



Designation: E 360 – 96 (Reapproved 2001)

Standard Test Methods for Chemical Analysis of Silicon and Ferrosilicon¹

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 Quinolate 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 Ferrosilicon²

E 29 Practice for Using Significant Digits in Test Data to

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.

Determine Conformance with Specifications³

E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition⁴

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials⁴

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry⁴

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals⁵

E 362 Test Methods for Chemical Analysis of Silicomanganese and Ferrosilicon Manganese⁴

E 363 Methods for Chemical Analysis of Chromium and Ferrochromium⁴

E 364 Test Methods for Chemical Analysis of Ferrochrome-Silicon⁴

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.

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.

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 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 ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$) 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.

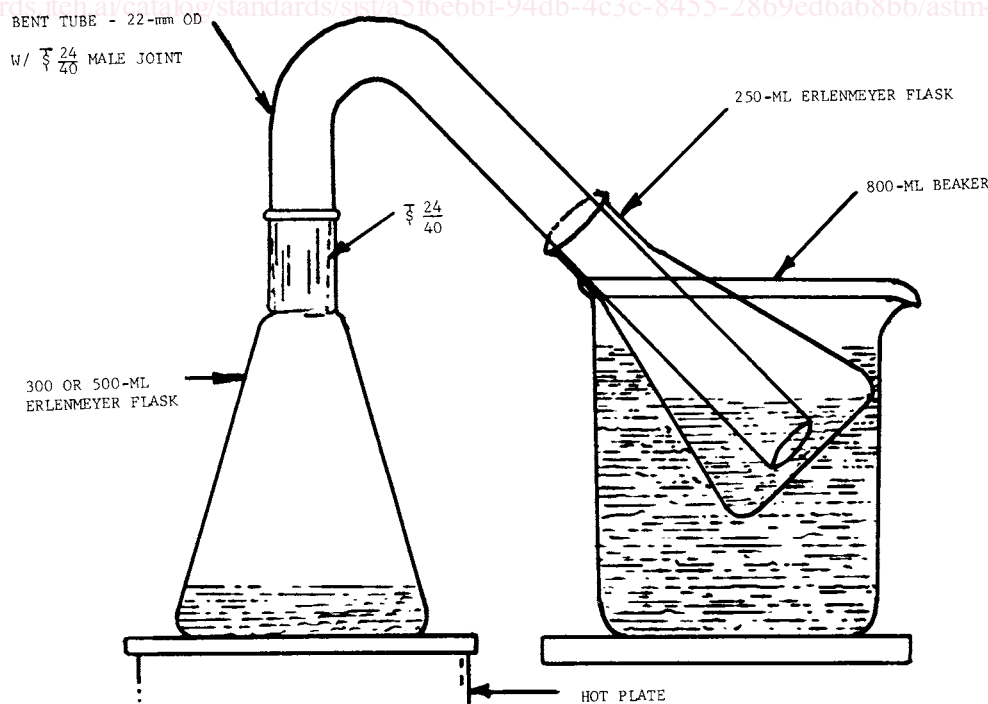


FIG. 1 Arsenic Distillation Apparatus

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* ((NH₂)₂·H₂SO₄).

15.7 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ((NH₂)₂·H₂SO₄) in water, dilute to 1 L, and mix. Do not use a solution that has stood more than 1 day.

15.8 *Sodium Carbonate* (Na₂CO₃).

15.9 *Sodium Peroxide* (Na₂O₂).

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 HNO₃ 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 HNO₃ 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 Na₂O₂ and 1 g of Na₂CO₃ if ferrosilicon, or 8 g of Na₂O₂ plus 2 g of Na₂CO₃ 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 unattached 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 H₂SO₄ (1+1) and 200 mL of water. Dissolve the melt; remove and rinse the crucible.

17.1.3 If manganese dioxide is present, add H₂SO₃ dropwise until the solution clears.

17.1.4 Heat to boiling, and cool. While stirring vigorously, add NH₄OH 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 HNO₃ (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 NH₄Br and 0.75 g of hydrazine sulfate. Add 20 mL of HNO₃ (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

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

materials, if available, that the precision and bias of this method is adequate for the contemplated use.

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