INTERNATIONAL STANDARD

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Metallurgical-grade fluorspar — Determination of available fluorine content — Modified Willard-Winter method

Spaths fluor utilisables dans l'industrie métallurgique — Dosage du fluor utilisable — Méthode de Willard-Winter modifiée

Reference number
ISO 9503:1991(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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Metallurgical-grade fluorspar — Determination of available fluorine content — Modified Willard-Winter method

1 Scope

This International Standard specifies a modified Willard-Winter method for the determination of the available fluorine content of metallurgical-grade fluorspar.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*.

ISO 8868:1989, *Fluorspar — Sampling and sample preparation*.

3 Principle

Perchloric acid is added to a test portion of the sample and the test portion is subjected to steam distillation. After fluorine has been separated, the solution is titrated with standard thorium nitrate solution to determine the available fluorine.

4 Reagents

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

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

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general.

4.2 Sodium alizarinsulfonate, 0,5 g/l solution.

Dissolve 0,05 g of sodium alizarinsulfonate in water and dilute to 100 ml.

4.3 Sodium hydroxide, 4 g/l solution.

4.4 Hydrochloric acid, diluted 1 + 200.

Dilute 1 volume of hydrochloric acid, ρ approximately 1,19 g/ml, about 36 % (m/m) solution, with 200 volumes of water.

4.5 Buffer solution, pH 3.

Dissolve 9,45 g of monochloroacetic acid in a cold solution of 2,0 g of sodium hydroxide (as NaOH 100 %) in about 50 ml of water and dilute with water to 100 ml.

The pH of the buffer solution shall be checked regularly and carefully readjusted if necessary.

4.6 Sodium fluoride, primary standard substance.

4.7 Thorium nitrate, standard volumetric solution, $c[Th(NO_3)_4.4H_2O] = 0,025$ mol/l.

Dissolve about 14 g of thorium nitrate tetrahydrate $[Th(NO_3)_4.4H_2O]$ in 1 000 ml of water. To overcome any tendency to ageing, allow the solution to stand for one week and then pass it through a filter to give a clear filtrate. Prior to using it, determine the equivalent of the clear filtrate to calcium fluoride by the following procedure. Dry the proper amount of sodium fluoride (4.6) in a platinum crucible at 500 °C to 550 °C for 40 min to 50 min, and allow to cool in an H_2SO_4 desiccator. Treat the sodium fluor-

ide in accordance with the procedure described in clause 7, and calculate the equivalent of 1 ml of this solution to calcium fluoride, m_2, using the equation

$$m_2 = \frac{0{,}929\ 7 \times m_1}{V_1} \times \frac{1}{10}$$

where

m_1 is the mass, in grams, of sodium fluoride (4.6) taken;

V_1 is the volume, in millilitres, of thorium nitrate solution consumed in the titration.

Ensure that the same lighting conditions are used for the standardization of the thorium nitrate solution and for the titration (7.3).

4.8 Standard colour solution.

Dissolve 2,33 g of cobalt(II) nitrate and 0,027 9 g of potassium chromate in water and dilute with water to 1 000 ml to prepare the standard colour stock solution. To 75 ml of this stock solution, add 0,05 g of sodium fluoride dissolved in 25 ml of water. Add 8 ml of the thorium nitrate solution (4.7) and shake well. This standard colour solution shall be prepared prior to use.

5 Apparatus

5.1 Distillation apparatus, as shown in figure 1, for instance.

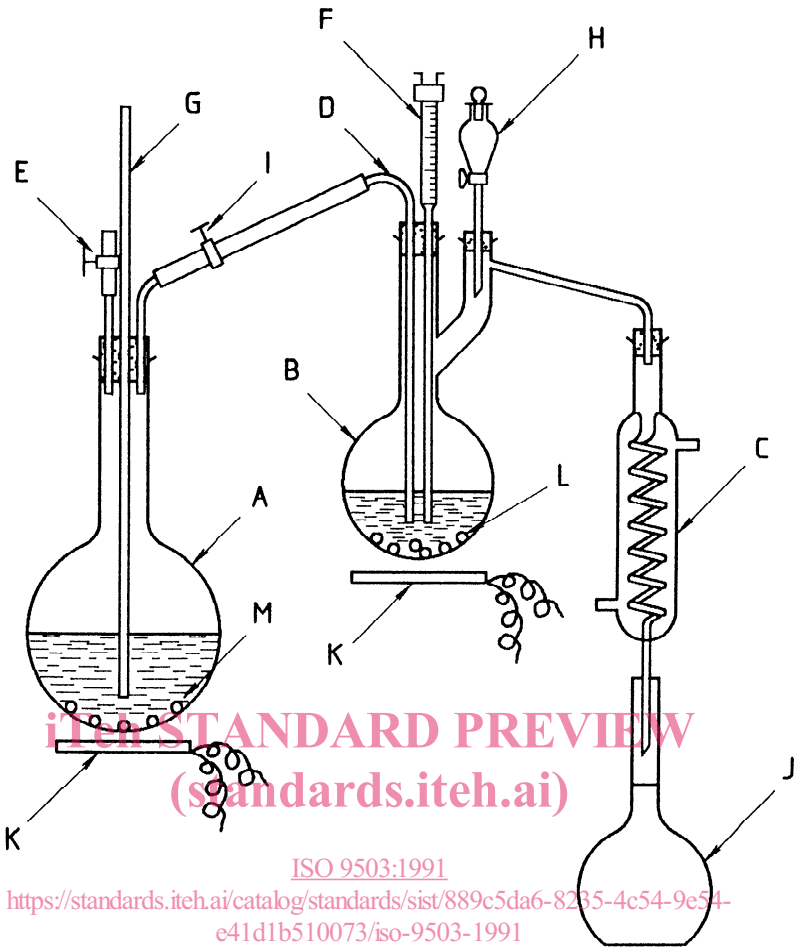
5.2 Magnetic stirrer.

5.3 Burette, of capacity 10 ml, graduated at 0,02 ml intervals.

5.4 Electric oven, capable of being maintained at a temperature of 105 °C ± 2 °C.

6 Test sample

Prepare the test sample in accordance with the procedure given in ISO 8868:1989, subclause 9.3.



Key

A: Steam generator, consisting of a 3 000 ml to 5 000 ml round-bottom flask, filled with the correct amount of water and containing several boiling bubble stones (M). Sodium hydroxide is added to make the water slightly alkaline.

B: Claisen distillation flask, 250 ml capacity, made of hard glass No. 1, equipped with a side tube to accommodate a dropping funnel (H). A main tube is coupled to a steam inlet tube (D) and this tube (D) together with a contact thermometer (F) is inserted through a rubber stopper in the neck of the flask.

C: Condenser with coiled tube, 300 mm in length.

D: Steam inlet tube, about 6 mm in outside diameter, inserted to the bottom of a Claisen distillation flask.

E: Screw stopcock.

F: Contact thermometer, designed on the principle of a maximum thermometer. The required temperature in the Claisen distillation flask (B) is 135 °C and is controlled in the following manner:

Current to the electric heater (K) is supplied via the temperature-regulating circuit (see figure 2). This temperature-regulating circuit is connected to the platinium wires in the contact thermometer. The temperature is controlled by means of the mercury thread in the contact thermometer, which connects or disconnects the platinum wires in the thermometer as the temperature falls below or rises above 135 °C and this causes the current to the electric heater (K) to be switched on or off.

G: Glass safety tube, about 6 mm in outside diameter and about 1 m in length.

H: Dropping funnel, consisting of a 100 ml separating funnel.

I: Screw stopcock.

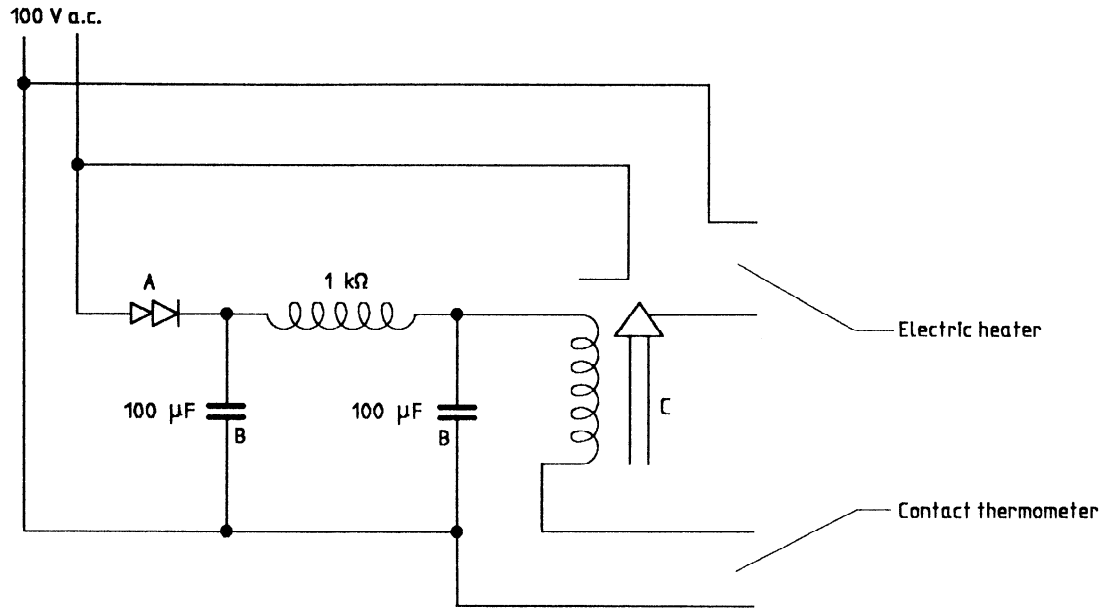
J: Receiver, consisting of a 500 ml volumetric flask.

K: Electric heater.

L: Soft glass beads, about 3 mm in diameter.

M: Boiling bubble stones.

Figure 1 — Distillation apparatus



Key

A: Selenium rectifier (80 mA).

B: Electrolytic capacitors (working voltage 150 V, 100 µF × 2).

C: Microswitch for 100 V d.c.

Figure 2 — Temperature-regulating circuit

7 Procedure

WARNING — Due to the danger of serious accidents when perchloric acid is used, it should be handled in a special fume cupboard with an absorber unit in the exhaust.

7.1 Test portion

Grind several grams of the test sample (clause 6) in an agate or similar mortar until it passes through a 63 µm mesh sieve (see ISO 565). Dry the sieved material for 2 h in the oven (5.4) maintained at 105 °C ± 2 °C, allow to cool in a desiccator and weigh, to the nearest 0,1 mg, about 0,2 g as the test portion.

7.2 Distillation

Open screw stopcock E, close screw stopcock I and heat the steam generator (A) to boil the water.

Wash the test portion into the Claisen distillation flask (B) with about 50 ml of water and drop about 10 glass beads (L) into the flask. Fit the steam inlet tube (D) and the contact thermometer (F) to the flask (B) through a rubber stopper.

Pour 50 ml of perchloric acid (4.1) into the dropping funnel (H).

Connect the steam generator (A) and the condenser (C) to the Claisen distillation flask (B), place the receiver (J) beneath the condenser (C), connect the contact thermometer (F) and the electric heater (K) to the temperature-regulating circuit.

Circulate water through the condenser (C) and open the stopcock of the dropping funnel (H) to permit all the perchloric acid to run gently into the flask (B), then close the stopcock.

Gently swirl the flask (B) and then switch on the heater.

When the temperature in the flask (B) reaches 135 °C, open screw stopcock I and close screw stopcock E to introduce the steam into the flask (B). Continue the distillation at a rate of not more than 4 ml per minute until the distillate measures almost 500 ml. Generally 2 h to 2,5 h are required for this distillation. Dilute the distillate with water to exactly 500 ml and mix.

7.3 Titration

Transfer a 50,0 ml aliquot portion from the 500 ml volumetric flask (J) to a 300 ml conical beaker. Add

50 ml of water and 1,0 ml of sodium alizarinsulfonate solution (4.2). Add sodium hydroxide solution (4.3) till the appearance of a red colour, followed by hydrochloric acid (4.4) until the colour changes to orange-yellow, and then add 1,0 ml of the buffer solution (4.5).

Switch on the magnetic stirrer (5.2) to agitate the solution vigorously and titrate with the thorium nitrate solution (4.7). Add 1 or 2 drops per second, until the colour of the solution matches that of the standard colour solution (4.8).

Ensure that the same lighting conditions are used for the standardization of the thorium nitrate solution (4.7) and for the titration.

8 Expression of results

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

$$\frac{m_2 \times V_2}{m_0} \times 1\,000$$

where

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

m_2 is the mass, in grams, of calcium fluoride corresponding to 1 ml of thorium nitrate solution (4.7);

V_2 is the volume, in millilitres, of thorium nitrate solution (4.7) consumed in the titration (7.3).

9 Test report

The test report shall include the following information:

a) an identification of the sample;

b) a reference to this International Standard;

c) the results and the units in which they are expressed;

d) any unusual features noted during the determination;

e) any operating details not included in this International Standard, or in the International Standards to which reference is made, as well as any operations regarded as optional.

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Descriptors: minerals and ores, fluorspar, chemical analysis, determination of content, fluorine, volumetric analysis.

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