



Standard Test Method for Calcium and Magnesium in Iron Ores by Atomic Absorption Spectrometry¹

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1. Scope

1.1 This test method covers the determination of calcium and magnesium in iron ores, concentrates, and agglomerates in the concentration range from 0.05 to 5 % of calcium and 0.05 to 3 % of magnesium.

1.2 *This standard does not purport to address all of the safety problems, 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.*

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

E 50 Practices for Apparatus, Reagents, and Safety Precautions for Chemical Analysis of Metals³

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores and Related Materials³

E 276 Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials³

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory⁴

2.2 Other Documents

E 663-86 (1991) Practice for Flame Atomic Absorption Analysis⁵

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E 135.

¹ This test method is under the jurisdiction of ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

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² *Annual Book of ASTM Standards*, Vol 11.01.

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

⁴ *Annual Book of ASTM Standards*, Vol 03.06.

⁵ Available from Global Engineering Documents, 15 Inverness Way, East Englewood, CO 80112-5704

4. Summary of Test Method

4.1 The sample is dissolved in hydrochloric acid with the addition of a small amount of nitric acid. After evaporation and dehydration, any insoluble residue is filtered, treated for the recovery of calcium and magnesium, and added to the main solution. The solution is aspirated into the flame of the atomic absorption spectrometer. For calcium, a nitrous oxide-acetylene burner is used, for magnesium, an air-acetylene burner is preferred (Note 1). The absorbed energy at the resonance line of the spectrum of calcium or magnesium, or both, is measured by atomic absorption spectrophotometry and compared with that of the calibration solutions of the two elements.

NOTE 1—If a nitrous oxide burner is used for the determination of magnesium, the sensitivity is decreased by a factor of about three.

If an air-acetylene burner is used for the determination of calcium, several elements, if present in percent amounts, interfere with the calcium determination. Also, lanthanum chloride must be employed and the sensitivity is decreased by a factor of about two.

5. Significance and Use

5.1 This test method is intended as a referee method for compliance with compositional specifications for impurity content. It is assumed that all who use this procedure will be trained analysts capable of performing common laboratory practices skillfully and safely. It is expected that work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Follow appropriate quality control practices such as those described in Guide E 882.

6. Interferences

6.1 None of the elements normally found in iron ores interfere with this test method (Note 1).

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*, meeting the following criteria:

7.1.1 *Minimum Sensitivity*—The absorbance of the highest calibration solution (see 8.4) must be at least 0.3.

7.1.2 *Curve-Linearity*—The difference between the readings of the highest calibration solutions must be more than 1.4 times the difference between the readings for the zero solutions and the lowest calibration solution.

7.1.3 *Minimum Stability*—The coefficient of variation of a number of measurements of the highest calibration solution and of the zero calibration solution must be less than 1.5 % and 0.5 % respectively, relative to the measurement of the highest calibration solution.

NOTE 2—Use of a strip chart recorder or digital readout device, or both, is advisable.

NOTE 3—Instrument parameters will vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. In the case of calcium, solutions were aspirated into a nitrous oxide-acetylene flame of a premix burner. For magnesium an air-acetylene burner was used.

	Ca	Mg
Hollow cathode lamp, mA	15	15
Wavelength, λ , Å	4227	2852
Nitrous oxide flow rate, L/min	13.8	...
Air flow rate, L/min	...	22
Acetylene flow rate, L/min	6.6	4.2

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available⁶. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D 1193.

8.3 *Calcium, Standard Solution* (1 mL = 25 μ g Ca)—Dissolve 1.2487 g of anhydrous calcium carbonate in 100 mL of dilute hydrochloric acid (HCl) (1+3). When solution is complete, cool and dilute to 1 L in a volumetric flask. Transfer 10 mL of this solution to a 200-mL volumetric flask. Dilute to volume, and mix.

8.4 *Calcium and Magnesium Calibration Solutions*—Using pipets, transfer, 5.0, 10.0, 20.0, 40.0, and 50.0-mL portions of the standard calcium and magnesium solutions to 200-mL volumetric flasks (Note 4). Dilute to 90 mL, add 6 mL of HCl (sp gr 1.19), 60 mL of background solution, and 40 mL of lanthanum chloride solution. Dilute to volume, and mix.

8.5 *Iron, Background Solution* (10 g/L)—Dissolve 10 g of high-purity iron in 50 mL of HCl, (sp gr 1.19) and oxidize by the dropwise addition of nitric acid (HNO₃, sp gr 1.42). Evaporate to a syrupy consistency. Add 20 mL of HCl (sp gr 1.19) and dilute to 200 mL with water. Add 20 g of sodium chloride (NaCl) dissolved in 200 mL water and dilute to 1 L with water.

8.6 *Lanthanum Chloride Solution* (50 g/L)—Dissolve 50 g of lanthanum chloride in 50 mL of HCl (sp gr 1.19) and 300 mL of hot water. Cool and dilute to 1 L.

8.7 *Magnesium, Standard Solution* (1 mL = 17.5 μ g Mg)—Dissolve 0.3500 g of high-purity magnesium by slowly adding 75 mL of HCl (1+3). When dissolved, dilute with water to 1 L in a volumetric flask. Transfer 10 mL of this solution to a 200-mL volumetric flask, dilute to volume, and mix.

8.8 *Zero Calibration Solution*—Transfer 60 mL of the background solution to a 200-mL volumetric flask, add 6 mL of HCl (sp gr 1.19), 40 mL of lanthanum chloride solution, dilute to volume, and mix.

NOTE 4—The range of calcium or magnesium that can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 7.1.

9. Hazards

9.1 For precautions to be observed in this method, refer to Practice E 50.

10. Sample Preparation

10.1 The analytical sample shall be pulverized to pass a No. 100 (150- μ m) sieve (see Test Method E 276).

NOTE 5—To facilitate decomposition, some ores, such as specular hematite, require grinding to pass a No. 200 (75- μ m) sieve.

11. Procedure

11.1 Transfer approximately 1.0 g of the sample to a small weighing bottle previously dried at about 150°C. Dry the bottle and contents for 1 h at 105 to 110°C. Cap the bottle and cool to room temperature in a desiccator. Momentarily release the cap to equalize the pressure and weigh the capped bottle and sample to the nearest 0.1 mg. Repeat the drying and weighing until there is no further weight loss. Transfer the sample to a 250-mL beaker and reweigh the capped bottle to the nearest 0.1 mg. The difference between the two weights is the weight of the sample taken for analysis.

11.2 Carry a reagent blank through all steps of the procedure starting with 11.3.

11.3 *Decomposition of Sample*—Moisten the sample with a few milliliters of water, add 25 mL of HCl, cover, and digest below the boiling point until no further attack is apparent. Add 2 mL of HNO₃ and digest for several minutes. Remove the cover and evaporate the solution to dryness. Heat the salts on a hot plate at 105 to 110°C for 15 min. Add 5 mL of HCl, cover the beaker, and warm for several minutes. Add 50 mL of water and warm until soluble salts are in solution. Filter on a fine-textured paper, and collect the filtrate in a 250-mL beaker. Transfer the residue quantitatively to the filter paper. Wash alternately three times with hot HCl (1+9) and hot water until the yellow color of ferric chloride is no longer apparent. Transfer the paper and residue to a platinum crucible. Reserve the filtrate.

11.4 *Treatment of Residue*—Ignite the paper and residue in the platinum crucible. Cool, moisten with several drops of water, add 3 or 4 drops of dilute sulfuric acid (H₂SO₄, 1+1) and 10 mL of hydrofluoric acid (HF). Evaporate slowly to expel silica and then fume off the excess of H₂SO₄. Finally ignite at

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

about 700°C. Add 1 g of anhydrous sodium carbonate (Na₂CO₃) to the residue, cover the crucible, and fuse over a burner or in a muffle furnace until a clear melt is obtained. Dissolve the cool melt in the reserved filtrate from 11.3, remove and wash the crucible and cover. Transfer the solution to a 200-mL volumetric flask, dilute to volume, and mix. If the solution is cloudy at this stage, indicating the presence of titania, filter a portion of the solution through a dry paper into a dry beaker. Transfer a proper aliquot of this solution (see Table 1) to a 200-mL volumetric flask and add 40 mL of the lanthanum chloride solution. Add the amount of background solution and HCl indicated in Table 1, dilute to volume, and mix.

until a steady signal is obtained and adjust the instrument readout system to obtain zero absorption or absorbance.

NOTE 7—The manufacturer’s instructions for igniting and extinguishing the nitrous oxide-acetylene burner should be strictly followed to avoid possible explosion hazards. Tinted safety glasses should be worn by the operator whenever the flame is burning.

11.6 *Measurements*—Aspirate water until the initial reading is again obtained. Aspirate the calibration solutions in the order of increasing absorption or absorbance starting with the zero calibration solution. When a stable response is obtained for each solution, record the readings. Aspirate the test solutions at the proper points in the calibration series. Aspirate water

TABLE 1 Dilution Guide for Test Solution

Element	Expected Percentage of Element in Sample	Aliquot, mL	Equivalent Weight of Sample, g	Background Solution to Be Added, mL	Hydrochloric Acid Added, mL
Calcium	0.05 to 0.5	50	0.25	45	4
Calcium	0.5 to 2.5	10	0.05	60	6
Calcium	2.5 to 10.0	2	0.01	60	6
Magnesium	0.05 to 0.25	40	0.20	50	4
Magnesium	0.25 to 1.25	10	0.05	60	6
Magnesium	1.25 to 5.00	2	0.01	60	6

NOTE 6—Dilutions shown in Table 1 will provide concentrations of calcium and magnesium falling within the range of the calibration solutions.

between each calibration and test solution. Repeat all measurements at least two more times.

TABLE 2 Precision

Average Concentration ^A of Element, %	Relative Standard Deviation ^B Within Laboratories, %	Relative Standard Deviation ^B Between Laboratories, %	Number of Laboratories	Number of Determinations
0.074 Ca	8.11	13.51	31	88
0.342 Ca	2.92	4.97	30	87
0.483 Ca	3.11	5.38	31	89
3.59 Ca	2.37	2.79	28	81
4.04 Ca	1.68	2.97	33	94
4.52 Ca	1.28	3.32	12	32
0.298 Mg	3.19	3.69	31	90
0.316 Mg	2.85	3.16	31	90
0.589 Mg	2.20	2.38	27	79
0.99 Mg	2.22	3.74	33	95
1.28 Mg	2.03	2.97	31	90
3.14 Mg	0.86	3.41	10	29

^A Each concentration of calcium and magnesium represents a different kind of iron ore.

^B Relative standard deviation (RSD), in this test method is calculated as follows:

$$\% \text{RSD} = (100/\bar{X}) \sqrt{\sum d^2/(n-1)}$$

where:

\bar{X} = average concentration, %,

d = difference of the determination from the mean, and

n = number of determinations.

11.5 *Adjustment of Atomic Absorption Spectrophotometer*—In accordance with Practice E 663 (discontinued 1997), set the initial instrument parameters to the values in Note 3. Light the burner and aspirate water until the instrument comes to thermal equilibrium. Optimize instrument response by adjusting the wavelength, fuel, air, burner, and nebulizer while aspirating the highest calibration solution to obtain maximum absorption or absorbance. Aspirate water

12. Calculation

12.1 Only if necessary, convert the average of the readings for each calibration solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the average absorbance of the zero calibration solution. In a similar manner, obtain the net absorbance of the test solution by subtracting the absorbance of the reagent blank solution.

12.2 Prepare calibration curves for calcium and magnesium by plotting the net absorbance values of the calibration solutions against micrograms of calcium or magnesium per millilitre.

12.3 Convert the net absorbance values of the sample solution to micrograms of calcium and magnesium per millilitre by means of the calibration curves.

12.4 Calculate the percentage of calcium and magnesium as follows:

$$\text{Calcium or magnesium, \%} = (A \times 200)/(B \times 10\,000) \quad (1)$$

where:

A = calcium or magnesium per mL, μg , and

B = sample represented in the 200-mL volume of the final test solution, g.

13. Precision and Bias ⁷

13.1 *Precision*—Table 2 indicates the precision of the test method within and between laboratories when applied to a number of samples of iron ore.

13.2 *Bias*—No information on the accuracy of this test method is known. The accuracy of this test method may be judged by comparison of accepted values for standard reference materials with the mean determined through interlaboratory testing.

14. Keywords

14.1 atomic absorption spectroscopy; calcium; iron ores; magnesium

⁷ Supporting data giving the results of cooperative testing have been filed at ASTM Headquarters. Request RR XXX-XXXX.

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