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Metallurgical-grade fluorspar — Determination of silica content — Reduced-molybdosilicate spectrometric method

iTeh STANDARD PREVIEW

*Spaths fluor utilisables dans l'industrie métallurgique — Dosage de la
silice — Méthode spectrométrique au molybdosilicate réduit*

ISO 9502:1989

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 9502 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

Annex A of this International Standard is for information only.

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Metallurgical-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 metallurgical-grade fluorspar.

The method is applicable to products having silica contents, expressed as SiO_2 , in the range 0,2 % (m/m) to 30 % (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 565:1983, *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

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 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 absorbance of the coloured complex at a wavelength of approximately 650 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, $c(\text{HCl}) \approx 7 \text{ mol/l}$.

4.4 Sulfuric acid, $c(0,5\text{H}_2\text{SO}_4) \approx 7 \text{ mol/l}$.

4.5 Sulfuric acid, $c(0,5\text{H}_2\text{SO}_4) \approx 18 \text{ mol/l}$.

4.6 Molybdate, solution, equivalent to 55 g of Mo per litre, prepared using one of the following procedures.

a) Dissolve 28 g of sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) 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.

b) Dissolve 20 g of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ 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 750 mg of SiO₂ per litre.

Weigh, to the nearest 0,2 mg, into a platinum crucible (5.1),

either

0,375 g of silica (SiO₂), obtained by heating pure silicic acid (H₂SiO₃) at 1000 °C to constant mass (i.e. until the results of two consecutive weighings do not differ by more than 1 mg),

or

0,375 g of pure quartz, finely ground and previously heated for 1 h at 1000 °C and allowed to cool in a desiccator.

Add 4 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 750 µg of SiO₂.

4.10 Diluting solution.

In a 600 ml beaker (5.2), dissolve 4 g of sodium carbonate (4.1) 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 1000 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, flattened at one end, of material free from silica.

5.6 Spectrometer, with a radiation selector for continuous variation, fitted with cells of optical path length 1 cm, or

5.7 Spectrometer, with a radiation selector for discontinuous variation, fitted with the same cells and with filters giving a maximum transmission at a wavelength of about 650 nm.

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

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

The residue from the determination of the loss in mass at 105 °C (see ISO 4282) shall be used as the test sample.

NOTE 1 ISO 4282, although it specifies acid-grade fluorspar, is equally applicable to metallurgical-grade fluorspar.

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 through a 63 µm mesh sieve (see ISO 565). Dry the sieved 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 0,2 mg, about 0,2 g of this sample into a platinum crucible (5.1).

Add 4 g of the sodium carbonate (4.1) and 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 it 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. 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, allow it 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 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 the calibration solutions

Into a series of five 600 ml beakers (5.2) place the volumes of the standard silicate solution (4.9) shown in table 1.

Table 1 — Calibration solutions

Volume of standard silicate solution (4.9) ml	Mass of silica in the aliquot portion used to prepare the absorbing compound (see 7.3.3) µg
0 ¹⁾	0
5	150
10	300
15	450
20	600
1) Compensation solution	

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, while stirring, add hydrochloric acid (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.

7.3.2 Preliminary test and correction of pH

Place 20 ml of the most concentrated calibration solution (see table 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 approximately 7 mol/l sulfuric acid (4.4).

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

7.3.3 Formation of the absorbing compound

Into a series of five 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 approximately 7 mol/l sulfuric acid (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 approximately 18 mol/l sulfuric acid (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

Using the spectrometer (5.6), at a wavelength of approximately 650 nm, or the spectrometer (5.7), fitted with suitable filters, carry out the spectrometric measurements, after having adjusted the instrument to zero absorbance against water.

7.3.5 Plotting the calibration graph

Deduct the absorbance of the compensation solution (see table 1) from that of each of the calibration solutions to yield the net absorbance.

Plot a calibration graph showing, for example, the masses, in micrograms, of silica (SiO₂) in the calibration 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 approximately 7 mol/l sulfuric acid (4.4).

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

7.4.2 Formation of the absorbing compound

Transfer the appropriate volume of the test solution (7.1) shown in table 2 into a 100 ml one-mark volumetric flask (5.4). When less than 20 ml are used, add the diluting solution (4.10) to obtain accurately a total volume of 20 ml. Dilute to about 60 ml with water, add the volume of the approximately 7 mol/l sulfuric acid (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 approximately 18 mol/l sulfuric acid (4.5) and 2 ml of the ascorbic acid sol-

ution (4.8). Dilute to the mark with water, mix and allow to stand for 30 min.

Table 2 — Volume of test solution to be used for the formation of the absorbing compound

Silica content % (m/m)	Allquot portion to be taken ml
less than 6	20
6 to 12	10
greater than 12	5

7.4.3 Spectrometric measurements

Carry out the spectrometric measurements on the test solution (7.4.2) and on the blank test solution (7.2), following 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 (SiO₂) content corresponding to the absorbances of the test solution and the blank test solution.

The silica content, expressed as a percentage by mass of SiO₂, 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 (7.1);

m_1 is the mass, in micrograms, of silica (SiO₂) found in the aliquot portion of the test solution taken for formation of the absorbing compound;

m_2 is the mass, in micrograms, of silica (SiO₂) found in the corresponding aliquot portion of the blank test solution;

r_D is the ratio of the volume of the test solution to the volume of the aliquot portion taken for formation of the absorbing compound.

9 Test report

The test report shall include the following particulars:

- an identification of the sample;
- the method used (a reference to this International Standard);
- the results and the units in which they have been expressed;
- any unusual features noted during the determination;
- 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)

Interlaboratory test results

The method specified in this International Standard is a modification of the method given in ISO 5438:1985, *Acid-grade and ceramic-grade fluorspar — Determination of silica content — Reduced molybdsilicate spectrometric method*, for application to metallurgical-grade fluorspar.

In order to confirm the analytical precision of the modified version, eight laboratories in Japan have

carried out a co-operative test calling for the duplicate analysis of six kinds of metallurgical-grade fluorspar.

The analytical results and statistical evaluation are summarized in table A.1.

Table A.1 shows that the modified spectrometric method of ISO 5438 is suitable for metallurgical-grade fluorspar.

Table A.1 — Results of the co-operative test using the spectrometric method of ISO 5438

Lab	Sample																	
	Mexico			China-1			China-2			Thailand			China-3			China-4		
	x	\bar{x}	σ_x	x	\bar{x}	σ_x	x	\bar{x}	σ_x	x	\bar{x}	σ_x	x	\bar{x}	σ_x	x	\bar{x}	σ_x
A	21,24 21,04	21,140	0,141	20,40 20,32	20,360	0,057	15,62 15,46	15,540	0,113	14,38 14,30	14,340	0,057	6,73 6,75	6,740	0,014	1,30 1,35	1,325	0,035
B	21,00 21,04	21,020	0,028	20,04 19,89	19,965	0,057	15,67 15,57	15,620	0,071	14,39 14,46	14,425	0,049	6,92 6,81	6,865	0,078	1,47 1,43	1,450	0,028
C	21,40 21,45	21,425	0,035	20,10 20,45	20,275	0,247	15,57 15,95	15,760	0,269	14,36 14,47	14,415	0,078	6,86 6,86	6,860	0	1,44 1,44	1,440	0
D	21,17 21,18	21,175	0,007	20,28 20,22	20,250	0,042	15,56 15,62	15,590	0,042	14,22 14,19	14,205	0,021	6,61 6,64	6,625	0,021	1,42 1,42	1,420	0
E	21,10 21,25	21,175	0,106	20,25 20,25	20,250	0	15,50 15,50	15,500	0	14,40 14,50	14,450	0,071	6,63 6,75	6,690	0,085	1,46 1,44	1,450	0,014
F	21,15 21,00	21,075	0,106	19,90 19,85	19,875	0,035	15,30 15,40	15,350	0,071	14,20 14,25	14,225	0,035	6,72 6,75	6,735	0,021	1,44 1,50	1,470	0,042
G	20,98 20,95	20,965	0,021	20,26 20,05	20,155	0,148	15,51 15,35	15,430	0,113	14,05 14,12	14,085	0,049	6,64 6,58	6,610	0,042	1,47 1,53	1,500	0,042
H	21,34 21,20	21,270	0,099	20,24 20,00	20,120	0,170	15,74 15,70	15,720	0,028	14,55 14,65	14,605	0,071	6,69 6,68	6,685	0,007	1,40 1,50	1,450	0,071
$\bar{\bar{x}}$	21,156			20,156			15,564			14,343			6,726			1,438		
σ_r	0,088			0,132			0,126			0,060			0,048			0,039		
σ_R	0,158			0,189			0,165			0,169			0,102			0,058		

where

- x is the determined value;
- \bar{x} is the laboratory mean;
- σ_x is the cell standard deviation calculated in accordance with ISO 57251);
- $\bar{\bar{x}}$ is the grand mean of \bar{x} for each sample;
- σ_r and σ_R are the repeatability and reproducibility standard deviations calculated in accordance with ISO 57251).

1) ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

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