INTERNATIONAL STANDARD

ISO 5438

Second edition
1993-04-01

Acid-grade and ceramic-grade fluorspar — Determination of silica content — Reduced-molybdosilicate spectrometric method

Spaths fluor pour la fabrication de l'acide fluorhydrique et spaths fluor utilisables dans l'industrie céramique — Dosage de la silice — Méthode spectrométrique au molybdosilicate réduit

Reference number
ISO 5438:1993(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 5438 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

This second edition cancels and replaces the first edition (ISO 5438:1985), which has been updated.

Annex A of this International Standard is for information only.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

Acid-grade and ceramic-grade fluorspar — Determination of silica content — Reduced-molybdosilicate spectrometric method

1 Scope

This International Standard specifies a reduced molybdosilicate spectrometric method for the determination of the silica content of acid-grade and ceramic-grade fluorspar.

The method is applicable to products having silica contents, expressed as SiO_2, in the range 0,05 % (*m/m*) to 4,0 % (*m/m*).

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

Decomposition of a test portion by fusion with sodium carbonate and subsequent acidification with hydrochloric acid in the presence of boric acid to complex fluoride. Formation of the molybdosilicic acid and selective reduction to the blue molybdosilicic acid complex with addition of tartaric acid to prevent interference from phosphate.

Spectrometric measurement of the coloured complex at the wavelength of maximum absorption (about 795 nm).

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity. All the reagents shall have very low silica contents.

4.1 Sodium carbonate, anhydrous.

4.2 Boric acid, 40 g/l solution.

4.3 Hydrochloric acid solution, $c(\mathrm{HCl}) \approx 7$ mol/l.

4.4 Sulfuric acid solution, $c(0{,}5\mathrm{H_2SO_4}) \approx 7$ mol/l.

4.5 Sulfuric acid solution, $c(0{,}5\mathrm{H_2SO_4}) \approx 18$ mol/l.

4.6 Molybdate solution, equivalent to 55 g of Mo per litre, prepared by one of the following methods:

a) Dissolve 28 g of sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) in 150 ml of water and dilute to 200 ml.

or

b) Dissolve 20 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in 150 ml of water and dilute to 200 ml.

Store the solution in a bottle (5.3) and discard if a precipitate appears in the solution.

4.7 Tartaric acid, 100 g/l solution.

4.8 Ascorbic acid, 20 g/l solution.

Prepare this solution on the day of use.

4.9 Silicate, standard solution, corresponding to 500 mg of SiO_2 per litre.

Weigh, to the nearest 0,000 2 g, into a platinum crucible (5.1), either

> 0,250 g of silica (SiO_2), obtained by heating pure silicic acid (H_2SiO_3) at 1 000 °C to constant mass, (i.e. until the results of two consecutive weighings do not differ by more than 0,001 g),

or

> 0,250 g of pure quartz, finely ground and previously heated for 1 h at 1 000 °C and allowed to cool in a desiccator.

Add 2,5 g of the sodium carbonate (4.1) to the crucible. Mix well with the stirring rod (5.5) and carefully fuse the mixture. Add warm water directly to the crucible, heat gently until the contents are completely dissolved and transfer quantitatively to a beaker (5.2) of suitable capacity.

Cool, dilute the solution to about 400 ml, transfer quantitatively to a 500 ml one-mark volumetric flask (5.4), dilute to the mark and mix. Transfer the solution immediately to a bottle (5.3).

1 ml of this standard solution contains 500 µg of SiO_2.

4.10 Silicate, standard solution, corresponding to 100 mg of SiO_2 per litre.

Place 100 ml of the standard silicate solution (4.9), in a 500 ml one-mark volumetric flask (5.4), dilute to the mark with water and mix.

1 ml of this standard solution contains 100 µg of SiO_2.

Prepare this solution just before use.

4.11 Diluting solution.

In a 600 ml beaker (5.2), dissolve 4 g of sodium carbonate with approximately 300 ml of water, add 20 ml of boric acid solution (4.2), adjust to approximately pH 2 with hydrochloric acid (4.3) using indicator paper and dilute to 500 ml with water. Store the solution in a bottle (5.3).

5 Apparatus

Ordinary laboratory apparatus and

5.1 Platinum crucibles, of diameter about 40 mm and depth about 30 mm, fitted with platinum lids.

5.2 Beakers, of capacity 100 ml, 250 ml, 600 ml and 1 000 ml, of material free from silica.

5.3 Bottles, of material free from silica.

5.4 Volumetric flasks, of material free from silica.

5.5 Stirring rod, of material free from silica, flattened at one end.

5.6 Spectrometer, with a radiation selector for continuous variation, fitted with cells of thickness 2 cm, or

5.7 Spectrometer, with a radiation selector for discontinuous variation, fitted with the same cells and with filters allowing a maximum transmission of about 795 nm.

If such filters are not available, operate at about 680 nm with cells of thickness 4 cm.

5.8 pH meter, fitted with a glass measuring electrode and a calomel electrode, sensitivity 0,05 pH unit.

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

5.10 Pestle and mortar, of material free from silica, e.g. aluminium oxide or tungsten carbide.

6 Test sample

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

7 Procedure

7.1 Test portion and preparation of the test solution

Grind several grams of the test sample (clause 6) using the pestle and mortar (5.10) until it passes a 63 µm mesh sieve (see ISO 565).

Dry the ground material for 2 h in the oven (5.9), maintained at 105 °C ± 2 °C, allow to cool in a desiccator and weigh, to the nearest 0,000 2 g, about 0,2 g of this sample into a platinum crucible (5.1). Add 4 g of the sodium carbonate (4.1).

Mix the contents of the crucible using the stirring rod (5.5). Cover the crucible with its lid and heat with a gas burner, gently at first, then to dull red. After having attained a clear melt, maintain at red heat for 5 min to 10 min. Ensure that the test portion comes into contact with the molten sodium carbonate by swirling the contents of the crucible.

Chill the crucible by placing in cold water to loosen the melt from the walls of the crucible. Transfer the solid melt to a 600 ml beaker (5.2), then carefully rinse any remaining solid into the beaker. Finally, bring the volume of the solution in the beaker to approximately 200 ml by addition of water. Place the beaker on a steam bath, allow to stand for 30 min and break any lumps using the stirring rod (5.5). Allow to cool, dilute to approximately 300 ml with water and add 20 ml of the boric acid solution (4.2). During stirring, add the hydrochloric acid (4.3) to adjust the pH to approximately 2 (suitable indicator paper). Transfer the solution, which may occasionally appear slightly opalescent, to a 500 ml one-mark volumetric flask (5.4), dilute to the mark with water and mix.

If any white sediment of barium sulfate is observed, it should be allowed to settle before proceeding.

7.2 Blank test

Carry out a blank test at the same time as the determination (7.4), following the same procedure and using the same quantities of all the reagents as used for the determination, but replacing the volume of the test solution by an equal volume of water.

7.3 Preparation of calibration graph

7.3.1 Preparation of standard colorimetric solutions for spectrometric measurements

Into a series of six 600 ml beakers (5.2) place the volumes of the standard silicate solution (4.10) shown in table 1.

Add 4 g of the sodium carbonate (4.1), dilute to approximately 300 ml with water, add 20 ml of the boric acid solution (4.2) and, during stirring, add the hydrochloric acid solution (4.3) to adjust the pH to approximately 2 (suitable indicator paper). Transfer the solution to a 500 ml one-mark volumetric flask (5.4), dilute to the mark with water and mix.

Table 1 — Calibration solutions

Volume of standard silicate solution (4.10) ml	Corresponding mass of silica, related to the volume to be applied for measurement (7.3.3) µg
0[1]	0
2,0	8
5,0	20
10,0	40
20,0	80
25,0	100

[1] Zero calibration solution (blank solution for the calibration-graph reagents).

7.3.2 Preliminary test and correction of pH

Place 20 ml of the standard colorimetric solution containing 100 µg of SiO_2 (7.3.1) into one of the 100 ml beakers (5.2). Dilute to about 60 ml with water and, while stirring, adjust the pH to 1,1 with the sulfuric acid solution (4.4).

Note the volume of sulfuric acid solution (4.4) required and discard the solution.

7.3.3 Formation of the absorbing compound

Into each of six 100 ml one-mark volumetric flasks (5.4) measure 20 ml of the solutions, obtained as described in 7.3.1.

Dilute to about 60 ml with water. Then add the volume of the sulfuric acid solution (4.4) recorded in 7.3.2 and 10 ml of the molybdate solution (4.6). Mix and allow to stand for 15 min. Add 5 ml of the tartaric acid solution (4.7), mix and allow to stand for 5 min. Then add 10 ml of the sulfuric acid solution (4.5) and 2 ml of the ascorbic acid solution (4.8). Dilute to the mark with water, mix and allow to stand for 30 min.

7.3.4 Spectrometric measurements

Measure the absorbance of each of the standard solutions, using the spectrometer (5.6) at a wavelength of maximum absorption (approximately 795 nm), or the spectrometer (5.7) fitted with suitable filters, after having adjusted the instrument to zero absorbance against water.

7.3.5 Plotting of the calibration graph

Deduct the absorbance of the zero calibration solution from that of each of the other standard colorimetric solutions (see table 1) in order to obtain net absorbance.

Plot a graph having, for example, the masses, in micrograms, of silica (SiO_2) in the standard colorimetric solutions as abscissae and the corresponding values of the net absorbance as ordinates.

7.4 Determination

7.4.1 Preliminary test and correction of pH

Place 20 ml of the test solution (7.1) into one of the 100 ml beakers (5.2). Dilute to about 60 ml with water and, while stirring, adjust the pH to 1,1 with the sulfuric acid solution (4.4).

Note the volume of the sulfuric acid solution (4.4) required and discard the solution.

7.4.2 Colour development

Transfer a volume of the test solution (7.1) not greater than 20 ml and containing no more than 100 µg of SiO_2 into a 100 ml one-mark volumetric flask (5.4). If less than 20 ml are used, add the diluting solution (4.11) to obtain accurately a total volume of 20 ml. Dilute to about 60 ml with water, add the volume of the sulfuric acid solution (4.4) recorded in 7.4.1. Add 10 ml of the molybdate solution (4.6), mix well and allow to stand for 15 min. Add 5 ml of the tartaric acid solution (4.7), mix and allow to stand for 5 min. Then add 10 ml of the sulfuric acid solution (4.5) and 2 ml of the ascorbic acid solution (4.8). Dilute to the mark with water, mix and allow to stand for 30 min.

7.4.3 Spectrometric measurements

Measure the absorbances of the test solution (7.4.2) and of the blank test solution (7.2) by the procedure specified in 7.3.4, after having adjusted the instrument to zero absorbance against water.

8 Expression of results

By reference to the calibration graph (7.3.5), determine the silica (SiO_2) content corresponding to the net absorbances of the test solution and of the blank test solution.

The silica content, expressed as a percentage by mass of SiO_2, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times r_D \times 10^{-4}$$

where

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

m_1 is the mass, in micrograms, of silica (SiO_2) found in the aliquot portion of the test solution (see 7.1) taken for the colour development;

m_2 is the mass, in micrograms, of silica (SiO_2) found in the corresponding aliquot portion of the blank test solution (7.2);

r_D is the ratio between the volume of test solution and the volume of the aliquot portion taken for the colour development (7.4.2).

NOTE 1 Examples of silica contents obtained by different test methods 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, or regarded as optional.