Designation: E 372 – 01

Standard Test Method for Determination of Calcium and Magnesium in Magnesium Ferrosilicon[1]

This standard is issued under the fixed designation E 372; 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 This test method covers the chemical analysis of magnesium ferrosilicon having chemical compositions within the following limits:

Element	Concentration Range, %
Aluminum	2.0 max
Calcium	0.25 to 3.00
Carbon	0.50 max
Cerium	1.0 max
Chromium	0.50 max
Magnesium	2.00 to 12.00
Manganese	1.0 max
Silicon	40.00 to 55.00
Sulfur	0.025 max
Titanium	0.2 max

1.2 *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.* For general precautions to be observed in this test method, refer to Practices E 50.

2. Referenced Documents

2.1 *ASTM Standards:*

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[2]

E 32 Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition[3]

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[3]

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals[4]

3. Significance and Use

3.1 This test method for the chemical analysis of metals and alloys is primarily intended to test such materials for compliance with compositional specifications. It is assumed that all who use this test method 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 this test method shall conform to Practice E 60.

5. Sampling

5.1 For procedures for sampling the material, refer to Methods E 32.

6. Rounding Calculated Values

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

7. Interlaboratory Studies

7.1 This test method has been evaluated in accordance with Practice E 173, unless otherwise noted in the precision and bias section.

CALCIUM AND MAGNESIUM BY THE (ETHYLENEDINITRILO)TETRAACETIC ACID (EDTA) TITRIMETRIC METHOD

8. Scope

8.1 This test method covers the determination of magnesium in concentrations from 2 to 12 % and calcium in concentrations from 0.25 to 3.0 %.

9. Summary of Test Method

9.1 After dissolution of the sample in nitric and hydrofluoric

[1] This test method is 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.

Current edition approved May 10, 2001. Published July 2001. Originally published as E 568 – 76 T. Redesignated E 372 in 1980. Last previous edition E 372 – 84 (1996).

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

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

[4] Discontinued; see *1997 Annual Book of ASTM Standards*, Vol 03.05.

acids, an ammonium hydroxide precipitation is made to separate other elements from calcium and magnesium. Calcium, and magnesium plus calcium are titrated in separate aliquot portions after adding triethanolamine and potassium cyanide to mask residual traces of iron, copper, nickel, manganese, and aluminum that may be present. Calcium is titrated with disodium (ethylenedinitrilo)tetraacetate (EDTA) at pH 12. Magnesium plus calcium is titrated with EDTA at pH 10.0 and the magnesium concentration is calculated by correcting for the volume of EDTA required to titrate the calcium.

10. Interferences

10.1 Provision is made for the removal or masking of interfering elements ordinarily present in magnesium ferrosilicon.

11. Apparatus

11.1 *Beakers*, TFE-fluorocarbon 500-mL.

11.2 *pH Meter*—Apparatus No. 3A.

12. Reagents

12.1 *Ammonium Chloride Buffer Solution* (pH 10.0)—Dissolve 60 g of ammonium chloride (NH_4Cl) in 200 mL of water, add 570 mL of NH_4OH, and dilute to 1 L.

12.2 *Calcium, Standard Solution* (1 mL = 0.2002 mg Ca)—Dissolve 0.5000 g of calcium carbonate ($CaCO_3$) (purity: 99.9 % min) in 100 mL of HCl (5+95). Boil 1 min, cool, transfer to a 1-L volumetric flask, dilute to volume, and mix.

12.3 *Disodium Ethylenedinitrilo-Tetraacetate Dihydrate (EDTA), Standard Solution* (0.005 *M*)—Prepare a solution as directed for Reagent No. 22, using 1.8613 g instead of the specified weight.

12.3.1 Standardize the solution as follows: Using a pipet, tranfer 25 mL of the calcium solution (1 mL = 0.2002 mg Ca) to a 250-mL beaker, add 1 mL of $MgCl_2$ solution and 100 mL of water, and proceed as directed in 13.4.

NOTE 1—Containers used for the storage of dilute solutions of EDTA should be pretreated with a hot alkaline EDTA solution (10 g/L), and rinsed with water.

12.3.2 Calculate the calcium equivalent of the EDTA solution as follows:

$$\text{Calcium equivalent, mg/mL} = A/B \quad (1)$$

where:

A = calcium, mg, and

B = EDTA solution required to titrate the calcium solution, mL.

12.3.3 Calculate the magnesium equivalent of the solution as follows:

$$\text{Magnesium equivalent, mg/mL} = C \times 0.6068 \quad (2)$$

where C = calcium equivalent (12.3.2).

12.4 *Eriochrome Black-T Indicator Solution* (6 g/L of methanol)—Dissolve 0.3 g of Eriochrome Black-T and 1 g of sodium borate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) in 50 mL of methanol. Do not use a solution that has stood for more than 8 h.

12.5 *Hydroxy Naphthol Blue Mixture*—Add 1.0 g of indicator to 100 g NaCl and mix thoroughly.

12.6 *Magnesium Chloride* (2.5 g/L)—Dissolve 0.25 g of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) in 50 mL of water, and dilute to 100 mL.

12.7 *Potassium Cyanide Solution* (50 g/L)—Dissolve 2 g of potassium hydroxide (KOH) in water, add 5 g of potassium cyanide (KCN) (**Warning;** see 12.7.1), dilute to 100 mL, and transfer to a plastic bottle.

12.7.1 **Warning:** The preparation, storage, and use of KCN 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 7 of Practices E 50.

12.8 *Potassium Hydroxide Buffer Solution* (pH 12.5)—Dissolve 531 g of KOH in water, add 50 g of KCN (**Warning;** see 12.7.1), and dilute to 1 L. Store the solution in a plastic container.

12.9 *Triethanolamine Solution* (200 mL/L)—Dilute 20 mL of triethanolamine to 100 mL with water.

13. Procedure

13.1 Transfer a 1.0-g sample, weighed to the nearest 0.1 mg, to a dry 500-mL TFE-fluorocarbon beaker. Add 10 mL of HNO_3. Cautiously add 10 mL of HF, and heat gently until the sample is dissolved. Wash the sides of the beaker with a fine stream of water. Add 20 mL of $HClO_4$, place on a hot plate with a surface temperature not exceeding 300°C, and evaporate to dense fumes of $HClO_4$. Cool, add 10 mL of HCl (1+1), and heat to dissolve salts. Transfer to a 600-mL glass beaker and evaporate to moderate dryness on a hot plate. Place on a burner and evaporate to complete *dryness* (indicated by the absence of fumes). Add 20 mL of HCl (1+1), wash the sides of the beaker with a fine stream of water, and heat to dissolve salts.

13.2 Add 200 mL of water and 5 g of NH_4Cl. Heat to boiling. Remove from the hot plate and cool. Add NH_4OH until the iron begins to precipitate. Using a pH meter, adjust the pH to 4.25 + 0.25 by adding NH_4OH dropwise. Cool to room temperature, transfer to a 500-mL volumetric flask, dilute to volume, and mix. Let stand 1 h to allow the precipitate to settle.

13.3 Dry-filter approximately 200 mL of the solution through a 12.5-cm medium filter paper into a dry beaker. Using a pipet, transfer 50 mL of the solution to a 250-mL beaker.

13.4 *Titration of Calcium*—Add 5 mL of triethanolamine solution, stir, and immediately add 5 mL of the KOH buffer solution (**Warning;** see 12.7.1). Add 100 mg of hydroxy naphthol blue indicator mixture. Titrate with EDTA solution (0.005 *M*) to the disappearance of the last trace of the red color.

13.5 *Titration of Calcium and Magnesium*—Using a pipet, transfer a second aliquot portion of the filtered solution from 13.3 to a 250-mL beaker in accordance with the following:

Magnesium, %	Sample Weight, g	Aliquot for Magnesium Determination, mL
2.0 to 5.0	1.0	50
5.0 to 12.0	1.0	25

13.6 Add 5 mL of triethanolamine solution, stir, and immediately add 10 mL of the NH_4Cl buffer solution. Add 5 mL of the KCN solution (**Warning;** see 12.7.1), and 3 to 5 drops of Eriochrome Black-T solution. Titrate with the EDTA solution (0.005 *M*) to the disappearance of the last trace of the red color.

NOTE 2—In going through the end point, the color changes from red to blue to blue-green. The appearance of a blue-green color indicates over-titration.

14. Calculation

14.1 Calculate the percentage of calcium as follows:

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

where:

A = EDTA solution required to titrate the calcium (13.4), mL
B = calcium equivalent of the EDTA solution, mg/mL (12.3.2), and
C = sample represented in the final aliquot, mg.

14.2 Calculate the percentage of magnesium as follows:

$$\text{Magnesium, \%} = \frac{[D - (A/E)] \times F}{G} \times 100 \quad (4)$$

where:

A = EDTA solution required to titrate the calcium (13.4), mL,
D = EDTA solution required to titrate the magnesium and calcium (13.6), mL,
E = 50 divided by millilitres of aliquot taken for titration of magnesium and calcium (13.5),
F = magnesium equivalent of the EDTA solution, mg/mL (12.3.3), and
G = sample represented in the final aliquot, mg.

15. Precision and Bias [5]

15.1 *Precision*—Eight laboratories cooperated in testing this method and obtained the data summarized in Table 1 and

TABLE 1 Statistical Information—Calcium

Test Specimen	Calcium Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1. 48Si-45Fe	0.496	0.035	0.044
2. 46Si-43Fe	1.06	0.04	0.08

Table 2. Samples with calcium and magnesium concentrations

TABLE 2 Statistical Information—Magnesium

Test Specimen	Magnesium Found, %	Repeatability (R_1, E 173)	Reproducibility (R_2, E 173)
1. 48Si-45Fe	5.16	0.13	0.15
2. 46Si-43Fe	8.98	0.18	0.30

near the upper limit of the scope were not available for testing.

15.2 *Bias*—The bias of this 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.

16. Keywords

16.1 chemical analysis; ferrosilicon; magnesium ferrosilicon; titrimetric method

[5] Supporting data have been filed at ASTM Headquarters. Request RR:E03—1005.