INTERNATIONAL STANDARD

ISO 4284

Third edition
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Acid-grade and ceramic-grade fluorspar — Determination of sulfide content — Iodometric method

Spaths fluor pour la fabrication de l'acide fluorhydrique et spaths fluor utilisables dans l'industrie céramique — Dosage des sulfures — Méthode iodométrique

Reference number
ISO 4284:1993(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.

International Standard ISO 4284 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

This third edition cancels and replaces the second edition (ISO 4284:1988), which has been updated.

Annex A of this International Standard is for information only.

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Acid-grade and ceramic-grade fluorspar — Determination of sulfide content — Iodometric method

1 Scope

This International Standard specifies an iodometric method for the determination of the sulfide content of acid-grade and ceramic-grade fluorspar.

The method is applicable to products having a sulfide content, expressed as sulfur (S), equal to or greater than 0,001 % (m/m).

Acid-grade and ceramic-grade fluorspars do not normally contain polysulfides. The method is not applicable if their presence is suspected.

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

Digestion of a test portion in a sealed apparatus in a mixture of hydrochloric acid, tin(II) chloride and boric acid solutions. Absorption of the liberated hydrogen sulfide, entrained in a stream of oxygen-free argon or nitrogen, in zinc acetate solution and iodometric determination of the zinc sulfide formed.

4 Reagents

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

4.1 Boric acid.

4.2 Nitrogen or **argon**, oxygen-free.

If the presence of oxygen is suspected, first pass the gas through a wash-bottle containing alkaline pyrogallol solution.

4.3 Hydrochloric acid, solution.

Dilute 1 volume of hydrochloric acid (ρ approximately 1,18 g/ml) with 2 volumes of water.

4.4 Tin(II) chloride, 200 g/l solution.

Dissolve 200 g of tin(II) chloride dihydrate ($SnCl_2.2H_2O$) in 300 ml of hydrochloric acid (ρ approximately 1,18 g/ml) and dilute with water to 1 000 ml.

4.5 Zinc acetate, 30 g/l solution.

Dissolve 30 g of zinc acetate dihydrate plus 6 ml of glacial acetic acid in water and dilute to 1 000 ml.

4.6 Iodine, standard volumetric solution, $c(0{,}5\ I_2) = 0{,}005$ mol/l.

It is essential that this solution be freshly prepared by dilution of a standard volumetric solution of iodine, $c(0{,}5\ I_2) = 0{,}05$ mol/l.

4.7 Sodium thiosulfate, standard volumetric solution, $c(Na_2S_2O_3)$ = 0,01 mol/l.

It is essential that this solution be freshly prepared by dilution of a standard volumetric solution of sodium thiosulfate, $c(Na_2S_2O_3)$ = 0,10 mol/l.

4.8 Starch, solution.

Triturate 1 g of soluble starch with about 10 ml of water, and add the suspension slowly to 200 ml of boiling water. Continue boiling for 1 min. Cool and filter into a glass-stoppered bottle.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Gas evolution and absorption apparatus (as illustrated in figure 1), consisting of the following components:

5.1.1 Washing bottle.

5.1.2 Flat-bottom flask, fitted with a dropping funnel and a reflux water condenser.

5.2 Electric oven, capable of being maintained at 105 °C ± 2 °C.

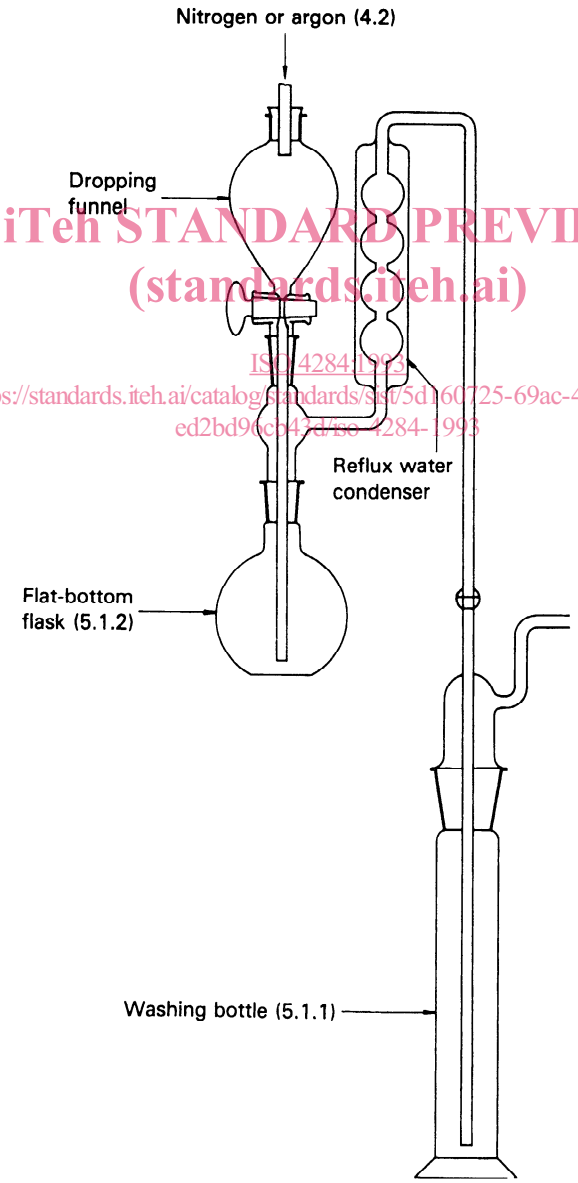

Figure 1 — Typical gas evolution and absorption apparatus

6 Test sample

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

7 Procedure

7.1 Test portion

Grind several grams of the test sample (see clause 6) in an agate mortar until it all passes through a 63 µm mesh sieve (see ISO 565). Dry the sieved material for 2 h in the oven (5.2), maintained at 105 °C ± 2 °C. Allow to cool in a desiccator. Weigh, to the nearest 1 mg, about 3 g of this sample.

It is essential that the total amount of sulfide, expressed as sulfur (S), in the test portion does not exceed about 0,8 mg. For samples containing more than about 0,03 % (*m*/*m*) of sulfur, the mass of the test portion shall 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

Place 50 ml of the zinc acetate solution (4.5) in the washing bottle (5.1.1). Place the test portion (7.1) in the flat-bottom flask (5.1.2), add 3 g of the boric acid (4.1) and assemble the apparatus (5.1).

Add a mixture of 50 ml of the hydrochloric acid solution (4.3) and 10 ml of the tin(II) chloride solution (4.4) through the dropping funnel. Insert a one-holed bung fitted with a piece of glass tubing into the neck of the dropping funnel, and pass a stream of the nitrogen or argon (4.2) through the apparatus at a rate of 50 ml/min for 15 min.

Boil the contents of the flask gently for 1 h, without interrupting the gas stream, then disconnect the washing bottle from the apparatus.

Remove the gas inlet tube of the washing bottle and quickly add 10,0 ml of the iodine solution (4.6) and 8 to 10 ml of the hydrochloric acid solution (4.3). Immediately dip the gas inlet tube into the washing bottle, seal the inlet and the outlet of the washing bottle, and allow to stand for about 10 min. Then remove the seals and rinse the gas inlet tube carefully, collecting the washings in the bottle. Take great care that all the zinc sulfide adhering to the inlet tube has been dissolved completely.

Back-titrate the unreacted iodine with the sodium thiosulfate solution (4.7), adding 1 ml of starch solution (4.8) just before the end-point is reached.

8 Expression of results

The sulfide content, expressed as a percentage by mass of sulfur (S), is given by the formula

$$\frac{(10{,}0 - V_1) - (10{,}0 - V_0)}{m} \times 100 \times 0{,}000\,16$$

$$= \frac{V_0 - V_1}{m} \times 0{,}016$$

where

V_0 is the volume, in millilitres, of the sodium thiosulfate solution (4.7) used for the blank test;

V_1 is the volume, in millilitres, of the sodium thiosulfate solution (4.7) used for the determination;

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

10,0 is the volume, in millilitres, of the iodine solution (4.6) added to the washing bottle;

0,000 16 is the mass, in grams, of sulfur corresponding to 1,00 ml of sodium thiosulfate solution, $c(Na_2S_2O_3) = 0{,}010$ mol/l.

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

NOTE 1 Examples of the values obtained for sulfide content using the methods specified in the first and second editions of this International Standard are given in annex A.

9 Test report

The test report shall include the following particulars:

a) all information necessary for the identification of the sample;

b) a reference to the method used (reference to this International Standard);

c) the results and the form in which they have been expressed;

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, as well as any operation regarded as optional.

Annex A
(informative)

Comparative test results

The results presented in table A.1 were obtained from comparative tests carried out by the member body for Germany.

Table A.1 — Sulfur contents of various samples

S [% (*m/m*)]

Sample	Results obtained using method specified in ISO 4284:1978	Results obtained using method specified in ISO 4284:1988
SARM 14	0,000 5; 0,000 5	0,000 5; 0,000 5
SARM 15	0,004 7; 0,004 9; 0,005 0	0,004 9; 0,004 9; 0,005 1
Shipment A	0,044	0,044; 0,043
Shipment B	0,036	0,038; 0,037
Shipment C	0,028	0,027; 0,028
Shipment D	0,13	0,12; 0,13

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Descriptors: minerals and ores, fluorspar, chemical analysis, determination of content, sulphides, iodometry.

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