175

INTERNATIONAL STANDARD

ISO 4284

Second edition
1988-12-01

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

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 : 1988 (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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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

This second edition cancels and replaces the first edition (ISO 4284 : 1978), of which it constitutes a minor revision. The scope has been extended to include ceramic-grade fluorspar, and an annex has been added giving the results of comparative tests.

Annex A of this International Standard is for information only.

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*).

NOTE — 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 listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 565 : 1983, *Test sieves — Woven metal wire cloth, perforated plate and electroformed sheet — Nominal sizes of openings.*

ISO 4282 : 1977, *Acid-grade fluorspar — Determination of loss in mass at* 105 °C.

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.

NOTE — 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 1 000 ml of water.

4.6 Iodine, standard volumetric solution, $c(1/2\ I_2) = 0{,}005$ mol/l.

It is essential that this solution be freshly prepared by dilution of a standard volumetric solution of iodine, $c(1/2\ I_2) = 0{,}05$ 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, 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.

NOTE — A typical apparatus is shown in figure 1.

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

6 Test sample

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

NOTE — ISO 4282, although specified for acid-grade fluorspar, is equally applicable to ceramic-grade fluorspar.

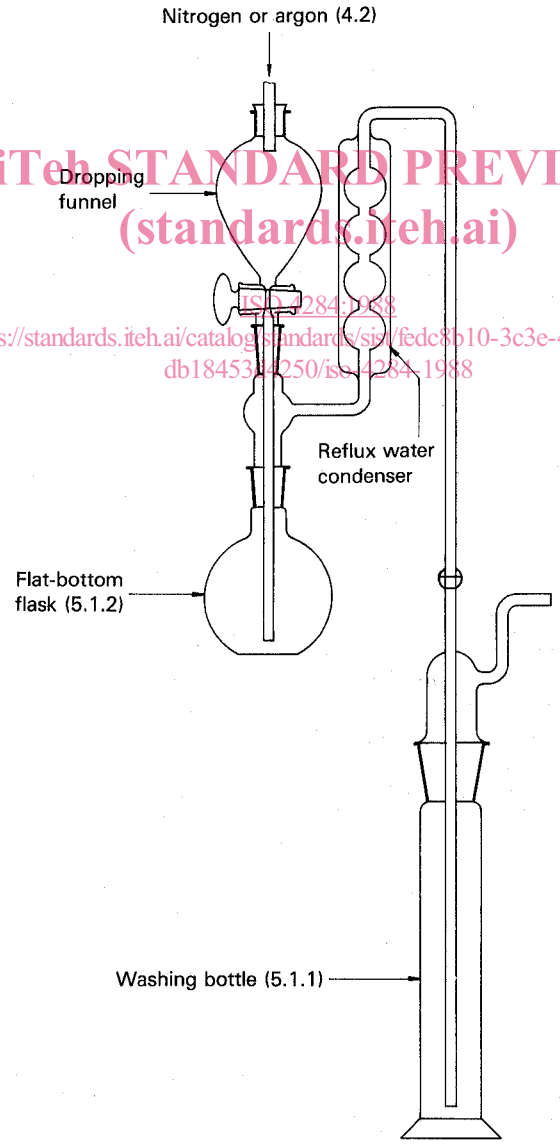

Figure 1 — Typical gas evolution and absorption apparatus

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.

NOTE — The total amount of sulfide, expressed as sulfur (S), in the test portion should not exceed about 0,8 mg. For samples containing more than about 0,03 % (m/m) of sulfur, therefore, the mass of the test portion should 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.

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.

See annex A for the results of comparative tests using the method specified in this International Standard.

9 Test report

The test report shall include the following particulars:

a) identification of the sample;

b) reference to the method used;

c) the results and the way 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 from comparative tests carried out by the member body for Germany, F.R.

Table A.1 — Sulfur contents of various samples

Values in % (*m*/*m*) of S

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

UDC 553.634.12 : 543.242.3 : 546.221

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

Price based on 4 pages