INTERNATIONAL STANDARD ISO 5439

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

Acid-grade fluorspar — Determination of available fluorine content — Potentiometric method after distillation

Spaths fluor pour la fabrication de l'acide fluorhydrique — Dosage du fluor utilisable — Méthode potentiométrique après distillation

First edition 1978-09-15

UDC 553.634 : 546.16 : 543.257

Ref. No. ISO 5439-1978 (E)

Descriptors : fluorspar, chemical analysis, quantitative analysis, determination of content, fluorine, potentiometric analysis, distillation.

Price based on 6 pages

FOREWORD

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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 5439 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
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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 available fluorine content — Potentiometric method after distillation

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a potentiometric titration method, using an ion-selective electrode, after distillation, for the determination of the available fluorine content of acid-grade fluorspar.

The method is applicable to products having a calcium fluoride (CaF_2) content equal to or greater than 90 % (*m/m*).

2 REFERENCES

ISO 2362, *Aluminium fluoride for industrial use — Determination of fluorine content — Modified Willard-Winter method.*

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

Separation of fluorine from a test portion by distillation in the presence of perchloric acid using a temperature-controlled distillation apparatus. Potentiometric titration of the distillate with lanthanum nitrate solution using a fluoride ion-selective electrode.

5 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water, or water of equivalent purity. Use carbon dioxide-free water for the preparation of the lanthanum nitrate solution (5.7).

5.1 Potassium permanganate, crystalline.

5.2 Sodium fluoride, recrystallized as follows :

Dissolve about 5 g of sodium fluoride in 125 ml of water and filter the solution under vacuum through a small Buchner funnel. Evaporate the solution in a platinum dish to approximately 60 ml. Cool to about 50 °C and separate the recrystallized sodium fluoride by centrifuging. Wash the crystals three times by centrifuging, with small quantities of cold water. Transfer the product to a platinum dish and dry in the electric oven (6.9), controlled at 105 ± 2 °C. Remove the dish from the oven, cool in a desiccator, grind the product in an agate mortar, and then pass it through a sieve with an aperture size of 355 µm (see ISO 565). Place the sieved sodium fluoride in a platinum dish, heat for 2 h in an electric furnace controlled at approximately 600 °C and allow to cool in a desiccator.

5.3 Ethanol or **propan-2-ol.**

5.4 Perchloric acid, ρ approximately 1,54 g/ml, about 60 % (*m/m*) solution.

5.5 Perchloric acid, approximately 10 % (*m/m*) solution.

Dilute 16,5 ml of the perchloric acid solution (5.4) to 100 ml.

5.6 Sodium hydroxide, approximately 1 N solution.

Store the solution in a plastic bottle.

5.7 Lanthanum nitrate, approximately 0,01 M standard volumetric solution.

5.7.1 *Preparation of the solution*

Dissolve 4,33 g of lanthanum nitrate hexahydrate [$La(NO_3)_3.6H_2O$] in water. Add 10 ml of 0,001 N nitric acid solution, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

5.7.2 *Standardization of the solution*

See 7.4.

5.8 Buffer solution, pH 6,5.

Dissolve 79 g of pyridine in about 800 ml of water and neutralize with the perchloric acid solution (5.5) to pH 6,5 ± 0,2. Dilute to 1 000 ml with water and, if necessary, readjust the pH to 6,5.

5.9 Phenolphthalein, 5 g/l solution in 95 % (*V/V*) ethanol.

6 APPARATUS

6.1 Distillation apparatus, incorporating a steam generator, two electric heating jackets and a contact thermometer with relay (see figure 1), capable of controlling the temperature in the distillation flask at 135 ± 2 °C.

The power required for the heating jackets is

a) for the distillation flask — approximately 150 W;

b) for the steam generator — a minimum of 500 W.

It is advisable to equip the steam generator heating jacket with a regulator in order to adjust the power input to give the desired steam rate.

Alternatively, the apparatus specified in ISO 2362 for the determination of the fluorine content of aluminium fluoride may be used.

6.2 Magnetic stirrer.

6.3 pH meter, fitted with glass and saturated calomel electrodes.

6.4 Burette, of capacity 20 ml, graduated at 0,02 ml intervals.

6.5 Fluoride ion-selective electrode.

6.6 Reference electrode, saturated calomel or other type.

6.7 Potentiometer, sensitivity 0,5 mV, covering the range − 500 mV to + 500 mV.

For fixed end-point measurements, the equipment, using a specific set of electrodes, should reproduce the end-point to ± 0,5 mV.

Automatic apparatus for registering titration graphs or for titrations to a pre-determined end-point potential are available commercially and may be used as alternatives.

6.8 Cups, of borosilicate glass, with straight sides and flat bases, with the following approximate dimensions :

Internal diameter : 10 mm

Depth : 10 to 12 mm

Wall thickness : 1 mm

6.9 Electric oven, capable of being controlled at 105 ± 2 °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 (6.9), controlled at 105 ± 2 °C, allow to cool in a desiccator and weigh, to the nearest 0,000 2 g, about 0,2 g into one of the cups (6.8).

7.2 Distillation

Assemble the distillation apparatus (6.1). Remove the contact thermometer and still-head from the distillation apparatus and add a few crystals of the potassium permanganate (5.1) to the distillation flask. Transfer the glass cup containing the test portion (7.1) into the distillation flask. Add 15 ml of water and 35 ml of the perchloric acid solution (5.4) to the distillation flask and immediately close the apparatus with the still-head and contact thermometer.

Place a 500 ml one-mark volumetric flask, containing 25 ml of the sodium hydroxide solution (5.6) and 40 ml of water, under the delivery tube, which should dip into the liquid.

Turn the stopcock between the steam generator and the distillation apparatus to position 1, set the contact thermometer to 135 °C and switch on the electric heating to the distillation flask and the steam generator. Heat the contents of the distillation flask to 135 °C for approximately 15 min, turn the stopcock to position 2 and pass steam into the distillation flask at a rate corresponding to about 10 ml of water per minute. Collect about 400 ml of distillate and then stop the distillation.

Rinse the delivery tube inside and outside with water, collecting the washings in the 500 ml one-mark volumetric flask. Neutralize the distillate with the perchloric acid solution (5.5), using a few drops of the phenolphthalein indicator solution (5.9) as indicator. Dilute to the mark with water and mix.

7.3 Potentiometric titration

Place a 50,0 ml aliquot portion from the 500 ml one-mark volumetric flask in a 250 ml beaker. Add 10 ml of the buffer solution (5.8) and 60 ml of the ethanol or propan-2-ol (5.3). Introduce the magnetized follower of the magnetic stirrer (6.2) into the beaker, place the beaker on the stirrer, immerse the fluoride ion-selective electrode (6.5) and the reference electrode (6.6) (unless a combined electrode is used) in the solution and connect the potentiometer (6.7). Start the magnetic stirrer and titrate with the lanthanum nitrate solution (5.7) at a titration rate of not more than 3,0 ml/min, recording the volume of titrant and the corresponding potentiometer reading. Titrate more slowly in the vicinity of sharply accelerating potential change. Evaluate the end-point graphically from either the drawn or the recorded titration graph. Alternatively, titrate to a pre-determined end-point potential derived from model titration curves, established under identical conditions.

An example of a typical titration graph is given in figure 2.

7.4 Standardization

Follow the procedure specified in 7.2 and 7.3 using approximately 0,200 g, weighed to the nearest 0,000 1 g, of the recrystallized sodium fluoride (5.2) instead of the test portion (7.1). Calculate the mass of sodium fluoride corresponding to 1 ml of the lanthanum nitrate solution (5.7), taking account of the blank test (7.5).

7.5 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 in the determination but omitting the test portion.

8 EXPRESSION OF RESULTS

8.1 Calculation

The available fluorine content, expressed as a percentage by mass of calcium fluoride (CaF_2), is given by the formula

$$\frac{0{,}929\,7 \times m_1\ (V_1 - V_0) \times 1\,000}{m_0}$$

and expressed as a percentage by mass of fluorine (F), by the formula

$$\frac{0{,}452\,4 \times m_1\ (V_1 - V_0) \times 1\,000}{m_0}$$

where

m_0 is the mass, in grams, of the test portion (7.1);

m_1 is the mass, in grams, of the recrystallized sodium fluoride (5.2) corresponding to 1 ml of the lanthanum nitrate solution (5.7);

V_0 is the volume, in millilitres, of the standard volumetric lanthanum nitrate solution (5.7) used for the blank test;

V_1 is the volume, in millilitres, of the standard volumetric lanthanum nitrate solution (5.7) used for the determination.

8.2 Repeatability and reproducibility

Comparative analyses carried out in 5 laboratories on 3 samples gave the statistical information shown in the following table :

Sample		**1**	**2**	**3**
Mean % (*m*/*m*) of CaF_2		97,04	96,79	96,41
Standard deviation	**of repeatability σ_r**	0,85	0,77	0,56
	of reproducibility σ_R	1,22	0,82	0,76

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 Standards to which reference is made, or regarded as optional.

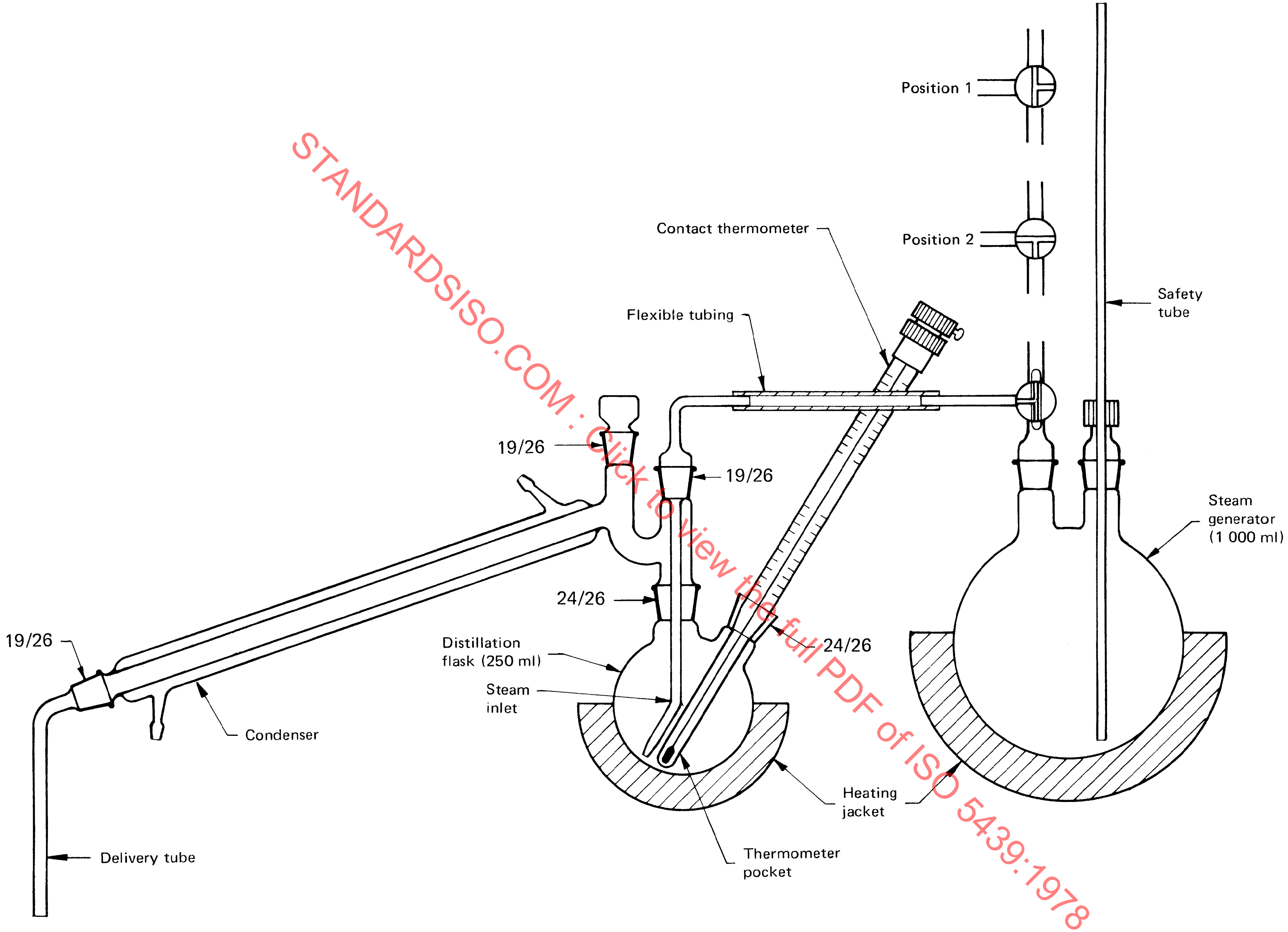

FIGURE 1 — **Distillation apparatus**

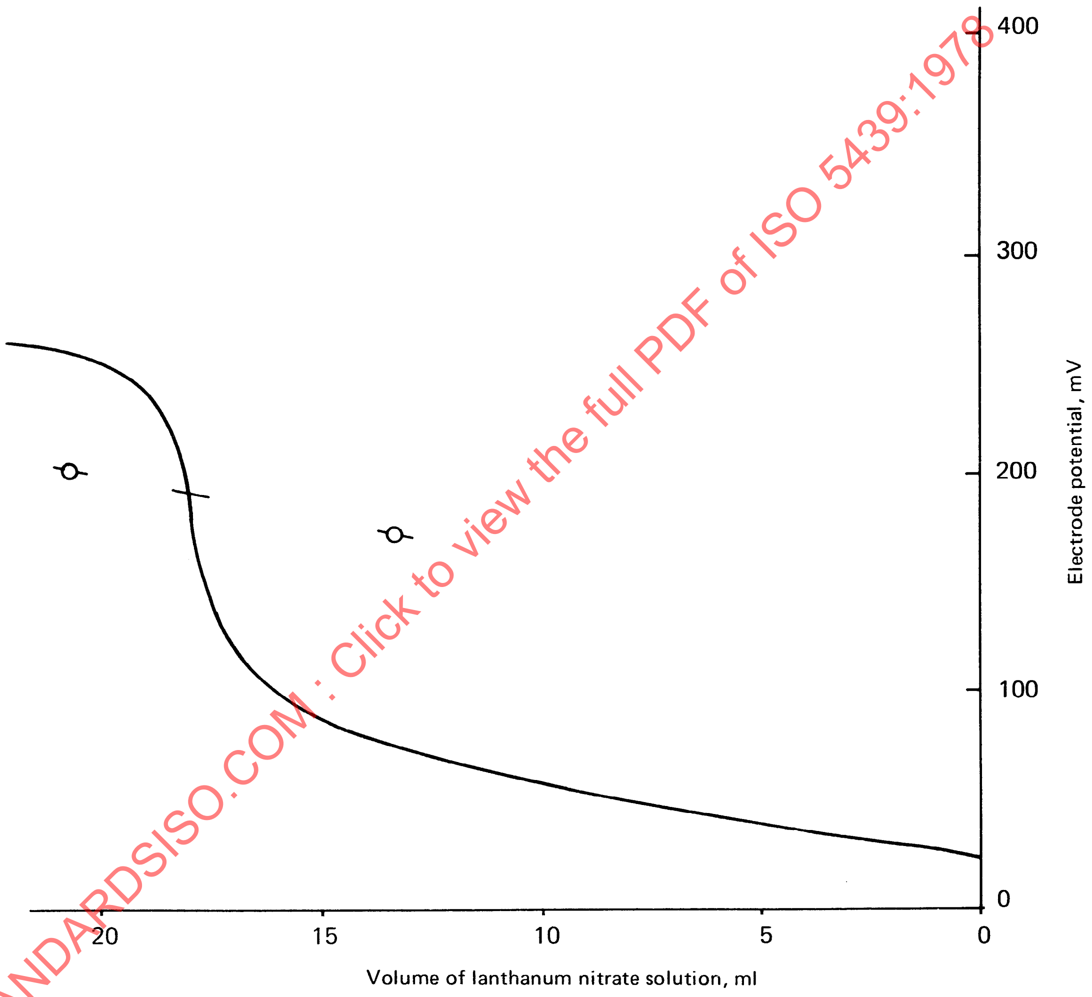

FIGURE 2 — **Example of typical titration graph**

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 sulphides 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.

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