



Designation: E372 – 21

Standard Test Method for Determination of Calcium and Magnesium in Magnesium Ferrosilicon by EDTA Titrimetry¹

This standard is issued under the fixed designation E372; 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	Composition 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For general precautions to be observed in this test method, refer to Practices E50.

1.3 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*²

- E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
- E32 Practices for Sampling Ferrous Alloys and Steel Additives

¹ This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.01 on Iron, Steel, and Ferrous Alloys.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- for Determination of Chemical Composition
- E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
- E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
- E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals (Withdrawn 1998)³

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology E135.

4. Significance and Use

4.1 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.

5. Hazards

5.1 For precautions to be observed in the use of certain reagents and equipment in this test method, refer to Practices E50.

5.2 Specific hazard statements are given in 13.7.1 and 14.1.

6. Sampling

6.1 For procedures to sample the material, refer to Practices E32.

7. Rounding Calculated Values

7.1 Rounding of test results obtained using this test method shall be performed as directed in Practice E29, Rounding Method, unless an alternative rounding method is specified by the customer or applicable material specification.

³ The last approved version of this historical standard is referenced on www.astm.org.

8. Interlaboratory Studies

8.1 This test method has been evaluated in accordance with Practice E173, unless otherwise noted in the precision and bias section.

CALCIUM AND MAGNESIUM BY THE (ETHYLENEDINITRILLO) TETRAACETIC ACID DISODIUM SALT (EDTA) TITRIMETRY METHOD

9. Scope

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

10. Summary of Test Method

10.1 After dissolution of the sample in HNO₃ and HF, an NH₄OH 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 (ethylenedinitrilo) tetraacetic acid disodium salt (EDTA) at pH 12.5. Magnesium plus calcium is titrated with EDTA at pH 10.0, and the magnesium content is calculated by correcting for the volume of EDTA required to titrate the calcium.

11. Interferences

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

12. Apparatus

12.1 *Beakers*, TFE-fluorocarbon 500 mL.

12.2 *pH Meter*.

13. Reagents

13.1 *Ammonium Chloride Buffer Solution* (pH 10.0)—Dissolve 60 g of ammonium chloride (NH₄Cl) in 200 mL of water, add 570 mL of NH₄OH, and dilute to 1 L.

13.2 *Calcium, Standard Solution* (1 mL = 0.2002 mg Ca)—Dissolve 0.5000 g of calcium carbonate (CaCO₃) (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.

13.3 *(Ethylenedinitrilo) Tetraacetic Acid, Disodium Salt (EDTA), Standard Solution*: (0.005 M)

NOTE 1—The complete chemical compound name, (ethylenedinitrilo) tetraacetic acid disodium salt, is commonly referred to as EDTA.

13.3.1 Dissolve 1.8613 g of EDTA in water; transfer to a 1 L volumetric flask; dilute to volume; and mix. The solution will remain stable for several months when stored in plastic or borosilicate glass bottles. 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.

13.3.2 Standardize the solution as follows: Using a pipet, transfer 25 mL of the calcium solution (1 mL = 0.2002 mg Ca)

to a 250 mL beaker, add 1 mL of MgCl₂ (13.6) solution and 100 mL of water, and proceed as directed in 14.4.

13.3.3 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.

13.3.4 Calculate the magnesium equivalent of the solution as follows:

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

where C = calcium equivalent (13.3.3).

13.4 *Eriochrome Black-T Indicator Solution* (6 g/L in methanol)—Dissolve 0.3 g of Eriochrome Black-T and 1 g of sodium borate decahydrate (Na₂B₄O₇·10H₂O) in 50 mL of methanol. Do not use a solution that has stood for more than 8 h.

13.5 *Hydroxy Naphthol Blue Mixture*—Add 1.0 g of hydroxy naphthol blue indicator to 100 g NaCl and mix thoroughly.

13.6 *Magnesium Chloride* (2.5 g/L)—Dissolve 0.25 g of magnesium chloride hexahydrate (MgCl₂·6H₂O) in 50 mL of water, and dilute to 100 mL.

13.7 *Potassium Cyanide Solution* (50 g/L)—Dissolve 2 g of KOH in water, add 5 g of potassium cyanide (KCN) (**Warning**; see 13.7.1), dilute to 100 mL, and transfer to a plastic bottle.

13.7.1 **Warning**: The preparation, storage, and use of KCN requires 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 8 of Practices E50.

13.8 *KOH Buffer Solution* (pH 12.5)—Dissolve 531 g of KOH in water, add 50 g of KCN (**Warning**; see 13.7.1), and dilute to 1 L. Store the solution in a plastic container.

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

14. Procedure

14.1 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 HNO₃. 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 HClO₄, place on a hot plate with a surface temperature not exceeding 300 °C, and evaporate to dense fumes of HClO₄. 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 hot plate 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.

(Warning: HF produces very serious burns which may or may not be painful on first contact. Such burns often damage

bone and other tissue within the body. Standard procedure is to use gloves and protective clothing when handling this reagent. After the material is added, the closed container, gloves, and all surfaces that may later be touched are rinsed with large quantities of water. Even one drop of HF on the skin or fingernail must receive immediate first aid and medical attention should be promptly sought.)

14.2 Add 200 mL of water and 5 g of NH₄Cl. Heat to boiling. Remove from the hot plate and cool. Add NH₄OH until the iron begins to precipitate. Using a pH meter, adjust the pH to 4.25 ± 0.25 by adding NH₄OH 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.

14.3 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.

14.4 *Titration of Calcium*—Add 5 mL of triethanolamine solution, stir, and immediately add 5 mL of the KOH buffer solution (**Warning**; see 13.7.1). 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.

14.5 *Titration of Calcium and Magnesium*—Using a pipet, transfer a second aliquot portion of the filtered solution from 14.3 to a 250 mL beaker as follows:

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

14.6 Add 5 mL of triethanolamine solution, stir, and immediately add 10 mL of the NH₄Cl buffer solution. Add 5 mL of the KCN solution (**Warning**; see 13.7.1), and 3 drops 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—Passing through the end point, the color changes from red to blue to blue-green. The appearance of a blue-green color indicates over-titration.

TABLE 1 Statistical Information—Calcium

Test Specimen	Calcium Found, %	Repeatability (R ₁ , E173)	Reproducibility (R ₂ , E173)
1. 48Si-45Fe	0.496	0.035	0.044
2. 46Si-43Fe	1.06	0.04	0.08

TABLE 2 Statistical Information—Magnesium

Test Specimen	Magnesium Found, %	Repeatability (R ₁ , E173)	Reproducibility (R ₂ , E173)
1. 48Si-45Fe	5.16	0.13	0.15
2. 46Si-43Fe	8.98	0.18	0.30

15. Calculation

15.1 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 (14.4), mL
- B = calcium equivalent of the EDTA solution, mg/mL (13.3.3), and
- C = sample represented in the final aliquot, mg.

15.2 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 (14.4), mL,
- D = EDTA solution required to titrate the magnesium and calcium (14.6), mL,
- E = 50 divided by millilitres of aliquot taken for titration of magnesium and calcium (14.5),
- F = magnesium equivalent of the EDTA solution, mg/mL (13.3.4), and
- G = sample represented in the final aliquot, mg.

16. Precision and Bias⁴

16.1 *Precision*—Eight laboratories cooperated in testing this method and obtained the data summarized in Table 1 and Table 2. Samples with calcium and magnesium compositions near the upper limit of the scope were not available for testing.

16.2 *Bias*—The bias of this method could not be evaluated because adequate certified 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 intended use.

17. Keywords

17.1 calcium; chemical analysis; EDTA; ferrosilicon; magnesium; magnesium ferrosilicon; titration; titrimetry

⁴ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1005. Contact ASTM Customer Service at service@astm.org.