INTERNATIONAL STANDARD ISO 4283

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

# Acid-grade fluorspar — Determination of carbonate content — Titrimetric method

*Spaths fluor pour la fabrication de l'acide fluorhydrique — Dosage des carbonates — Méthode titrimétrique*

First edition — 1978-09-15

UDC 553.634 : 546.264 : 543.24

Ref. No. ISO 4283-1978 (E)

**Descriptors** : fluorspar, chemical analysis, quantitative analysis, determination of content, carbonates, volumetric analysis.

Price based on 4 pages

ISO 4283-1978 (E)

## FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 4283 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in July 1976.

It has been approved by the member bodies of the following countries :

Belgium
Brazil
Bulgaria
Chile
Czechoslovakia
France
Germany
Hungary
India
Israel
Italy
Mexico
Netherlands
Poland
Romania
South Africa, Rep. of
Spain
Switzerland
Thailand
Turkey
United Kingdom
Yugoslavia

No member body expressed disapproval of the document.

This International Standard has also been approved by the International Union of pure and Applied Chemistry (IUPAC).

Printed in Switzerland

# Acid-grade fluorspar — Determination of carbonate content — Titrimetric method

## 1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a titrimetric method for the determination of the carbonate content of acid-grade fluorspar.

The method is applicable to products having carbonate contents, expressed as calcium carbonate ($CaCO_3$), equal to or greater than 0,04 % (*m/m*).

## 2 REFERENCE

ISO 4282, *Acid-grade fluorspar — Determination of loss in mass at* 105 °C.

## 3 TEST SAMPLE

Use the residue from the determination of the loss in mass at 105 °C (see ISO 4282) to prepare the test sample.

## 4 PRINCIPLE

Treatment of a test portion with hydrochloric acid solution, absorption of the evolved carbon dioxide in barium hydroxide solution, neutralization of excess alkali with hydrochloric acid solution, addition of an exactly measured excess of a standard volumetric hydrochloric acid solution to dissolve the precipitated barium carbonate and back-titration with a standard volumetric sodium hydroxide solution using methyl orange or screened methyl orange as indicator.

## 5 REAGENTS

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

**5.1 Butan-1-ol.**

**5.2 Nitrogen,** free from carbon dioxide.

**5.3 Boric acid.**

**5.4 Barium chloride** dihydrate ($BaCl_2.2H_2O$), 122 g/l solution.

**5.5 Hydrochloric acid,** $\rho$ approximately 1,12 g/ml, about 25 % (*m/m*) solution, prepared by diluting 3 volumes of hydrochloric acid solution ($\rho$ approximately 1,19 g/ml) with 2 volumes of water.

**5.6 Mercury(II) chloride,** saturated solution.

**5.7 Potassium hydroxide,** about 20 % (*m/m*) solution.

**5.8 Hydrochloric acid,** approximately 36,5 g/l solution.

**5.9 Sodium hydroxide,** approximately 40 g/l solution.

**5.10 Hydrochloric acid,** standard volumetric solution, $c$ (HCl) = 0,1 mol/l.*

**5.11 Sodium hydroxide,** standard volumetric solution, $c$ (NaOH) = 0,1 mol/l.*

**5.12 Methyl orange,** 1 g/l solution, or

**5.13 Screened methyl orange** solution.

Dissolve 1 g of methyl orange and 1,4 g of xylene cyanole FF in 500 ml of 50 % (*V/V*) ethanol.

**5.14 Phenolphthalein,** 0,25 g/l solution in 50 % (*V/V*) ethanol.

## 6 APPARATUS

Ordinary laboratory apparatus and

**6.1 Gas evolution and absorption apparatus,** illustrated in the figure, and consisting of

**6.1.1 Washing bottle,** equipped with a sintered glass disk, porosity P1 or P2, as shown in the figure, or similar type, and containing the potassium hydroxide solution (5.7).

**6.1.2 Three-necked flask,** of capacity 500 ml, fitted with a dropping funnel and a reflux water condenser.

---

* Hitherto expressed as 0,1 N.

**6.1.3 and 6.1.4 Washing bottles,** Drechsel type.

**6.2 Electric oven,** capable of being controlled at 105 ± 1 °C.

## 7 PROCEDURE

### 7.1 Test portion

Grind several grams of the test sample (see clause 3) in an agate mortar until it all passes a 63 μm mesh sieve (see ISO 565). Dry the sieved material for 2 h in the oven (6.2), controlled at 105 ± 1 °C, allow to cool in a desiccator and weigh, to the nearest 0,001 g, about 5 g of this sample.

NOTE — It is essential that the total amount of carbon dioxide, expressed as calcium carbonate, in the test portion should not exceed 100 mg. For samples containing more than 2 % (*m/m*) of $CaCO_3$, the mass of the test portion should therefore be reduced in proportion.

### 7.2 Blank test

Carry out a blank test at the same time as the determination and following the same procedure, using the same reagents as used for the determination but omitting the test portion.

### 7.3 Determination

Transfer the test portion (7.1) to the flask (6.1.2), using about 100 ml of water. Add 4 g of the boric acid (5.3) and 5 ml of the mercury(II) chloride solution (5.6). Close the necks of the flask and pass a stream of the nitrogen (5.2) through the flask at a rate of 50 ml/min for 10 min.

Without interrupting the nitrogen stream, connect the washing bottles (6.1.3 and 6.1.4) each containing 10 ml of the sodium hydroxide solution (5.9), 10 ml of the barium chloride solution (5.4), 1 ml of the phenolphthalein solution (5.14), 1 ml of the butan-1-ol (5.1), and 20 ml of water. Introduce 30 ml of the hydrochloric acid solution (5.5) into the flask through the dropping funnel, if necessary by using a rubber bulb. Close the stopcock of the dropping funnel.

Heat the flask slowly and boil gently for 45 min. Stop heating and allow to cool for 10 min without interrupting the nitrogen flow.

Disconnect the second washing bottle (6.1.4) from the apparatus (6.1), remove and rinse the inlet tube, collecting the washing in the bottle. Titrate the contents of the bottle with the hydrochloric acid solution (5.8) until near the end-point.

NOTE — To avoid absorption of atmospheric carbon dioxide during titration of the excess sodium hydroxide in the absorption solution, pass a stream of the nitrogen (5.2) through the air space above the solution in the washing bottle.

Continue the titration with the hydrochloric acid solution (5.10) until the phenolphthalein is just colourless, taking care not to overshoot the end-point.

Add an exactly measured volume of the standard volumetric hydrochloric acid solution (5.10) until the precipitate dissolves completely. Dip the inlet tube into this solution so as to dissolve any adhering barium carbonate, remove and rinse again. Add a few drops of the methyl orange solution (5.12) or the screened methyl orange solution (5.13) and back-titrate the excess of hydrochloric acid with the standard volumetric sodium hydroxide solution (5.11).

Neutralize and titrate the contents of the first washing bottle (6.1.3) in the same manner.

## 8 EXPRESSION OF RESULTS

The carbonate content, expressed as a percentage by mass of calcium carbonate ($CaCO_3$), is given by the formula

$$\frac{[(V_1 - V_2) - (V_3 - V_4)] \times 0{,}500\,5}{m}$$

where

$V_1$ is the volume, in millilitres, of the standard volumetric hydrochloric acid solution (5.10) used to dissolve the barium carbonate in both washing bottles;

$V_2$ is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (5.11) used for the back-titration of the excess hydrochloric acid in both washing bottles;

$V_3$ and $V_4$ are the corresponding volumes, in millilitres, of the standard volumetric hydrochloric acid solution (5.10) and the standard volumetric sodium hydroxide solution (5.11) used for the blank test;

$m$ is the mass, in grams, of the test portion (7.1).

NOTE — If the concentrations of the standard volumetric solutions used are not exactly as specified in the list of reagents, appropriate corrections should be made.

## 9 TEST REPORT

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

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

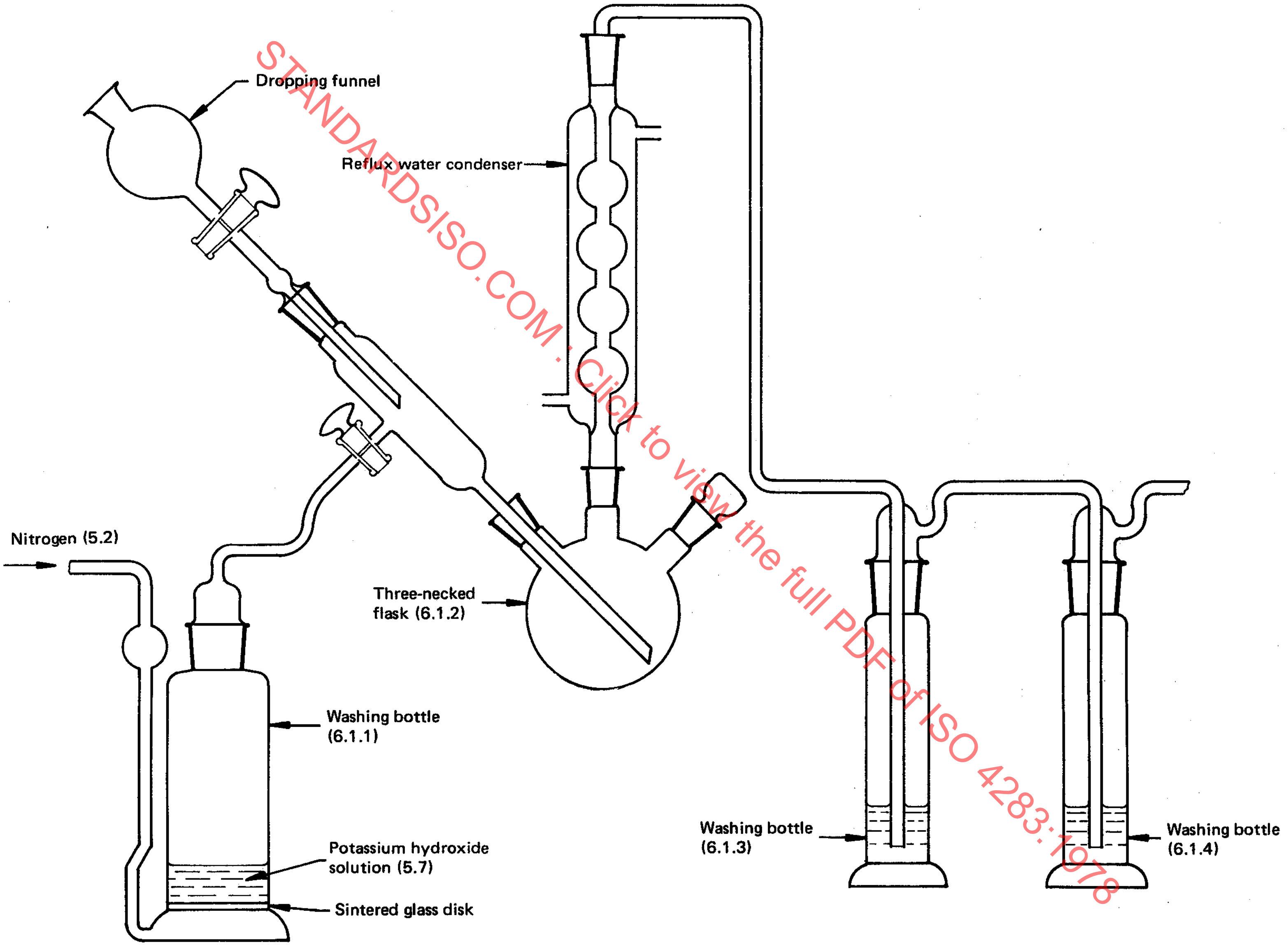

FIGURE — **Typical gas evolution and absorption apparatus**

## ANNEX

## ISO PUBLICATIONS RELATING TO ACID-GRADE FLUORSPAR

ISO 3703 – Determination of flotation agents.

ISO 4282 – Determination of loss in mass at 105 °C.

ISO 4283 – Determination of carbonate content – Titrimetric method.

ISO 4284 – Determination of sulphide content – Iodometric method.

ISO 5437 – Determination of barium sulphate – Gravimetric method.

ISO 5438 – Determination of silica content – Reduced molybdosilicate photometric method.

ISO 5439 – Determination of available fluorine – Potentiometric method after distillation.