



Designation: E 364 – 94 (Reapproved 2000)

## Standard Test Methods for Chemical Analysis of Ferrochrome-Silicon<sup>1</sup>

This standard is issued under the fixed designation E 364; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 These test methods cover the chemical analysis of ferrochrome-silicon having chemical compositions within the following limits:<sup>2</sup>

| Element    | Concentration,<br>% |
|------------|---------------------|
| Aluminum   | 0.50 max            |
| Antimony   | 0.005 max           |
| Arsenic    | 0.005 max           |
| Bismuth    | 0.005 max           |
| Boron      | 0.005 max           |
| Carbon     | 0.15 max            |
| Chromium   | 34.0 to 47.0        |
| Cobalt     | 0.10 max            |
| Columbium  | 0.050 max           |
| Copper     | 0.050 max           |
| Lead       | 0.005 max           |
| Manganese  | 0.75 max            |
| Molybdenum | 0.050 max           |
| Nickel     | 0.50 max            |
| Nitrogen   | 0.050 max           |
| Phosphorus | 0.030 max           |
| Silicon    | 30.0 to 45.0        |
| Silver     | 0.005 max           |
| Sulfur     | 0.030 max           |
| Tantalum   | 0.050 max           |
| Tin        | 0.005 max           |
| Titanium   | 0.50 max            |
| Vanadium   | 0.50 max            |
| Zinc       | 0.005 max           |
| Zirconium  | 0.050 max           |

1.2 The test methods appear in the following order:

|  | Sections |
|--|----------|
| Arsenic by the Molybdenum Blue Photometric Method                        | 8-18     |
| Chromium by the Acid Dissolution Titrimetric Method                      | 19-25    |
| Silicon by the Sodium Peroxide Fusion-Perchloric Acid Dehydration Method | 26-33    |

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 applica-*

*bility of regulatory limitations prior to use.* For precautions to be observed in these test methods, refer to Practices E 50, and to precautions included in the individual methods.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- A 482 Specification for Ferrochrome-Silicon<sup>3</sup>
- E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>4</sup>
- E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition<sup>5</sup>
- E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals<sup>5</sup>
- E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals<sup>5</sup>
- E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals<sup>5</sup>
- E 360 Test Methods for Chemical Analysis of Silicon and Ferrosilicon<sup>6</sup>

### 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.

<sup>1</sup> 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 E01.01 on Iron, Steel and Ferroalloys.

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<sup>2</sup> These test methods are intended for use in determining the composition of ferrochrome-silicon as specified in Specification A 482.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 01.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 03.05.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 03.06.



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

## 5. Sampling

5.1 For procedures for sampling the material, and for particle size of the sample for chemical analysis, refer to Practices E 32.

## 6. Rounding Off Calculated Values

6.1 Calculated values shall be rounded off to the desired number of places as directed in the Rounding Off and Special Case Rounding Off procedures in the Rounding-Off Method Section of Practice E 29.

## 7. Interlaboratory Studies

7.1 These 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

## 8. Scope

8.1 This method covers the determination of arsenic in ferrochrome-silicon in concentrations from 0.001 to 0.005 %.

8.2 The limits of the scope have been set at 0.001 to 0.005 % because test materials containing other arsenic concentrations were unavailable for testing. However, recognizing that the procedure should give satisfactory results at lower and higher concentrations, the calibration and procedure section cover the range from 0.001 to 0.1 %.

8.2.1 Users of this method are cautioned that its use on samples outside of the 0.001 to 0.005 % range is not supported by interlaboratory testing.

## 9. Summary of Method

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

## 10. Concentration Range

10.1 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.

## 11. Stability of Color

11.1 The color is stable for at least 2 h.

## 12. Interferences

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

## 13. Apparatus

13.1 *Distillation Apparatus*, Fig. 1, Methods E 360.

13.2 *Zirconium Crucibles*, 30-mL capacity.

## 14. Reagents

14.1 *Ammonium Bromide* ( $\text{NH}_4\text{Br}$ ).

14.2 *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  $\text{H}_2\text{SO}_4$  (1 + 3), dilute to 250 mL, and mix.

14.3 *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.

14.4 *Arsenic, Standard Solution A* (1 mL = 0.10 mg As)—Transfer 0.1320 g of arsenic trioxide ( $\text{As}_2\text{O}_3$ ) to a 1-L volumetric flask, dissolve in 100 mL of HCl, cool, dilute to volume, and mix.

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

14.6 *Hydrazine Sulfate*— $(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4$ .

14.7 *Hydrazine Sulfate Solution* (1.5 g/L)—Dissolve 1.5 g of hydrazine sulfate ( $(\text{NH}_2)_2\cdot\text{H}_2\text{SO}_4$ ) in water, dilute to 1 L, and mix. Do not use a solution that has stood more than 1 day.

14.8 *Sodium Carbonate* ( $\text{Na}_2\text{CO}_3$ ).

14.9 *Sodium Peroxide* ( $\text{Na}_2\text{O}_2$ ).

## 15. Preparation of Calibration Curve

### 15.1 Calibration Solutions:

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

15.1.2 Add 10 mL of  $\text{HNO}_3$  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 15.3.

15.2 *Reference Solution*—Transfer 10 mL of  $\text{HNO}_3$  to a 125-mL Erlenmeyer flask 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 the flask, warm gently to dissolve the residue, transfer to a 50-mL volumetric flask and proceed as directed in 15.3.

15.3 *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.

### 15.4 Photometry:

15.4.1 *Multiple-Cell Photometer*—Measure the cell correction with water 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 using the solution prepared in 15.2 as a reference.

15.4.2 *Single-Cell Photometer*—Transfer a suitable portion of the reference solution (15.2) to an absorption cell with a 1-cm light path and adjust the photometer to the initial setting, using a light band centered at approximately 850 nm. While

maintaining this adjustment, take the photometric readings of the calibration solutions.

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

**16. Procedure**

16.1 *Test Solution:*

16.1.1 Select and weigh a sample to the nearest 0.1 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<sub>2</sub>O<sub>2</sub> and 2 g of Na<sub>2</sub>CO<sub>3</sub> or 8 g of Na<sub>2</sub>O<sub>2</sub> plus 2 g of Na<sub>2</sub>CO<sub>3</sub>.

16.1.2 Mix thoroughly with a metal spatula (Note 2). 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 H<sub>2</sub>SO<sub>4</sub>(1 + 1) and 200 mL of water. Dissolve the melt; remove and rinse the crucible.

NOTE 2—**Precaution:** Use proper safety practices and equipment when performing sodium peroxide fusions.

16.1.3 If manganese dioxide is present, add H<sub>2</sub>SO<sub>3</sub> dropwise until the solution clears.

16.1.4 Heat to boiling, and cool. While stirring vigorously, add NH<sub>4</sub>OH 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 HCl 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.

16.1.5 Transfer the solution to the distillation flask, add 1 g of NH<sub>4</sub>Br and 0.75 g of hydrazine sulfate. Add 20 mL of HNO<sub>3</sub>(1 + 1) to the receiving flask, and place the flask in an 800-mL beaker containing cold water. Assemble the apparatus (Fig. 1, Methods E 360), heat the distillation flask, and distill into the receiving flask.

16.1.6 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 16.3.

16.2 *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.

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

16.4 *Photometry*—Take the photometric reading of the test solution as directed in 15.4.

**17. Calculation**

17.1 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:

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

where:

- A = arsenic found in 50 mL of final test solution, mg, and
- B = sample represented in 50 mL of final test solution, g.

**18. Precision and Bias**

18.1 *Precision*—Nine laboratories cooperated in testing this method and obtained the data summarized in Table 1. Samples with arsenic concentrations near the upper limit of the scope were not available for testing.

18.2 *Bias*—The accuracy of the method could not be evaluated because adequate certified standard reference materials were unavailable at the time of testing. The user is cautioned to verify by the use of certified reference materials, if available, that the accuracy of this method is adequate for the contemplated use.

**CHROMIUM BY THE ACID DISSOLUTION  
TITRIMETRIC METHOD**

**19. Scope**

19.1 This method covers the determination of chromium in ferrochrome-silicon in concentrations from 30 to 60 %.

**20. Summary of Method**

20.1 The alloy is dissolved in sulfuric, nitric, and hydrofluoric acids, and the excess of the latter is complexed with boric acid. The chromium and manganese ions are oxidized to dichromate and permanganate ions, respectively, by ammonium peroxydisulfate with silver nitrate as a catalyst. After adding HCl to reduce permanganate ions, the dichromate ions are reduced by adding an excess of standard ferrous ammonium sulfate (salt or solution). The excess ferrous ions are titrated with standard potassium permanganate solution.

**21. Interferences**

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

**22. Reagents**

- 22.1 *Ammonium Peroxydisulfate* —((NH<sub>4</sub>)<sub>2</sub>-S<sub>2</sub>O<sub>8</sub>).
- 22.2 *Boric Acid* (H<sub>3</sub>BO<sub>3</sub>).

**TABLE 1 Statistical Information—Arsenic**

| Ferroalloy Type | Arsenic Found, % | Repeatability (R <sub>1</sub> , E 173) | Reproducibility (R <sub>2</sub> , E 173) |
|-----------------|------------------|--|--|
| Cr40-Si42-C0.05 | 0.0018           | 0.0003                                 | 0.0003                                   |