL volumetric flask, dilute to volume, and mix.

80.1.3 Transfer an aliquot containing between 0.02 and 0.20 mg of iron to a 150-mL beaker, dilute to approximately 30 mL, and add 1 to 2 g of test lead. Boil gently until the iron is reduced to the ferrous state and the copper is displaced completely, approximately 5 to 8 min being required. Cool, transfer the solution to a 100-mL volumetric flask, and wash the residue by decantation.

80.2 *Reference Solution*—Carry a reagent blank through the entire procedure, using the same amounts of all reagents, for use as a reference solution.

80.3 *Color Development*—Proceed as directed in 79.3.



80.4 *Photometry*—Take the photometric reading of the test solution as directed in 79.4.

81. Calculation

81.1 Convert the photometric reading of the test solution to milligrams of iron by means of the calibration curve. Calculate the percentage of iron as follows:

$$\text{Iron, \%} = A/(B \times 10) \quad (3)$$

where:

A = iron found in 100 mL of the final solution, mg, and

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

MAGNESIUM BY THE PYROPHOSPHATE (GRAVIMETRIC) TEST METHOD

(This test method, which consisted of Sections 82 through 87 of this standard, was discontinued in 1981.)

MAGNESIUM BY THE ETHYLENEDIAMINE TETRAACETATE (TITRIMETRIC) TEST METHOD

88. Scope

88.1 This test method covers the determination of magnesium in concentrations from 0.1 to 5.0 %. The range may be extended by suitably varying the sample weight.

89. Summary of Test Method

89.1 Magnesium is separated from the bulk of the alloy constituents by treatment of the sample with sodium hydroxide in the presence of hydrogen peroxide and potassium cyanide. The magnesium hydroxide is dissolved in hydrochloric acid and any remaining aluminum is separated by precipitation with ammonium hydroxide. Manganese is oxidized with bromine and separated as manganese dioxide. Magnesium is then determined by titration with disodium ethylenediamine tetraacetate.

90. Interferences

90.1 The elements ordinarily present in aluminum and aluminum-base alloys, except calcium, do not interfere if their concentrations are under the maximum limits shown in 1.1. Calcium is rarely present in significantly high concentrations.

91. Reagents

91.1 *Bromine Water (Saturated).*

91.2 *Disodium Ethylenediamine Tetraacetate (EDTA), Standard Solution (0.05 M)*—Dissolve 18.61 g of disodium ethylenediamine tetraacetate dihydrate (EDTA) in water, transfer to a 1-L volumetric flask, dilute to volume, and mix. Standardize as follows: transfer a 20-mL aliquot of magnesium solution (1 mL = 1.00 mg Mg) to a 400-mL beaker. Add 40 mL of HCl (1+1) and neutralize with NH₄OH. Dilute to 250 mL with water, add 70 mL of NH₄OH, and proceed as directed in 92.1.3 and 92.2. Calculate the magnesium equivalent of the disodium ethylenediamine tetraacetate solution as follows:

$$\text{Magnesium equivalent, g/mL} = 0.020/(A - B) \quad (4)$$

where:

A = EDTA solution required for titration of the magnesium solution, mL, and

B = EDTA solution required for titration of the blank, mL.

91.3 *Eriochrome Black-T Indicator Solution (8 g/L)*—Dissolve 0.4 g of the sodium salt of Eriochrome Black-T in a

mixture of 20 mL of ethanol and 30 mL of triethanolamine. This solution is stable for at least 3 months when kept in a tightly closed plastic dropping bottle.

91.4 *Magnesium, Standard Solution (1 mL = 1.00 mg Mg)*—Dissolve 1.000 g of magnesium turnings (purity, 99.9 % min) in 25 mL of HCl (1+1). Transfer to a 1-L volumetric flask, dilute to volume, and mix.

91.5 *Potassium Cyanide Solution (250 g/L)*—Dissolve 250 g of potassium cyanide (KCN) in water and dilute to 1 L. Store in a plastic bottle.

NOTE 11—**Precaution:** The preparation, storage, and use of KCN solutions require care and attention. Avoid inhalation of fumes and exposure of the skin to the chemical or its solutions. Work in a well-ventilated hood.

91.6 *Sodium Hydroxide Solution, Low-Carbonate (200 g/L)*—Dissolve 200 g of sodium hydroxide (NaOH) (low-carbonate) in water in a nickel or stainless steel beaker. Cool, dilute to 1 L, and transfer to a plastic bottle.

92. Procedure

92.1 Test Solution:

92.1.1 Transfer 1.0 g of the sample, weighed to the nearest 1 mg, to a 250-mL beaker. Carefully add 30 mL of NaOH solution. When the reaction subsides, wash down the sides of the beaker with a small amount of water and boil until the reaction ceases. Add a few drops of H₂O₂, followed by 5 mL of KCN solution, and boil. Dilute to about 150 mL with hot water and filter using a hardened rapid paper. Wash well with hot water.

92.1.2 Dissolve the precipitate on the paper with 40 mL of hot HCl (1+1). Collect the solution in the original 250-mL beaker and wash the paper well with hot water. Add 10 mL of saturated bromine water, neutralize with NH₄OH until the bromine color disappears, and add 6 to 8 drops in excess. A large excess of NH₄OH must be avoided to prevent dissolution of any aluminum, which would interfere with the end point in the subsequent titration. Bring the solution to a boil to coagulate the precipitated MnO₂, and boil for at least 5 min to expel excess NH₃. Let settle for 1 min and filter through a medium paper with pulp, collecting the filtrate in a 400-mL beaker. Wash well with hot water. (If the manganese or iron content is high, as indicated by a large amount of a dark-colored precipitate, redissolve and reprecipitate as before.) Cool the filtrate to room temperature, dilute to 250 mL, and add 70 mL of NH₄OH.

92.1.3 Add 10 drops of KCN solution, 7 to 10 drops of Eriochrome Black-T indicator solution and titrate with 0.05 M EDTA solution.

92.2 *Blank Determination*—Neutralize 40 mL of HCl (1+1) with NH₄OH. Dilute to 250 mL with water and add 70 mL of NH₄OH. Proceed as directed in 92.1.3.

93. Calculation

93.1 Calculate the percentage of magnesium as follows:

$$\text{Magnesium, \%} = [(A - B)C/D] \times 100 \quad (5)$$

where:

A = EDTA solution required for titration of the test solution, mL,

B = EDTA solution required for titration of the blank, mL,



C = magnesium equivalent of the EDTA solution, g/mL, and
 D = sample used, g.

MANGANESE BY THE PERIODATE (PHOTOMETRIC) TEST METHOD

(This test method, which consisted of Sections 94 through 102 of this standard, was replaced in 1984 by Sections 293 through 302.)

NICKEL BY THE DIMETHYLGLYOXIME (PHOTOMETRIC) TEST METHOD

(This test method, which consisted of Sections 103 through 111 of this standard, was discontinued in 1983.)

NICKEL BY THE DIMETHYLGLYOXIME (GRAVIMETRIC) TEST METHOD

(This test method, which consisted of Sections 112 through 117 of this standard, was discontinued in 1981.)

SILICON BY THE MOLYBDISILICIC ACID (PHOTOMETRIC) TEST METHOD

118. Scope

118.1 This test method covers the determination of silicon in concentrations from 0.05 to 1.0 %.

119. Summary of Test Method

119.1 Silicic acid in a true (not colloidal) solution reacts with molybdate to form a soluble yellow-colored molybdisilicic acid. Maximum color development occurs over a pH range from 1.1 to 1.3. Photometric measurement is made at approximately 400 nm.

120. Concentration Range

120.1 The recommended concentration range is from 0.05 to 1.0 mg of silicon per 100 mL of solution, using a cell depth of 2 cm (see Note 6).

121. Stability of Color

121.1 The color develops in less than 5 min and does not fade appreciably for at least 20 min.

122. Interferences

122.1 The elements ordinarily present in aluminum and aluminum-base alloys do not interfere.

NOTE 12—If detergents are used for cleaning, all traces of the detergents must be removed by boiling with HCl followed by thorough rinsing. Many detergents contain phosphorus compounds, which also form a yellow color with ammonium molybdate, and would cause interference if not completely removed.

123. Apparatus

123.1 *Plastic Ware* (polyethylene, polypropylene, or tetrafluoroethylene):

123.1.1 *Beakers and Covers.*

123.1.2 *Bottles, 1-L capacity.*

123.1.3 *Graduated Cylinders, 10-mL and 1-L capacity.*

123.2 *Nickel Crucibles and Covers, 50-mL capacity.*

123.3 *Nickel or Stainless Steel Beakers and Covers, 250-mL and 1-L capacity.*

123.4 *pH Meter*—Any commercial instrument capable of determining pH in the range from 0 to 7 ± 0.1 is suitable.

124. Reagents

124.1 *Aluminum Nitrate Solution* ($\text{Al}(\text{NO}_3)_3$)—Transfer 1.0 g of aluminum, low-silicon,⁶ to a 250-mL nickel beaker. Add 100 mL of NaOH solution and cover. Allow to react without applying heat until the reaction subsides, and then warm gently to complete the dissolution. Cool, and transfer to a 400-mL beaker containing 125 mL of HNO_3 (1+1). Cover and warm gently until the salts dissolve and the solution becomes clear. Cool, transfer to a 250-mL volumetric flask, dilute to volume, and mix.

124.2 *Ammonium Molybdate Solution* (100 g/L)—Dissolve 100 g of ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) in water and dilute to 1 L. Store in a plastic bottle. Filter before using. If a precipitate forms on standing, the solution should be discarded.

124.3 *Silicon, Standard Solution* (1 mL = 0.05 mg Si)—Fuse 0.1070 g of anhydrous silicon dioxide (SiO_2) with 1.0 g of sodium carbonate (Na_2CO_3) in a covered platinum crucible. Cool, dissolve the melt completely in water in a plastic beaker, cover, and heat on a steam bath for $\frac{1}{2}$ to 1 h. Cool, transfer to a 1-L volumetric flask, dilute to volume, and mix. Store the solution in a plastic bottle. If anhydrous SiO_2 is not available, the weight should be adjusted according to the actual silicon content of the SiO_2 used, as determined by gravimetric analysis.

124.4 *Sodium Hydroxide Solution* (300 g/L)—Dissolve 300 g of sodium hydroxide (NaOH) in about 600 mL of water, using a nickel or stainless steel beaker. Cool and dilute to 1 L. Store in a plastic bottle.

125. Preparation of Calibration Curve

125.1 *Calibration Solutions*—Transfer 12.5 mL of $(\text{NO}_3)_3$ solution and 1.0 mL of HNO_3 (1+1) to seven 100-mL beakers. Transfer 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, and 20.0 mL of silicon solution (1 mL = 0.05 mg Si) to each of the 100-mL beakers. Dilute to about 80 mL and mix. Proceed as directed in 125.3.

125.2 *Reference Solution*—Transfer 12.5 mL of $\text{Al}(\text{NO}_3)_3$ solution and 1 mL of HNO_3 (1+1) to a 100-mL beaker, dilute to about 80 mL, and mix. Proceed as directed in 125.3.

125.3 *Color Development*—Using a pH meter, check the pH of the solution. If the pH is not within 1.1 to 1.3, adjust it to this range using HNO_3 (1+1) or NaOH solution as required. Add 10 mL of ammonium molybdate solution, transfer the solution to a 100-mL volumetric flask, dilute to volume, and mix. Let stand at least 5 min but no longer than 20 min before taking the photometric reading.

125.4 *Photometry*—Transfer a suitable portion of the reference solution to an absorption cell with a 2-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 400+. While maintaining this adjustment, take the photometric readings of the calibration solutions.

125.5 *Calibration Curve*—Plot the photometric readings of the calibration solutions against milligrams of silicon per 100 mL of solution.

⁶ National Bureau of Standards Sample No. 44c (melting point aluminum) has been found satisfactory for this purpose.



126. Procedure

126.1 Test Solution:

126.1.1 Transfer 0.10 g of the sample, weighed to the nearest 0.1 mg, to a 50-mL nickel crucible, add 10.00 mL of NaOH solution, and cover. Allow to react without applying heat until the reaction subsides, wash down the cover and sides of the crucible with a minimum amount of water, and boil gently until the reaction is complete and the silicon completely oxidized (Note 13). Cool, dilute to approximately 30 mL with water, and transfer quantitatively to a 150-mL beaker containing 12.5 mL of HNO₃ (1+1). Cover and warm gently until the solution becomes clear (Notes 14 and 15). Cool, transfer to a 100-mL volumetric flask, dilute to volume, and mix.

NOTE 13—With certain alloys it may be necessary to evaporate the caustic solution to pastiness in order to completely dissolve the silicon. Care should be taken to avoid mechanical loss by spattering.

NOTE 14—Cloudiness (gray) of the solution at this point usually indicates incomplete dissolution of the silicon and another portion of the sample must be taken. Prolonging the heating after the NaOH attack will probably correct the difficulty. However, excessively prolonged heating will tend to cause precipitation of the manganese.

NOTE 15—If the sample contains high manganese, the solution may be colored brownish-yellow due to suspended manganese dioxide (MnO₂). To bleach the color, add a saturated sodium sulfite (Na₂SO₃) solution dropwise to the hot solution. Avoid any appreciable excess. Add potassium permanganate (KMnO₄) solution (3.2 g/L) until the solution is tinted pink. Finally add just enough oxalic acid (10 g/L) to destroy the pink color. Transfer the solution to a 100-mL volumetric flask, dilute to volume, and mix.

126.1.2 Transfer a 50-mL aliquot to a 100-mL beaker, add 1.0 mL of HNO₃ (1+1), dilute to approximately 80 mL, and mix.

126.2 Reagent Blank:

126.2.1 Transfer 10.0 mL of NaOH solution to a 100-mL volumetric flask containing 11.5 mL of HNO₃ (1+1). Dilute to approximately 50 mL, cool, dilute to volume, and mix. Transfer a 50-mL aliquot to a 100-mL beaker, add 1 mL of HNO₃ (1+1), dilute to 80 mL, and mix.

126.2.2 To the remaining portion of the reagent blank add 1 mL of HNO₃ (1+1), dilute to volume, and mix. This portion is used as the reagent blank for the reference solution in 126.4.

126.3 Color Development—Proceed as directed in 125.3.

126.4 Reference Solution—To the remaining portion of the test solution add 1 mL of HNO₃ (1+1), dilute to volume, and mix. Take the photometric reading of the reference solution as directed in 125.4 using the reagent blank obtained in 126.2.2 for the initial setting of the photometer.

NOTE 16—For routine work, the reference solution correction may be omitted unless the test solution is colored yellow.

127. Calculation

127.1 Convert the photometric readings of the test and reference solutions to milligrams of silicon by means of the calibration curve. Calculate the percentage of silicon as follows:

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

where:

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

B = reference solution correction, expressed as milligrams of silicon, and

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

SILICON BY THE SODIUM HYDROXIDE-PERCHLORIC ACID (GRAVIMETRIC) TEST METHOD

128. Scope

128.1 This test method covers the determination of silicon in concentrations from 0.5 to 20.0 %.

129. Summary of Test Method

129.1 The sample is dissolved with sodium hydroxide and hydrogen peroxide, and the solution acidified with perchloric acid. The silica is dehydrated, ignited, weighed, and then volatilized with hydrofluoric acid. The residue is ignited and weighed. The loss in weight represents silicon dioxide.

130. Interferences

130.1 The elements ordinarily present in aluminum and aluminum-base alloys do not interfere if their concentrations are under the maximum limits shown in 1.1.

131. Reagents

131.1 Ammonium Acetate Wash Solution (250 g/L)—Dissolve 25 g of ammonium acetate in 1 mL of glacial acetic acid and 99 mL of water.

131.2 Sodium Hydroxide Solution (500 g/L)—Dissolve 500 g of sodium hydroxide (NaOH) in water in a nickel or stainless steel beaker, and dilute to 1 L. Store in a plastic bottle.

131.3 Sulfurous Acid (H₂SO₃)—Saturate water with sulfur dioxide (SO₂). Prepare fresh as needed.

132. Procedure

132.1 Test Solution:

132.1.1 Weigh, to the nearest 1 mg, a portion of the sample calculated to contain from 0.010 to 0.075 g of silicon, but weighing not less than 0.35 g and transfer to a covered 250-mL nickel beaker. Add 12 mL of NaOH solution for each gram of sample (Note 17). When the reaction is complete, wash down the cover and sides of the beaker with a small jet of hot water, keeping the volume as small as possible. Place the covered beaker on the hot plate and cautiously evaporate to a syrupy consistency. Cool, add H₂O₂ dropwise, and repeat the evaporation. Continue the addition of H₂O₂ and the evaporation until the silicon is completely oxidized as shown by the absence of any black or gray particles.

NOTE 17—The following procedure for decomposition may be used: add 6 g of NaOH pellets for each gram of sample and add 10 mL of water, in small increments.

132.1.2 Remove the beaker from the hot plate, cool, wash the cover and sides of the beaker with 10 mL of water, and pour the solution into a 400-mL glass beaker containing 40 mL of HClO₄ (3+2) (Notes 18 and 19). Rinse the nickel beaker, first with hot water and then with a few millilitres of HClO₄ (3+2) to which an equal volume of water has been added. Police the beaker thoroughly, and finally rinse with hot water. Add all the rinsings to the main solution. Add 5 mL of HNO₃ and 5 mL of H₂SO₃.

NOTE 18—Perchloric acid can be used safely as specified in the



procedure. It should not, however, be brought in contact with finely divided aluminum, silicon, or organic matter.

NOTE 19—The HClO_4 (3+2) may be replaced with the following $\text{H}_2\text{SO}_4\text{-HClO}_4$ mixture: 315 mL of water, 625 mL of H_2SO_4 , and 85 mL of HClO_4 . In this case, after fuming, dissolve the salts with 90 mL of water and 10 mL of H_2SO_4 solution (1+3).

132.1.3 Evaporate to dense white fumes, cover, and fume for 15 min (Note 20). Cool, add 100 mL of hot water, stir well, and heat until the salts are dissolved (Note 21). If manganese dioxide (MnO_2) is present, dissolve it by adding H_2O_2 or H_2SO_3 dropwise. Add ashless paper pulp, and filter using a medium, low-ash paper. Thoroughly police the beaker to remove all the SiO_2 . Wash the precipitate with hot water until the washings no longer give an acid reaction to litmus. Finally wash once with H_2SO_4 (1+9). Reserve the paper and precipitate.

NOTE 20—If lead is present, it may be removed after filtering and washing the precipitate with water and H_2SO_4 . Wash the precipitate on the paper with hot ammonium acetate wash solution. The ammonium acetate wash solution must be excluded from the silicon filtrate.

NOTE 21—If appreciable amounts of tin and antimony are present, make the dehydration with H_2SO_4 and dissolve the salts with HCl .

132.1.4 Evaporate the filtrate and washings and proceed as directed in 132.1.3.

132.1.5 Place the filter papers and precipitates in a platinum crucible, dry and char the paper at a low temperature, and then ignite at 1000°C or above to constant weight. Cool in a desiccator and weigh.

132.1.6 To the residue, add a few drops of H_2SO_4 (1+1) and about 5 mL of HF . Evaporate carefully to dryness on a hot plate, ignite at 1000°C or above, cool in a desiccator, and weigh. Repeat the treatment with HF and ignite to constant weight. The loss in weight represents silicon dioxide (SiO_2).

132.2 *Reagent Blank*—Make a blank determination, following the same procedure and using the same amounts of all reagents.

133. Calculation

133.1 Calculate the percentage of silicon as follows:

$$\text{Silicon, \%} = [(A - B) \times 0.4674]/C \times 100 \quad (7)$$

where:

A = silicon dioxide found, g,

B = correction for blank, g, and

C = sample used, g.

TIN BY THE IODATE (TITRIMETRIC) TEST METHOD

134. Scope

134.1 This test method covers the determination of tin in concentrations from 0.03 to 1.0 %.

135. Summary of Test Method

135.1 The sample is dissolved in hydrochloric acid and any insoluble material is removed. Tin is reduced with aluminum in the presence of antimony in an inert atmosphere. The stannous tin is titrated with iodate solution using starch as the indicator.

136. Interferences

136.1 The elements ordinarily present in aluminum and aluminum-base alloys do not interfere if their concentrations

are under the maximum limits shown in 1.1.

137. Apparatus

137.1 *Apparatus for Reduction of Tin*—Apparatus No. 7A.

138. Reagents

138.1 *Aluminum*, sheet or rolled foil.

138.2 *Antimony*, powdered.

138.3 *Potassium Iodate, Standard Solution* (approximately 0.017 N)—*Prepare as directed for Reagent No. 12, using 0.5945 g instead of the specified weight. Standardize against aliquots of tin solution (1 mL = 0.001 g Sn) containing approximately the same amount of tin as the samples to be tested. Carry the standard through the procedure as directed in 139.1.2 and 139.1.3 and 139.2. Calculate the tin equivalent of the potassium iodate (KIO_3) solution as follows:*

$$\text{Tin equivalent, g/mL} = A/B \quad (8)$$

where:

A = tin represented in the standard, g, and

B = KIO_3 solution required for titration of the tin, mL.

138.4 *Sodium Bicarbonate Solution* (100 g/L)—*Dissolve 100 g of sodium bicarbonate (NaHCO_3) in water and dilute to 1 L.*

138.5 *Sodium Bicarbonate Tablets* (10 grains).

138.6 *Starch-Potassium Iodide Solution*—*Prepare as directed for Reagent No. 110, using 40 g of KI instead of the specified weight.*

138.7 *Tin, Standard Solution* (1 mL = 0.001 g Sn)—*Reagent No. 19.*

139. Procedure

139.1 *Test Solution:*

139.1.1 Transfer 1.0 to 3.0 g of the sample, weighed to the nearest 1 mg, to a 500-mL flask. Add 0.25 g of antimony and 150 mL of HCl (1+2). When the reaction subsides, heat the solution and then boil it for about 10 min to ensure complete dissolution of the tin. Filter through a medium paper (Note 22) and wash with HCl (1+2).

NOTE 22—If the sample has no appreciable insoluble residue on dissolution with HCl , the filtration step may be omitted.

139.1.2 Return the filtrate to the original flask and add 0.25 g of antimony and 0.5 g of aluminum. Stopper the flask with the special stopper and syphon, as directed in Apparatus 7A.

139.1.3 Boil gently for 10 to 15 min (until all the metallic tin and aluminum are in solution). Place the flask in a cooling bath with the outlet of the syphon tube immersed in the NaHCO_3 solution. When the solution is cold, remove the stopper, immediately add 4 NaHCO_3 tablets and 5 mL of fresh starch-KI solution, and titrate rapidly with KIO_3 solution to a persistent blue end point.

139.2 *Reagent Blank*—Make a blank determination, following the same procedure and using the same amounts of all reagents.

140. Calculation

140.1 Calculate the percentage of tin as follows:

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

where:

A = KIO_3 solution required for titration of the test solution, mL,