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Cryolite, natural and artificial — Determination of calcium content — Flame atomic absorption method

Cryolithe, naturelle et artificielle — Dosage du calcium — Méthode par absorption atomique dans la flamme

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FOREWORD

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Cryolite, natural and artificial — Determination of calcium content — Flame atomic absorption method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a flame atomic absorption method for the determination of the calcium content of natural and artificial cryolite.

2 REFERENCE

ISO 1619, *Cryolite natural and artificial — Preparation and storage of test samples.*

3 PRINCIPLE

Dissolution of a test portion in concentrated sulphuric acid and treatment with concentrated hydrochloric acid.

Aspiration of the solution into an acetylene dinitrogen monoxide flame.

Determination of calcium content by spectrophotometric measurement of the absorption of the 422,7 nm line emitted by a calcium hollow cathode lamp.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Sulphuric acid, ρ approximately 1,84 g/ml, about 96 % (*m/m*) solution.

4.2 Hydrochloric acid, ρ approximately 1,19 g/ml, about 38 % (*m/m*) solution.

4.3 Complexant.

Either :

4.3.1 Lanthanum nitrate, 310 g/l solution.

Weigh, to the nearest 0,1 g, 31,0 g of lanthanum nitrate hexahydrate ($La(NO_3)_2.6H_2O$) and place a 100 ml one-mark volumetric flask. Dissolve in water dilute to the mark and mix.

NOTE — It is possible to use lanthanum chloride heptahydrate ($LaCl_3.7H_2O$), 270 g/l solution.

Or :

4.3.2 Triethanolamine, dilute solution.

Dilute 100 ml of triethanolamine [$(CH_2OHCH_2)_3N$] to 200 ml with water.

4.4 Sodium chloride solution, corresponding to 16,0 g of Na per litre.

Weigh, to the nearest 0,001 g, 4,067 g of sodium chloride, previously dried for 12 h at approximately 120 °C and cooled in a desiccator, into a 100 ml one-mark volumetric flask. Dissolve in water, dilute to the mark and mix.

4.5 Aluminium, acid solution corresponding to 6,6 g of Al per litre.

Weigh, to the nearest 0,001 g, 0,66 g of extra pure aluminium in the form of small shavings, and dissolve in 50,0 ml of hydrochloric acid solution, diluted 1 + 1 ($V + V$), in a porcelain dish. Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, cool, dilute to the mark and mix.

4.6 Calcium, standard solution, corresponding to 1,00 g of Ca per litre.

Weigh, to the nearest 0,000 1 g, 2,497 2 g of calcium carbonate, previously dried for 2 h at approximately 110 °C and cooled in a desiccator. Transfer to a 250 ml beaker and dissolve with care in 12 ml of the hydrochloric acid solution (4.2), previously diluted with 12 ml of water.

Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, cool, dilute to the mark and mix. Transfer to a flask of material free from calcium.

1 ml of this standard solution contains 1,00 mg of Ca.

4.7 Calcium, standard solution, corresponding to 0,10 g of Ca per litre.

Place 100,0 ml of the standard calcium solution (4.6) in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix. Transfer to a flask of material free from calcium.

1 ml of this standard solution contains 0,10 mg of Ca.

5 APPARATUS

Ordinary laboratory apparatus and :

5.1 Platinum dishes, diameter about 75 mm, height about 30 mm.

5.2 Atomic absorption spectrophotometer, fitted with a burner fed from cylinders of dinitrogen monoxide and acetylene (a 50/60 mm burner is suitable).

5.3 Calcium hollow cathode lamp.

6 PROCEDURE

6.1 Test portion

Weigh, to the nearest 0,000 1 g, 0,500 g of the dried test sample, prepared by the procedure specified in 3.3 of ISO 1619.

6.2 Blank test

Carry out a blank test at the same time as the determination, following the same procedure and using the same quantities of all the reagents used for the determination. Before introducing the sulphuric acid, add 10,0 ml of the aluminium solution (4.5) and 10,0 ml of the sodium chloride solution (4.4).

6.3 Preparation of calibration graph

6.3.1 *Preparation of the standard matching solutions*

Into a series of six of the platinum dishes (5.1), place the quantities of the standard calcium solution (4.7) indicated in the following table.

Standard calcium solution (4.7)	Corresponding mass of Ca	Corresponding to CaO in cryolite
ml	mg	%
0*	0	0
1,0	0,10	0,028
2,0	0,20	0,056
3,0	0,30	0,084
4,0	0,40	0,112
5,0	0,50	0,140

* Reagent blank for the calibration graph.

Add to each dish 10,0 ml of the acid aluminium solution (4.5), 10,0 ml of the sodium chloride solution (4.4) and 5,0 ml of the sulphuric acid solution (4.1). Warm with care on a sand bath or hot-plate to evaporate the free sulphuric acid.

NOTE — The 5,0 ml of the sulphuric acid solution (4.1) can be replaced by 10,0 ml of perchloric acid solution (ρ approximately 1,70 g/ml). In this case the spectrophotometric measurements are carried out using an air-acetylene flame (clear, non-luminous, oxidizing flame).

Introduce into each dish 1,0 ml of the hydrochloric acid solution (4.2) and 30 ml of water. Transfer the contents quantitatively to 100 ml one-mark volumetric flasks, add either 10 ml of the lanthanum nitrate or chloride solution (4.3.1) or 20 ml of the triethanolamine solution (4.3.2) and, after cooling, dilute to the mark and mix.

Store these solutions in flasks of material free from calcium.

6.3.2 *Spectrophotometric measurements*

Mount the calcium hollow cathode lamp (5.3). Switch on the apparatus (5.2) a sufficient time in advance for it to reach stabilization. Adjust the wavelength to 422,7 nm and the sensitivity and the aperture of the slit according to the characteristics of the apparatus. Adjust the gas pressures according to the characteristics of the burner so as to obtain an oxidizing flame. Control the rate of aspiration (for example, to 2 to 3 ml/min).

Aspirate the standard matching solutions (6.3.1) in the flame and measure the absorbance of each.

Take care to maintain the quantity of solution aspirated in the flame constant with respect to time during all the measurements.

Spray water through the burner after each measurement.

6.3.3 *Plotting of the calibration graph*

Plot a graph having, for example, the masses, expressed as milligrams of Ca in 100 ml of the standard matching solutions as abscissae and the corresponding values of absorbance, decreased by the value for the reagent blank for the calibration graph, as ordinates.

6.4 Determination

6.4.1 *Preparation of the test solution*

Place the test portion (6.1) in one of the platinum dishes (5.1) and add 5,0 ml of the sulphuric acid solution (4.1) (see note to 6.3.1). Warm with care on a sand bath or hot-plate until the hydrofluoric acid has evaporated (15 to 20 min). Allow the temperature to rise until the free sulphuric acid has evaporated.

Introduce into the dish 3,0 ml of the hydrochloric acid solution (4.2) and 30 ml of water and warm on a boiling water bath until completely dissolved.

Transfer the solution quantitatively to a 100 ml one-mark volumetric flask and add either 10 ml of the lanthanum nitrate or chloride solution (4.3.1) or 20 ml of the triethanolamine solution (4.3.2). After cooling, dilute to the mark and mix.

Store the solution in a flask of material free from calcium.

6.4.2 *Spectrophotometric measurements*

6.4.2.1 PRELIMINARY MEASUREMENT

Carry out a preliminary measurement on the test solution

(6.4.1) and on the blank solution (6.2) at the same time as the spectrophotometric measurements on the standard matching solutions (6.3.1) following the procedure specified in 6.3.2.

6.4.2.2 BRACKETING MEASUREMENT

Carry out a second measurement on the test solution (6.4.1) by bracketing between two standard matching solutions differing by only 0,10 mg, of Ca in 100 ml, one at a concentration above, and one at a concentration below, that of the test solution.

For the preparation of these standard matching solutions, follow the procedure specified in 6.3.1 using suitable quantities of the standard calcium solution (4.7).

Carry out at the same time, without bracketing, a second measurement of the blank test solution (6.2).

7 EXPRESSION OF RESULTS

The concentration of calcium (Ca), expressed as milligrams per 100 ml of solution used for the spectrophotometric measurement, is given by the formula

$$C = C_1 + (C_2 - C_1) \times \left[\frac{(A_4 - A_0) - (A_1 - A_3)}{(A_2 - A_1)} \right]$$

where

A_0 is the value of the spectrophotometric measurement on the blank test solution;

C_1 is the concentration, in milligrams per 100 ml of the weaker bracketing solution used for the test solution;

A_1 is the corresponding value of the spectrophotometric measurement;

C_2 is the concentration, in milligrams per 100 ml of the stronger bracketing solution used for the test solution;

A_2 is the corresponding value of the spectrophotometric measurement;

A_3 is the spectrophotometric measurement corresponding to the calibration blank.

A_4 is the spectrophotometric measurement corresponding to the test solution.

The calcium content, expressed as a percentage by mass of CaO, is given by the formula

$$\frac{C \times 1{,}399 \times 100}{1\,000 \times m} = 0{,}139\,9\,\frac{C}{m}$$

where

m is the mass, in grams of the test portion (6.1);

1,399 is the conversion factor from Ca to CaO.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard or in the International Standard to which reference is made, or regarded as optional.

ANNEX

ISO PUBLICATIONS RELATING TO CRYOLITE, NATURAL AND ARTIFICIAL

ISO 1619 – Preparation and storage of test samples.

ISO 1620 – Determination of silica content – Reduced molybdosilicate spectrophotometric method.

ISO 1693 – Determination of fluorine content – Modified Willard-Winter method.

ISO 1694 – Determination of iron content – 1,10-Phenanthroline photometric method.

ISO 2366 – Determination of sodium content – Flame emission and atomic absorption spectrophotometric methods.

ISO 2367 – Determination of aluminium content – 8-Hydroxyquinoline gravimetric method.

ISO 2830 – Determination of aluminium content – Atomic absorption method.

ISO 3391 – Determination of calcium content – Flame atomic absorption method.

ISO 3392 – Determination of water content – Electrometric method.

ISO 3393 – Determination of moisture content – Gravimetric method.

ISO 4280 – Determination of sulphates content – Barium sulphate gravimetric method.

ISO . . . – Sampling.