Designation: E 360 – 96 (Reapproved 2001)

Standard Test Methods for Chemical Analysis of Silicon and Ferrosilicon[1]

This standard is issued under the fixed designation E 360; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the chemical analysis of silicon and ferrosilicon having chemical compositions within the following limits:

Element	Concentration, %
Aluminum	2.0 max
Arsenic	0.10 max
Calcium	1.00 max
Carbon	0.50 max
Chromium	0.50 max
Copper	0.30 max
Manganese	1.00 max
Nickel	0.30 max
Phosphorus	0.10 max
Silicon	20.00 to 99.5
Sulfur	0.025 max
Titanium	0.20 max

1.2 The test methods appear in the following order:

	Sections
Arsenic by the Molybdenum Blue Photometric Method	9-19
Aluminum by the Quinolinate Photometric and Gravimetric Methods	20-30
Silicon by the Sodium Peroxide Fusion-Perchloric Acid Dehydration Method	31-38

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 5 and 26.8.1, 27.4.1.1, and 36.3.1.

2. Referenced Documents

2.1 *ASTM Standards:*

A 100 Specification for Ferrosilicon[2]

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[3]

E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition[4]

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials[4]

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry[4]

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[5]

E 362 Test Methods for Chemical Analysis of Silicomanganese and Ferrosilicon Manganese[4]

E 363 Methods for Chemical Analysis of Chromium and Ferrochromium[4]

E 364 Test Methods for Chemical Analysis of Ferrochrome-Silicon[4]

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 the 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. Safety Hazards

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

6. Sampling

6.1 For procedures for sampling the material, and for

[1] These 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 E01.01 on Iron, Steel, and Ferroalloys.

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[2] *Annual Book of ASTM Standards*, Vol 01.02.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 03.05.

[5] Discontinued; see *1997 Annual Book of ASTM Standards*, Vol 03.06.

particle size of the sample for chemical analysis, refer to Practices E 32.

7. Rounding Off Calculated Values

7.1 Calculated values shall be rounded off to the desired number of places as directed in 3.4 to 3.6 of Practice E 29.

8. Interlaboratory Studies

8.1 These test methods have been evaluated in accordance with Practice E 173, unless otherwise noted in the Precision and Bias section.

ARSENIC BY THE MOLYBDENUM BLUE PHOTOMETRIC METHOD

9. Scope

9.1 This method covers the determination of arsenic in silicon and ferrosilicon in concentrations from 0.001 to 0.10 %.

10. Summary of Method

10.1 Arsenic is first separated by distillation as the trivalent chloride. Ammonium molybdate is added to form arsenomolybdate which is then reduced by hydrazine sulfate to form the molybdenum blue complex. Photometric measurement is made at approximately 850 nm.

11. Concentration Range

11.1 The recommended concentration range is 0.01 to 0.15 mg of arsenic per 50 mL of solution using a 1-cm cell.

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

12. Stability of Color

12.1 The color is stable for at least 2 h.

13. Interferences

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

14. Apparatus

14.1 *Distillation Apparatus,* Fig. 1.

14.2 *Zirconium Crucibles,* 30-mL capacity.

15. Reagents

15.1 *Ammonium Bromide* (NH_4Br).

15.2 *Ammonium Molybdate Solution* (10 g/L)—Dissolve 2.5 g of ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in 40 mL of warm water. Add 128 mL of H_2SO_4 (1+3), dilute to 250 mL, and mix.

15.3 *Ammonium Molybdate-Hydrazine Sulfate Solution*—Dilute 100 mL of ammonium molybdate solution to 900 mL, add 10 mL of hydrazine sulfate solution, dilute to 1 L, and mix. Do not use a solution that has stood more than 1 h.

15.4 *Arsenic, Standard Solution A* (1 mL = 0.10 mg As)—Transfer 0.1320 g of arsenic trioxide (As_2O_3) to a 1-L volumetric flask, dissolve in 100 mL of HCl, cool, dilute to volume, and mix.

15.5 *Arsenic, Standard Solution B* (1 mL = 0.01 mg As)—Using a pipet, transfer 100 mL of arsenic Solution A (1 mL = 0.10 mg As) to a 1-L volumetric flask, dilute to volume, and mix.

15.6 *Hydrazine Sulfate* ($(NH_2)_2\cdot H_2SO_4$).

15.7 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ($(NH_2)_2\cdot H_2SO_4$) in water, dilute to 1 L, and mix. Do not use a solution that has stood more than 1 day.

15.8 *Sodium Carbonate* (Na_2CO_3).

15.9 *Sodium Peroxide* (Na_2O_2).

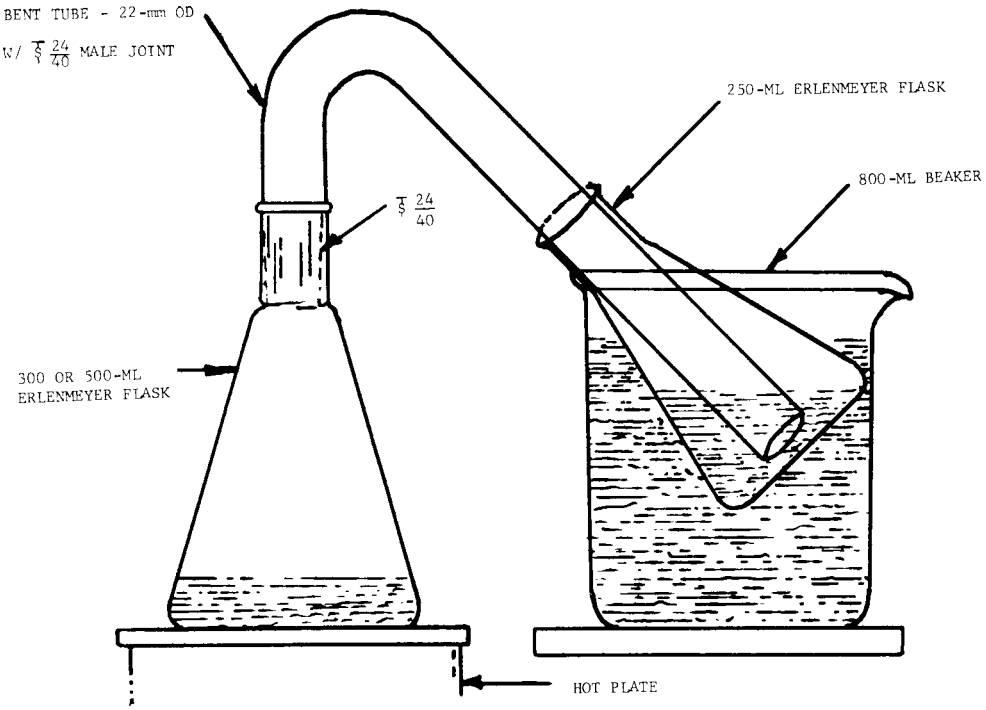

FIG. 1 Arsenic Distillation Apparatus

16. Preparation of Calibration Curve

16.1 *Calibration Solutions*:

16.1.1 Using pipets, transfer 1, 2, 5, 10, and 15 mL of arsenic Solution B (1 mL = 0.01 mg As) to 125-mL Erlenmeyer flasks.

16.1.2 Add 10 mL of HNO_3 and evaporate the solution to dryness on a hot plate. Bake for 30 min at 150 to 180°C. Remove from the hot plate. Add 45 mL of ammonium molybdate-hydrazine sulfate solution to each flask, warm gently to dissolve the residue, and transfer the solution to a 50-mL volumetric flask. Proceed as directed in 16.3.

16.2 *Reference Solution*—Transfer 10 mL of HNO_3 to a 125-mL Erlenmeyer flask and proceed as directed in 16.1.2.

16.3 *Color Development*—Heat the flask in a boiling water bath for 15 min. Remove the flask, cool to room temperature, dilute to volume with ammonium molybdate-hydrazine sulfate solution and mix.

16.4 *Photometry*:

16.4.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 850 nm. Using the test cell, take the photometric readings of the calibration solutions.

16.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 850 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions.

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

17. Procedure

17.1 *Test Solution*:

17.1.1 Select and weigh a sample to the nearest 0.2 mg in accordance with the following:

Arsenic, %	Sample Weight, g
0.001 to 0.015	0.500
0.01 to 0.04	0.250
0.035 to 0.10	0.125

Transfer the sample to a 30-mL zirconium crucible containing 10 g of Na_2O_2 and 1 g of Na_2CO_3 if ferrosilicon, or 8 g of Na_2O_2 plus 2 g of Na_2CO_3 if silicon metal.

17.1.2 Mix thoroughly with a metal spatula. Fuse carefully over a free flame by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have melted down quietly; raise the temperature gradually to avoid spattering. When the contents are molten, give the crucible a rotary motion to stir up any unattacked particles of the alloy adhering to the bottom or sides. Finally, increase the temperature until the crucible is bright red for 1 min. Cool the crucible to room temperature. Transfer the crucible to an 800-mL beaker containing 60 mL of H_2SO_4 (1+1) and 200 mL of water. Dissolve the melt; remove and rinse the crucible.

17.1.3 If manganese dioxide is present, add H_2SO_3 dropwise until the solution clears.

17.1.4 Heat to boiling, and cool. While stirring vigorously, add NH_4OH until the solution is alkaline to litmus, and then add 3 to 5 mL in excess. Heat to boiling, remove from the heat, and allow the precipitate to settle. Filter on a coarse filter paper and wash five times with hot water. Discard the filtrate. Remove the filter paper, carefully open it, and place it on the inside wall of the original 800-mL beaker. Wash the precipitate from the paper using a fine stream of water. Pass 25 mL of HNO_3 (1+1) over the paper, and wash well with water but do not exceed a total volume of 40 mL. Discard the paper. Warm gently until the precipitate dissolves.

17.1.5 Transfer the solution to the distillation flask, add 1 g of NH_4Br and 0.75 g of hydrazine sulfate. Add 20 mL of HNO_3 (1+1) to the receiving flask, and place the flask in an 800-mL beaker containing cold water. Assemble the apparatus (Fig. 1), heat the distillation flask, and distill into the receiving flask.

17.1.6 Distill until the volume is reduced to 10 mL or until oxides of nitrogen are noted in the distillation flask. Remove the distillation flask from the heat source. Place the receiving flask on a hot plate and evaporate the solution to dryness. Bake for 30 min at 150 to 180°C. Add 45 mL of ammonium molybdate-hydrazine sulfate solution to the flask, warm gently to dissolve the residue, and transfer the solution to a 50-mL volumetric flask. Proceed as directed in 17.3.

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

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

17.4 *Photometry*—Take the photometric reading of the test solution as directed in 16.4.

18. Calculation

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

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

where:

A = milligrams of arsenic found in 50 mL of final test solution, and

B = grams of sample represented in 50 mL of final test solution.

19. Precision and Bias

19.1 Although samples covered by this method were not available for testing, the precision data obtained for other types of alloys, using the methods indicated in Table 1, should apply. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this method is adequate for the contemplated use.

TABLE 1 Statistical Information—Arsenic

Ferroalloy Type	Arsenic Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1. No. 1, E 363	0.0015	0.0001	0.0005
2. No. 1, E 364	0.0018	0.0003	0.0003
3. No. 1, E 362	0.025	0.001	0.002
4. No. 2, E 362	0.039	0.001	0.002

ALUMINUM BY THE QUINOLINATE PHOTOMETRIC AND GRAVIMETRIC METHODS

20. Scope

20.1 This method covers the determination of aluminum in concentrations from 0.01 to 2.0 %.

21. Summary of Method

21.1 The sample is dissolved in nitric and hydrofluoric acids and fumed with perchloric acid. After the removal of interfering elements, aluminum is separated as the quinolinate. The determination is completed gravimetrically when aluminum is present in concentrations greater than 0.2 % or photometrically when aluminum is present in concentrations less than 0.2 %. Photometric measurement is made at approximately 395 nm.

22. Concentration Range (Photometric Method)

22.1 The recommended concentration range is 0.005 to 0.10 mg of aluminum per 25 mL of solution, using a 1-cm cell.

NOTE 2—See Note 1.

23. Stability of Color (Photometric Method)

23.1 The color is relatively stable, but readings should be made within 5 min.

24. Interferences

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

25. Apparatus

25.1 *Glassware*—To prevent contamination of the sample, all glassware must be cleaned with hot HCl (1+1) before use. It is recommended that a set of glassware be reserved for the determination of aluminum at concentrations below 0.01 %.

25.2 *Mercury Cathode*—Apparatus No. 10B.

25.3 *Platinum Dishes and Covers*, 150 or 200 and 400-mL capacity.

25.4 *Plastic Beakers*, TFE-fluorocarbon, 400-mL capacity.

25.5 *Plastic Funnels.*

25.6 *Spectrophotometer*—A spectrophotometer is recommended rather than a filter instrument because of the increased sensitivity that it provides.

26. Reagents

26.1 *Aluminum, Standard Solution* (1 mL = 0.005 mg Al)—Transfer 0.4396 g of potassium aluminum sulfate ($K_2Al_2(SO_4)_4 \cdot 24H_2O$) to a 250-mL volumetric flask, dissolve in water, add 15 mL of HCL (1+1), dilute to volume, and mix. Using a pipet, transfer 50 mL to a 1-L volumetric flask, dilute to volume, and mix. Store the solution in a polyethylene bottle.

26.2 *Ammonium Acetate Buffer Solution* (180 g/L)—Dissolve 90 g of ammonium acetate in water and dilute to 500 mL.

26.3 *Bromine Water (Saturated)*—Add 20 mL of bromine to 400 mL of water, and shake. Store in a glass stoppered bottle.

26.4 *Bromocresol Purple Indicator Solution* (0.4 g/L)—Reagent No. 120.

26.5 *Chloroform* ($CHCl_3$).

26.6 *Cupferron Solution* (60 g/L)—Reagent No. 115.

26.7 *8-Quinolinol Solution* (50 g/L)—Dissolve 25 g of 8-quinolinol in 60 mL of acetic acid, dilute to 300 mL with warm water, mix, filter through a medium filter paper, and dilute to 500 mL. Store in an amber bottle away from direct sunlight. Do not use a solution that has stood for more than one month.

26.8 *Sodium Cyanide Solution* (100 g/L)—Dissolve 100 g of sodium cyanide (NaCN) in 800 mL of water and dilute to 1 L. Store in a polyethylene bottle.

26.8.1 **Warning:** The preparation, storage, and use of NaCN solution require care and attention. Avoid inhalation of fumes and exposure of the skin to the chemical and its solutions. Work in a well-ventilated hood. Refer to Section 6 of Practices E 50. Because of the strongly alkaline properties of NaCN solution, contact with glass may result in appreciable contamination of the reagent with aluminum.

26.9 *Sodium Hydroxide Solution* (200 g/L)—Dissolve 40 g of sodium hydroxide (NaOH) in 150 mL of water in a plastic beaker and dilute to 200 mL.

26.10 *Tartaric Acid Solution* (100 g/L)—Dissolve 50 g of tartaric acid in 400 mL of water and dilute to 500 mL.

27. Preparation of Calibration Curve

27.1 *Calibration Solutions*—Using pipets, transfer 2, 5, 10, 15, and 20 mL of aluminum solution (1 mL = 0.005 mg Al) to 150 mL beakers each containing 40 mL of water and 2 mL of H_2SO_4 (1+1). Proceed as directed in 27.4.

27.2 *Reagent Blank*—Add 40 mL of water and 2 mL of H_2SO_4 (1+1) to a 150-mL beaker. Proceed as directed in 27.4.

27.3 *Reference Solution*—Chloroform ($CHCl_3$).

27.4 *Color Development*:

27.4.1 Treat the solutions singly as follows: Add 1 mL of ammonium acetate buffer solution and 10 mL of NaCN solution (**Warning:** see 27.4.1.1). Using a pH meter, adjust the pH to 9.0± 0.2 with NH_4OH (1+1) or HCl (1+1).

27.4.1.1 **Warning:** The solution must be kept under a hood after the NaCN solution is added and until the $CHCl_3$ extraction is completed.

27.4.2 Transfer the solution to a 125-mL pear-shaped separatory funnel. Add 1 mL of 8-quinolinol solution, mix, add 10-mL of $CHCl_3$, and shake vigorously for 20 s. Allow the phases to separate and drain the $CHCl_3$ layer into a dry 50-mL beaker. Add 10 mL of $CHCl_3$ to the separatory funnel and extract as before. Combine the two $CHCl_3$ extracts.

27.4.3 Sprinkle 0.5 g of anhydrous sodium sulfate (Na_2SO_4) over the surface of the $CHCl_3$ extracts and then decant the $CHCl_3$ into a 25-mL volumetric flask (Note 3). Rinse the beaker with 3 to 5 mL of $CHCl_3$ and transfer to the 25-mL volumetric flask. Dilute to volume with $CHCl_3$, and mix.

NOTE 3—Avoid transferring any Na_2SO_4 to the volumetric flask when decanting the $CHCl_3$ extracts and rinsings.

27.5 *Photometry*:

27.5.1 *Multiple-Cell Photometer*—Measure the cell correction using absorption cells with a 1-cm light path and a light band centered at approximately 395 nm. Using the test cell, take the photometric readings of the calibration solutions, and

of the reagent blank solution.

27.5.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 395 nm. While maintaining this adjustment, take the photometric readings of the calibration solutions and of the reagent blank solution.

27.6 *Calibration Curve*—Plot the net photometric readings of the calibration solutions against milligrams of aluminum per 25 mL of solution.

28. Procedure

28.1 *Test Solution*:

28.1.1 Transfer a 2.00-g sample, weighed to the nearest 1 mg, to a 150 or 200-mL platinum dish. Add 50 mL of HNO_3 (1+1) and partially cover the dish. Add 30 mL of HF in small portions. After each addition, swirl the dish and allow the reaction to subside. When all the HF has been added and the reaction has subsided, place the dish on a low-temperature hot plate and digest until dissolution is complete.

28.1.2 Remove and rinse the cover. Add 15 mL of $HClO_4$, and evaporate to copious fumes. Cool, wash down the sides of the dish with water, and swirl to dissolve the salts. Repeat the evaporation to copious fumes.

28.1.3 Cool, add 75 mL of water, digest until all soluble salts are in solution, and heat to boiling. Filter, using a 12.5-cm fine filter paper, into a 400-mL beaker. Wash the dish and paper 10 times with hot water. Reserve the filtrate.

28.1.4 Transfer the paper to a platinum crucible, dry the paper and residue, and then heat at about 600°C until the carbon is removed. Finally ignite at 1100°C to remove volatile oxides. Cool, add 2 to 3 drops of H_2SO_4 (1+1), 2 to 3 mL of HF, evaporate to dryness, and then heat at a gradually increasing rate until the H_2SO_4 is removed. Cool, add 2 to 3 g of sodium hydrogen sulfate ($NaHSO_4$) and fuse. Leach the fused melt in the reserved filtrate (28.1.3).

28.1.5 Cool, transfer the solution to a mercury cathode cell and dilute to 150 to 200 mL. Electrolyze at 10 to 15 A for 2 h or until a spot test for iron (Note 4) indicates the solution to be essentially iron-free. Without interrupting the current, transfer the solution back to the original beaker, and rinse the cell and electrodes several times with water and add the rinsings to the solution. Filter through a 12.5-cm medium filter paper containing paper pulp into a 600-mL beaker and wash 3 or 4 times with hot water.

NOTE 4—*Spot Test*—Transfer 1 drop of the electrolyte to a cover glass or spot test plate. Add 1 drop of H_2SO_4 (1+1), 1 drop of saturated potassium permanganate ($KMnO_4$) solution, and 1 drop of sodium thiocyanate (NaSCN) solution (500 g/L). When only a faint pink color is obtained, the electrolysis may be considered to be complete.

28.1.6 Add 10 mL of H_2SO_4 (1+1), 15 mL of bromine water, and a boiling stone. Boil gently and evaporate the solution to about 75 mL. Cool in an ice bath to 5°C.

28.1.7 Transfer the solution to a 250-mL conical separatory funnel, and without delay, add 15 mL of cupferron solution. Shake for 30 s. Add 20 mL of $CHCl_3$, shake for 1 min, allow to settle, draw off the $CHCl_3$ layer and discard it. Repeat the extraction again with 20 mL of $CHCl_3$. If any color remains in the aqueous layer, again add 15 mL of cupferron solution and repeat the $CHCl_3$ extractions. When the aqueous layer is colorless, continue the $CHCl_3$ extractions until the $CHCl_3$ layer is colorless. Transfer the aqueous layer to the original 600-mL beaker, add 25 mL of HNO_3, and evaporate to fumes of SO_3.

NOTE 5—**Caution:** The $CHCl_3$ extracts may contain enough perchlorate to be subject to spontaneous ignition upon prolonged standing. They should therefore be disposed of immediately.

28.1.8 Cool, dilute to 20 to 30 mL, and boil to remove chlorine. Cool, transfer to a 400-mL plastic (TFE-fluorocarbon) beaker or a platinum dish, police the beaker or dish, and rinse. Add the rinsings to the main solution. Neutralize with NaOH solution, and then add 10 mL in excess. Add 1 mL of H_2O_2 and digest at 80 to 90°C for 5 to 7 min to coagulate the manganese precipitate. Allow to cool at room temperature for 10 min. Filter through a plastic funnel containing an 11-cm fine filter paper previously washed with hot NaOH solution (20 g/L), and collect the filtrate in a 400-mL plastic beaker. Wash the paper and precipitate 4 or 5 times with hot water. Neutralize with HCl (1+1) and then add 3 to 5 mL of HCl in excess. Transfer to a 200-mL volumetric flask, dilute to volume, and mix. Proceed as directed in 28.3 or 28.4 depending on the aluminum concentration.

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

28.3 *Gravimetric Procedure* (for aluminum concentrations greater than 0.2 %):

28.3.1 Using a pipet, transfer a portion of the solution reserved in 28.1.8 to a 400-mL beaker, and dilute to 200 mL. Select the solution in accordance with the following:

Aluminum, %	Aliquot, Volume, mL	Equivalent Sample Weight, g	8-Quinolinol, mL
0.20 to 1.00	100	1.00	10
1.00 to 1.50	100	1.00	15
1.50 to 2.0	50	0.50	15

28.3.2 Add 5 mL of tartaric acid solution and 4 to 6 drops of bromocresol purple solution. Add NH_4OH (1+1) dropwise until the solution turns just purple.

NOTE 6—It is imperative that the solution be made just purple. If the end point has been passed, add HCl (1+1) until the solution turns yellow, then add NH_4OH (1+1) until it is just purple.

28.3.3 Add 1 mL of H_2O_2(Note 7). Heat on a low-temperature hot plate to 50 to 60°C. With stirring, slowly add the volume of 8-quinolinol solution specified in 28.3.1. While stirring vigorously, slowly add 35 mL of ammonium acetate buffer solution. Stir frequently and digest for 10 min, maintaining the temperature below 70°C (Note 8). Remove and let stand at room temperature for at least 40 but no longer than 90 min.

NOTE 7—Do not precipitate the aluminum in more than three samples at one time.

NOTE 8—It is important that the temperature of the solution does not exceed 70°C.

28.3.4 Filter using a tared medium-porosity fritted-glass crucible. Scrub the beaker with a rubber policeman and rinse with water. Wash the precipitate five or six times with water using a total volume of about 60 mL. Dry the precipitate at

135°C for 1½h. Cool and weigh as aluminum quinolinate.

28.4 *Photometric Procedure* (for concentrations less than 0.2 %):

28.4.1 *Test Solution*:

28.4.1.1 Using a pipet, transfer a portion of the solution reserved in 28.1.8 to a 250-mL beaker. Select the solution in accordance with the following:

Aluminum, %	Aliquot Volume, mL	Equivalent Sample Weight, g
0.003 to 0.02	50	0.500
0.01 to 0.04	25	0.250
0.02 to 0.10	10	0.100
0.08 to 0.20	5	0.050

28.4.1.2 If necessary, dilute to 50 mL. Proceed as directed in 28.4.4.

NOTE 9—Proceed with each solution one at a time through all the remaining steps.

28.4.2 *Reagent Blank*—Transfer an aliquot of the reagent blank (28.2) of the same volume as that taken for the test solution to a 250-mL beaker. Proceed as directed in 28.4.4.

28.4.3 *Reference Solution*—Chloroform ($CHCl_3$).

28.4.4 *Color Development*—Proceed as directed in 27.4.

28.4.5 *Photometry*—Take the photometric readings of the reagent blank and test solution as directed in 27.5.

29. Calculation

29.1 *Gravimetric Finish*:

29.1.1 Calculate the percentage of aluminum as follows:

$$\text{Aluminum, \%} = [((A - B) \times 0.587)/C] \times 100 \quad (2)$$

where:

A = grams of aluminum quinolinate found,
B = correction for blank, in grams, and
C = grams of sample represented in the aliquot taken.

29.2 *Photometric Finish*:

29.2.1 Convert the net photometric reading of the test solution to milligrams of aluminum and the net photometric reading of the reagent blank to the equivalent milligrams of aluminum by means of the calibration curve. Calculate the percentage of aluminum as follows:

$$\text{Aluminum, \%} = (D - E)/(F \times 10) \quad (3)$$

where:

D = milligrams of aluminum found in 25 mL of the final test solution,
E = equivalent milligrams of aluminum found in 25 mL of the reagent blank, and
F = grams of sample represented in 25 mL of the final test solution.

30. Precision and Bias

30.1 Eight laboratories cooperated in testing this method and obtained the data summarized in Table 2. Samples with aluminum concentrations near the limits of the scope were not available for testing. The user is cautioned to verify by the use of reference materials, if available, that the precision and bias of this method is adequate for the contemplated use.

TABLE 2 Statistical Information—Aluminum

Test Sample	Aluminum Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1. Ferrosilicon, 70 % Si	0.026	0.004	0.005
2. Ferrosilicon, 70 % Si	0.075	0.005	0.010
3. Ferrosilicon, 50 % Si	0.47	0.03	0.07
4. Ferrosilicon, 50 % Si	0.94	0.05	0.09
5. Ferrosilicon, 50 % Si	1.49	0.07	0.13

SILICON BY THE SODIUM PEROXIDE FUSION-PERCHLORIC ACID DEHYDRATION METHOD

31. Scope

31.1 This method covers the determination of silicon in ferrosilicon in concentrations from 40 to 80 %.

32. Summary of Method

32.1 The sample is fused with sodium peroxide and leached with water. Silicic acid is dehydrated by fuming with perchloric acid. The solution is filtered and the residue is ignited and weighed. The silica in the residue is volatilized with hydrofluoric acid. The residue is ignited and reweighed; the loss in weight is used to calculate the silicon content of the sample.

33. Interferences

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

34. Apparatus

34.1 *Crucible*, 40 mL, made of silicon-free iron, zirconium, nickel, or vitreous carbon. A crucible made from No. 20 gage ingot iron 0.965 mm (0.038 in.) in thickness is suitable.

35. Reagents

35.1 *Silver Nitrate* (10 g/L)—Dissolve 10 g of silver nitrate ($AgNO_3$) in water and dilute to 1 L.

35.2 *Sodium Peroxide* (Na_2O_2), 35 mesh or finer.

35.3 *Sodium Carbonate* (Na_2CO_3), anhydrous powder.

36. Procedure

36.1 Select and weigh a sample to the nearest 0.2 mg in accordance with the following:

Silicon, %	Sample Weight, g
20 to 25	1.0
25 to 50	0.5
40 to 80	0.25

36.2 Transfer the sample to a 40-mL crucible containing a mixture of 10 g of Na_2O_2 and 3 g of Na_2CO_3. Mix thoroughly. Carry a blank test through the same procedure, using the same quantities of reagents.

36.3 Heat the crucible and contents on a hot plate at 350 to 400°C until the melt darkens (see 36.3.1). Carefully fuse over a low flame by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have melted down. When the contents are completely molten, rotate the crucible carefully to stir up any particles of sample on the bottom or sides, keeping the crucible and

contents at a low, red heat (see36.3.1). Just before completion of the fusion, which requires approximately 3 or 4 min, increase the temperature to bright redness for 5 min. Allow the crucible to cool almost to room temperature.

36.3.1 **Warning:** Use proper safety practices and equipment when performing sodium peroxide fusions.

NOTE 10—If the reaction proceeds violently with spattering of the contents because of too rapid heating, the use of insufficient Na_2CO_3, or the lack of thorough mixing, appreciable loss may occur and the work should be repeated.

36.4 Dissolve the fusion as directed in 36.4.1 or 36.4.2.

36.4.1 *Alternative 1*—Transfer the crucible and contents to a 600-mL beaker (polytetrafluoroethylene, stainless steel, or high purity nickel) containing 200 mL of water. Cover with a watch glass. When the effervescence has ceased, remove and rinse the crucible with hot water. Cautiously, with stirring, transfer the solution to a 600- or 800-mL glass beaker containing 30 mL of HCl. Add 100 mL of $HClO_4$ and proceed as directed in 36.5.

36.4.2 *Alternative 2*—Cover the crucible and tap it on a hard surface to loosen the melt. Transfer the melt to a clean 600-mL glass beaker. Add 100 mL of $HClO_4$ to the beaker and cover with a watch glass. Fill the crucible with hot water and, after effervescence has ceased in the beaker, add the contents of the crucible to the beaker. Transfer any residue from the crucible to the beaker using a rubber policeman and a minimum amount of water (Note 11). Proceed as directed in 36.5.

NOTE 11—If an iron crucible was used, add 30 mL HCl to the beaker at this point. Proceed as directed in 36.5.

36.5 Place the beaker on a hot plate and heat to fumes of $HClO_4$. Continue heating until the residue begins to crystallize. Remove from the hot plate and allow to cool. Carefully add 20 mL of HCl down the wall of the beaker. Stir and dilute to 250 mL with hot water. Stir well and allow to settle.

36.6 Filter the solution through a 12.5-cm ashless, medium-porosity filter paper placed in a 75-mm fluted glass funnel, collecting the filtrate in a 600-mL beaker. Scrub the original beaker thoroughly with a rubber-tipped rod. Wash the paper and precipitate with hot HCl (1+19) until the yellow color of the iron salts disappears, then finally wash several times with hot water until the chloride ions disappear (verified by means of a spot test with silver nitrate solution).

NOTE 12—Thorough washing of the filter is necessary to remove any trace of $HClO_4$ that would cause the paper to flame up during ignition.

36.7 Transfer the filtrate and washings to the beaker used for the initial dehydration. Evaporate to a volume of about 250 mL. Add 20 mL of $HClO_4$ and carry out a second dehydration following the procedure described in 36.5. Filter and wash the precipitate as directed in 36.6, but use cold water instead of hot water.

36.8 Transfer the two filter papers to a 40-mL platinum crucible. Add 4 drops of ammonium hydroxide (Note 13). Heat gently at a maximum temperature of 400°C on a gas burner or other suitable means until the papers are dry. Partially cover the crucible with a platinum lid and continue heating the crucible and contents until the carbon is completely charred (Note 14). Cool and add 1 mL of H_2SO_4 (1+1). Evaporate to dryness on a sand bath or other suitable means. Transfer covered crucible to a muffle furnace and heat at 1100°C to constant weight. Cool in a desiccator and weigh.

NOTE 13—The addition of the ammonium hydroxide reduces the hazard from the reaction of perchlorates during ignition which may cause spattering of the silica from the crucible.

NOTE 14—Great care should be exercised in igniting the papers since the current of air produced by a burning filter paper is sufficient to carry SiO_2 out of the crucible.

36.9 Moisten the impure silica with a few drops of water. Add approximately 10 mL of HF plus 2 to 3 drops of concentrated H_2SO_4. Evaporate until fumes cease to be evolved and then cool.

36.10 Repeat the procedure described in 36.9, but decreasing the volume of HF to 2 mL. Heat in a muffle furnace at 1100°C to constant weight. Cool in a desiccator and weigh.

37. Calculation

37.1 Calculate the percentage silicon as follows:

$$\text{Silicon, \%} = \frac{(A - B) - (C - D)}{E} \times 0.4674 \times 100 \qquad (4)$$

where:

A = weight of crucible plus impure silica, g,
B = weight of crucible plus impurities, g,
C = weight of crucible plus impure silica in blank test, g,
D = weight of crucible plus impurities in blank test, g, and
E = weight of sample, g.

38. Precision and Bias [6]

38.1 *Precision*—Nine laboratories cooperated in testing the method on test specimen BCS 305/1 (FeSi) and eleven laboratories cooperated on test specimen JK 26 (FeCrSi). Each laboratory analyzed the sample on six separate days. Repeatability (R_1) and reproducibility (R_2) were calculated by analysis of variance (Practice E 173) using $M = 1$. The data are summarized in Table 3.

TABLE 3 Statistical Information—Silicon

Test Specimen	Silicon Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
FeSi (BCS 305/1, 75.0 Si)	74.93	0.350	0.945
FeCrSi (JK 26, 45.5 Si)	45.24	0.469	0.793

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

39. Keywords

39.1 chemical analysis; ferrosilicon; gravimetric; silicon

[6] Supporting data are available from ASTM Headquarters. Request RR: E03–1043.

APPENDIX

(Nonmandatory Information)

X1. TYPICAL SPECIFICATIONS[A] COVERED BY THE METHODS IN ASTM METHODS E 360 (FERROSILICON AND SILICON METAL)

ASTM SPECIFICATIONS

A 100

To determine whether a specification that is not listed falls into this category, compare the range of concentration specified for each element with the range indicated in 1.1 of Methods E 360.