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Methods for chemical analysis of limestone and dolomite - Part 1: The determination of calcium oxide and magnesium oxide content - The complexometric titration method and the flame atomic absorption spectrometric method

石灰石及白云石化学分析方法 第 1 部分：氧化钙和氧化镁含量的测定 络合滴定法和火焰原子吸收光谱法

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Methods for chemical analysis of limestone and dolomite - Part 1: The determination of calcium oxide and magnesium oxide content - The complexometric titration method and the flame atomic absorption spectrometric method

WARNING: Personnel using this Part shall have formal laboratory work experience. This Part does not point out all possible safety issues. It is the responsibility of the user to take appropriate safety and health measures and ensure compliance with the conditions specified by relevant national laws and regulations.

1 Scope

This Part of GB/T 3286 specifies the determination of calcium oxide and magnesium oxide content by complexometric titration method and the determination of magnesium oxide content by atomic absorption spectrometric method.

This Part applies to the determination of calcium oxide content and magnesium oxide content in limestone and dolomite. It also applies to the determination of calcium oxide content and magnesium oxide content in metallurgical lime. Complexometric titration method, determination range (mass fraction): calcium oxide content is greater than 20 %, magnesium oxide content is greater than 2.5 %; atomic absorption spectrometric method, determination range (mass fraction): magnesium oxide content is 0.1 % ~ 2.5 %.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 2007.2 General rules for the sampling and sample preparation of

titrate the combined content of calcium oxide and magnesium oxide; or mask the calcium with slightly excessive EGTA standard titration solution, and use cyclohexane diamine tetraacetic acid (CyDTA) standard titration solution to titrate the magnesium oxide content.

For samples of which the iron oxide and alumina content is greater than 2.0 % or the manganese oxide content is greater than 0.10 %, use sodium diethylamine dithioformate (copper reagent) to precipitate and separate iron, aluminum and manganese ions, and take the filtrate to titrate the calcium oxide content and magnesium oxide content with EDTA or EGTA and CyDTA standard titration solutions.

3.2 Reagents

Unless otherwise specified in the analysis, only approved analytical reagents and distilled water of grade 3 or higher or water of equivalent purity that meets the requirements of GB/T 6682 shall be used.

3.2.1 Mixed flux: TAKE two portions of anhydrous sodium carbonate and one portion of boric acid, MIX well.

3.2.2 Hydrochloric acid (1 + 5).

3.2.3 Triethanolamine (1 + 4).

3.2.4 Ammonia water (1 + 1).

3.2.5 Potassium hydroxide solution (200 g/L), stored in plastic bottles. After preparation, it shall be placed for more than 12 h before use.

3.2.6 Sodium diethylamine dithioformate (copper reagent) solution (50 g/L).

3.2.7 Ammonia buffer solution (pH10): WEIGH 67.5 g of ammonium chloride and DISSOLVE in water, ADD 570 mL of ammonia water (ρ = 0.90 g/mL), DILUTE to 1 L with water, MIX well.

3.2.8 Calcium indicator (calcium carboxylic acid): TAKE 1 g of calcium indicator and GRIND with 100 g of sodium chloride, MIX well.

3.2.9 Acid chrome blue K-naphthol green B mixed indicator solution: TAKE 0.5 g of acid chrome blue K and 0.2 g of naphthol green B, DISSOLVE in water, DILUTE to 70 mL with water.

NOTE: The ratio of acid chrome blue K and naphthol green B can be appropriately adjusted according to the color development sensitivity of the indicator and the color discrimination ability of the operator.

(mL);

V_2 - the average value of the volume of EDTA standard titration solution consumed in the titration, in milliliters (mL);

V_{02} - the average value of the volume of EDTA standard titration solution consumed by the titration reagent blank, in milliliters (mL).

3.2.13 EGTA (ethylene glycol tetraacetic acid) standard titration solution [*c*(EGTA) = 0.01 mol/L]

3.2.13.1 Preparation

WEIGH 3.90 g of EGTA, PLACE it in a 500 mL beaker, ADD about 250 mL of water, HEAT at low temperature, dropwise ADD potassium hydroxide solution (3.2.5) under constant stirring until the reagent is dissolved, and COOL to room temperature. TRANSFER to a 1000 mL volumetric flask, DILUTE with water to the mark, and MIX well.

3.2.13.2 Calibration of the titer of EGTA standard titration solution to calcium oxide

Same as the calibration of the tire of EDTA standard titration solution to calcium oxide. OPERATE according to 3.2.12.2 and CALCULATE the titer T_3. USE EGTA standard titration solution (3.2.13.1) instead of EDTA standard titration solution (3.2.12.1).

3.2.14 CyDTA (cyclohexane diamine tetraacetic acid) standard titration solution [*c*(CyDTA) = 0.01 mol/L]

3.2.14.1 Preparation

WEIGH 3.70 g of CyDTA, PLACE it in a 500 mL beaker, ADD about 250 mL of water, HEAT at low temperature, dropwise ADD potassium hydroxide solution (3.2.5) under constant stirring until the reagent is dissolved, and COOL to room temperature. TRANSFER to a 1000 mL volumetric flask, DILUTE with water to the mark, and MIX well.

3.2.14.2 Calibration of the titer of CyDTA standard titration solution to magnesium oxide

Same as the calibration of the tire of EDTA standard titration solution to magnesium oxide. OPERATE according to 3.2.12.3 and CALCULATE the titer T_4. USE CyDTA standard titration solution (3.2.14.1) instead of EDTA standard titration solution (3.2.12.1).

3.3 Instruments

NOTE: This test solution can be used as a stock solution for the determination of calcium oxide, magnesium oxide, silicon dioxide, aluminum oxide and iron oxide. It can be used for GB/T 3286.1 the determination of calcium oxide and magnesium oxide content by complexometric titration method, GB/T 3286.2 the determination of silicon dioxide content by silicomolybdic blue spectrophotometric method, GB/T 3286.3 the determination of aluminium oxide content by chrome azurol S spectrophotometric method, GB/T 3286.4 the determination of iron oxide content by o-phenanthroline spectrophotometric method. If the content of these chemical components in the sample are determined at the same time, it may prepare only one portion of stock solution of the sample, and then the stock solution is divided for the determination according to each analysis method.

3.5.4.3 TAKE two portions of 25.00 mL of stock solution (3.5.4.2) (it may take two portions of 15.00 mL for metallurgical lime samples), PLACE them in 250 mL or 500 mL Erlenmeyer flasks respectively, ADD 25 mL of water. DETERMINE the calcium oxide content and magnesium oxide content by the method specified in 3.5.5 or 3.5.6.

3.5.4.4 When the alumina and iron oxide content in the sample is greater than 2.0 % or the manganese oxide content is greater than 0.10 %, use copper reagent to separate them: TAKE 100.00 mL of stock solution (3.5.4.2) into a 250 mL volumetric flask, ADD 50 mL of water, PUT a small piece of Congo red test paper into the solution, NEUTRALIZE most of the acid with potassium hydroxide solution (3.2.5), RINSE the bottleneck with water, dropwise ADD ammonia water (3.2.4) to neutralize until the test paper is red, ADD 10 mL of copper reagent solution (3.2.6), SHAKE vigorously for 1 min, COOL to room temperature, DILUTE to the mark with water, MIX well, LEAVE for 30 min. DRY filtrate with medium-speed quantitative filter paper, DISCARD the first 20 mL of filtrate. TAKE two portions of 50.00 mL of filtrate, PLACE them in 250 mL Erlenmeyer flasks respectively. DETERMINE the calcium oxide content and magnesium oxide content by the method specified in 3.5.5 or 3.5.6.

3.5.5 Titration of calcium oxide content and magnesium oxide content with EDTA

3.5.5.1 Titration of calcium oxide content

3.5.5.1.1 Limestone, metallurgical lime samples

In a portion of test solution (3.5.4.3 or 3.5.4.4), ADD 5 mL of triethanolamine (3.2.3), MIX well, ADD 20 mL of potassium hydroxide solution (3.2.5) and about 0.1 g of calcium indicator (3.2.8), MIX well. TITRATE with EDTA standard titration solution (3.2.12) until the test solution changes from red to bright blue, which is the end point. For blank test and samples containing less than 1.0 % magnesium oxide content, ADD 1.0 mL of magnesium oxide standard solution (3.2.11) before titration with EDTA standard titration solution.

3.5.6.1.2 Dolomite samples

In a portion of test solution (3.5.4.3 or 3.5.4.4), ADD 5 mL of triethanolamine (3.2.3), MIX well, ADD EGTA standard titration solution equivalent to 90 % to 95 % calcium oxide content in the titration solution (3.2.12), ADD 20 mL of potassium hydroxide solution (3.2.5) and about 0.1 g of calcium indicator (3.2.8), MIX well. Continue to TITRATE with EGTA standard titration solution (3.2.12) until the test solution changes from red to bright blue, which is the end point. Before the blank test titration, ADD 1.0 mL of magnesium oxide standard solution (3.2.11), no titrant is preset.

NOTE: Same as the note of 3.5.5.1.2.

3.5.6.2 Titration of magnesium oxide

In another portion of test solution (3.5.4.3 or 3.5.4.4), ADD 5 mL of triethanolamine (3.2.3), MIX well, ADD EGTA standard titration solution (3.2.13), of which the added amount is 0.4 mL more than the volume of EGTA standard titration solution consumed when titrating calcium oxide. ADD 20 mL of ammonia buffer solution (3.2.7), ADD 4 to 5 drops of acid chrome blue K-naphthol green B mixed indicator solution (3.2.9), TITRATE with CyDTA standard titration solution (3.2.14) until the test solution changed from dark red to blue green, which is the end point.

3.6 Calculation and representation of analysis results

3.6.1 Calculation of analysis results

3.6.1.1 Titration of calcium oxide content and magnesium oxide content with EDTA

3.6.1.1.1 CALCULATE the mass fraction of calcium oxide according to formula (3):

$$w(\mathrm{CaO}) = \frac{(V_3 - V_{03}) \times T_1}{m} \times 100\% \qquad \cdots\cdots (3)$$

where:

w(CaO) - the mass fraction of calcium oxide;

V_3 - the volume of EDTA standard titration solution consumed in the titration of calcium oxide, in milliliters (mL);

V_{03} - the volume of EDTA standard titration solution consumed in the titration of blank test solution, in milliliters (mL);

V_{05} - the volume of EGTA standard titration solution consumed in the titration of blank test solution, in milliliters (mL);

T_1 - the titer of EGTA standard titration solution to calcium oxide, in grams per milliliter (g/mL);

m - the sample amount corresponding to the taken test solution, in grams (g).

3.6.1.2.2 CALCULATE the mass fraction of magnesium oxide according to formula (6):

$$w(\mathrm{MgO}) = \frac{(V_6 - V_{06}) \times T_4}{m} \times 100\% \qquad \cdots\cdots (6)$$

where:

w(MgO) - the mass fraction of magnesium oxide;

V_6 - the volume of CyDTA standard titration solution consumed in the titration of magnesium oxide, in milliliters (mL);

V_{03} - the volume of CyDTA standard titration solution consumed in the titration of blank test solution, in milliliters (mL);

T_4 - the titer of CyDTA standard titration solution to magnesium oxide, in grams per milliliter (g/mL);

m - the sample amount corresponding to the taken test solution, in grams (g).

3.6.2 Determination and representation of analysis results

If the absolute value of the difference between the two independent analysis results of the same sample is not greater than the repeatability limit r value, the arithmetic mean is taken as the analysis result. If the absolute value of the difference between the two independent analysis results is greater than the r value, increase the number of measurements and determine the analysis result as specified in Annex A.

The analysis result is rounded off according to GB/T 8170, and the numerical value is rounded off to two decimal places.

3.7 Precision

The precision data is determined in 2011 by 8 laboratories on samples with 5 different levels of calcium oxide and magnesium oxide content. Each laboratory independently determines the calcium oxide and magnesium oxide content three times under repeatability conditions. The joint test data is statistically

than 5 %;

Under reproducibility conditions, the absolute value of the difference between the two independent analysis results obtained is not greater than the reproducibility limit *R*, and the probability of exceeding the reproducibility limit *R* is not greater than 5 %. For metallurgical lime samples, the interlaboratory reproducibility limit is not required.

The raw data of the precision joint test are shown in Table B.2 and Table B.4.

4 Flame atomic absorption spectrometric method

4.1 Principle

The sample is decomposed with hydrochloric acid and hydrofluoric acid. Perchloric acid smokes and drives out the hydrofluoric acid. In the presence of strontium chloride, the test solution is sprayed into an air-acetylene flame. A magnesium hollow cathode lamp is used as the light source. The absorbance is measured at a wavelength of 285.2 nm of an atomic absorption spectrometer.

4.2 Reagents

4.2.1 Hydrochloric acid (1 + 1).

4.2.2 Hydrofluoric acid (ρ = 1.13 g/mL).

4.2.3 Perchloric acid (ρ = 1.67 g/mL).

4.2.4 Strontium chloride solution (60 g/L): TAKE 100 g of strontium chloride ($SrCl_2 \cdot 6H_2O$) in a 600 mL beaker, DISSOLVE it with water, TRANSFER it to a 1000 mL volumetric flask, DILUTE to the mark with water, MIX well.

4.2.5 Magnesium oxide standard solution

4.2.5.1 WEIGH 0.1000 g of high-purity magnesia (the content is not less than 99.99 %, it is burned at 950 °C ~ 1000 °C for 1 h and cooled to room temperature in advance), PUT it in a 250mL beaker, ADD 10 mL of hydrochloric acid (4.2.1) to dissolve, TRANSFER to a 1000 mL volumetric flask, DILUTE to the mark with water, MIX well. 1.00 mL of this solution contains 100.0 μg of magnesium oxide.

4.2.5.2 PIPETTE 50.00 mL of magnesium oxide standard solution (4.2.5.1) into a 500 mL volumetric flask, ADD 10 mL of hydrochloric acid (4.2.1), DILUTE to the mark with water, MIX well. 1.00 mL of this solution contains 10.0 μg of magnesium oxide.

After the samples are made, they shall be immediately sealed in a ground-mouth bottle or plastic bag and stored in a desiccator. The samples are not be dried before analysis.

4.5 Analysis steps

4.5.1 Determination times

For a same sample (4.4.3 or 4.4.4), determine at least 2 times independently.

4.5.2 Sample amount

WEIGH 0.20 g of sample, to the nearest 0.0001 g. For metallurgical lime samples, the samples shall be quickly weighed.

4.5.3 Blank test

CARRY OUT the blank test along with the sample.

4.5.4 Sample decomposition and preparation of test solution

4.5.4.1 PLACE the sample (4.5.2) in a platinum dish or a 250 mL Teflon beaker, MOISTEN with a small amount of water, dropwise ADD hydrochloric acid (4.2.1) carefully until the intense reaction stops, and then dropwise ADD hydrochloric acid (4.2.1) until the total amount is 10 mL. ADD 5 mL of hydrofluoric acid (4.2.2) and 5 mL of perchloric acid (4.2.3), HEAT at low temperature, EVAPORATE and generate white perchloric acid smoke until almost dry, COOL.

4.5.4.2 ADD 10 mL of hydrochloric acid (4.2.1), HEAT at low temperature to dissolve the salts, COOL. TRANSFER the test solution into a 100 mL volumetric flask, DILUTE to the mark with water, MIX well.

NOTE: This test solution is the same as the test solution prepared in accordance with 4.5.4.2 of GB/T 3286.4, and can be used for the determination of iron oxide content at the same time.

4.5.4.3 Test solution

4.5.4.3.1 PIPETTE 10.00 mL of test solution (4.5.4.2) into a 100 mL volumetric flask, ADD 5 mL of hydrochloric acid (4.2.1) and 5.0 mL of strontium chloride solution (4.2.4), DILUTE to the mark with water, MIX well. This test solution is used for the determination of 0.1 % ~ 0.50 % of magnesium oxide content.

4.5.4.3.2 PIPETTE 20.00 mL of test solution (4.5.4.3.1) into a 100 mL volumetric flask, ADD 5 mL of hydrochloric acid (4.2.1) and 5.0 mL of strontium chloride solution (4.2.4), DILUTE to the mark with water, MIX well. This test solution is used for the determination of more than 0.50 % of magnesium oxide content.

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