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Metallurgical-grade fluorspar — Determination of total sulfur content — Iodometric method after combustion

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*Spathes fluor utilisables dans l'industrie métallurgique — Dosage du
soufre total — Méthode iodométrique après combustion*

ISO 9501:1991

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INTERNATIONAL

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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 9501 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

Annexes A and B of this International Standard are for information only.

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Metallurgical-grade fluorspar — Determination of total sulfur content — Iodometric method after combustion

1 Scope

This International Standard specifies an iodometric method after combustion for the determination of total sulfur content of metallurgical-grade fluorspar.

This method is applicable to fluorspars having sulfur contents, expressed as S, in the range 0,01 % (*m/m*) to 1,0 % (*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

Mixing of the test portion with tungsten(VI) oxide, and heating at 1200 °C in a sealed apparatus. Absorption of the evolved sulfur dioxide, entrained in a stream of nitrogen, in dilute hydrochloric acid solution containing starch and potassium iodide. Titration of the solution continuously during the evolution with a standard volumetric solution of potassium iodate.

4 Reagents and materials

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

4.1 Calcium fluoride (CaF_2), powdered, of high purity (as high as possible), and free from sulfur or having a very low and known sulfur content.

4.2 Tungsten(VI) oxide (WO_3).

4.3 Hydrochloric acid, solution.

Dilute 1 volume of hydrochloric acid, ρ 1,18 g/ml, with 66 volumes of water.

4.4 Potassium iodide, solution about 30 g/l.

4.5 Sulfur, standard solution, corresponding to 5,0 g of S per litre.

Dry a small amount of potassium sulfate (K_2SO_4) by heating in an oven (5.2), set at $105\text{ °C} \pm 2\text{ °C}$, for 2 h. Allow to cool in a desiccator.

Weigh, to the nearest 0,2 mg, 13,587 2 g of the dried potassium sulfate and dissolve in water. Cool, transfer to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 5,0 mg of S.

4.6 Potassium iodate, standard volumetric solution, $c(\text{KIO}_3) \approx 0,001\text{ mol/l}$.

Weigh, to the nearest 0,2 mg, 0,223 g of dried potassium iodate (KIO_3) and dissolve in water. Cool, transfer to a 1000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard volumetric solution is equivalent to about 0,10 mg of S.

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4.7 Starch, solution, 20 g/l.

Triturate 2,0 g of soluble starch with 10 ml of water, add to 50 ml of boiling water and stir. Cool, dilute to 100 ml and mix.

Prepare this solution immediately prior to use.

4.8 Carbon-dioxide-absorbing granules, particle size range 0,5 mm to 2 mm.

Ascarite or a similar reagent which does not contain asbestos should be used.

4.9 Magnesium perchlorate [$\text{Mg}(\text{ClO}_4)_2$], anhydrous, particle size range 0,5 mm to 2 mm.**5 Apparatus**

Ordinary laboratory apparatus, and

5.1 Combustion and titration apparatus (see figure 1), consisting of the following components.**5.1.1 Nitrogen supply****5.1.2 Drying tower**, containing carbon-dioxide-absorbing granules (4.8) and magnesium perchlorate (4.9).**5.1.3 Flowmeter**, graduated from 0 ml/min to 1 000 ml/min.**5.1.4 Resistance furnace**, capable of being maintained at $1200\text{ }^\circ\text{C} \pm 25\text{ }^\circ\text{C}$.**5.1.5 Refractory combustion tube**, capable of withstanding a temperature of $1200\text{ }^\circ\text{C} \pm 25\text{ }^\circ\text{C}$.**5.1.6 Refractory combustion boat**, with loose-fitting lid, or a refractory combustion boat capable of accommodating a porous cartridge, as shown in figure 2 and figure 3 respectively.

The following dimensions, expressed in millimetres, for the combustion boat and cartridge may be used as guidelines

Combustion boat	Cartridge
Length 80	Length 50
Width 13	Internal diameter 15
Height 9	

5.1.7 Absorption bottle, tall form, capacity 100 ml, with a plastic-plate multihole bubbler fitted to a glass tube at a position 15 mm under the surface of the solution.**5.1.8 Burette**, graduated at 0,05 ml intervals.**5.2 Electric oven**, capable of being maintained at $105\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$.**6 Test sample**

Prepare the test sample in accordance with the procedure given in ISO 8868:1989, subclause 9.3, *Preparation of test samples for chemical analysis*.

7 Procedure**7.1 Test portion**

Grind several grams of test sample (see clause 6) in an agate mortar until it all passes through a $63\text{ }\mu\text{m}$ mesh sieve (see ISO 565). Dry the sieved material for 2 h in the oven (5.2) maintained at $105\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$. Allow to cool in a desiccator. Weigh, to the nearest 0,2 mg, the quantity of above-prepared sample indicated in table 1, depending on total sulfur content.

Table 1

Total sulfur content % (m/m)	Mass of sample g
Up to 0,5	0,5
0,5 to 1	0,2

7.2 Blank test

Carry out a blank test simultaneously with the determination, following the same procedure and using the same quantities of all the reagents used in the determination, but omitting the test portion.

7.3 Preparation of calibration graph

Weigh 0,5 g of calcium fluoride (4.1) into each of five refractory combustion boats (5.1.6). Add 1 g of tungsten(VI) oxide (4.2) to each of the combustion boats. Mix the contents in the boats and add to each boat the volume of standard sulfur solution (4.5) shown in table 2.

Table 2

Volume of standard sulfur solution (4.5) μl	Mass of S mg
0	0
100	0,5
200	1,0
300	1,5
400	2,0

Dry at $105\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for 2 h and proceed with the determination as described in 7.4, starting at the second sentence: "Place 80 ml of the hydrochloric acid . . .".

Draw the calibration graph by plotting the mass, in milligrams, of sulfur in each of the calibration solutions along the x -axis, for instance, and the corresponding volume, in millilitres, of potassium iodate solution (4.6) along the y -axis.

7.4 Determination

Place the test portion (7.1) in a small weighing bottle containing 1 g of tungsten(VI) oxide (4.2) and mix thoroughly. Place 80 ml of the hydrochloric acid solution (4.3), 1 ml of the potassium iodide solution (4.4) and 1 ml of the starch solution (4.7) into the absorption bottle (5.1.7) and place the bottle in position at the end of the combustion train. Pass a stream of nitrogen (5.1.1) through the combustion train at a rate of 150 ml/min to 200 ml/min and titrate the absorbing solution with the potassium iodate solution (4.6) until the colour of the solution is just blue.

NOTE 1 A few drops of the potassium iodate solution should be sufficient.

Transfer the mixture of sample and tungsten(VI) oxide to a refractory combustion boat with loose-fitting lid (5.1.6) (see figure 2) and insert the boat into the hot zone of the resistance furnace (5.1.4).

NOTE 2 Alternatively, the mixture of sample and tungsten(VI) oxide may be placed inside a porous cartridge which is placed in a refractory combustion boat (see figure 3).

Leave the boat standing in the hot zone of the furnace for approximately 1 min, and then pass a stream of nitrogen at a rate of 150 ml/min to 200 ml/min. Without interrupting the nitrogen stream, titrate the absorbing solution with the potassium iodate solution so as to keep the solution just blue in colour. Continue to pass nitrogen through the apparatus for 5 min or until the absorbing solution remains permanently blue. Wash the inside of the multihole bubbler several times by releasing the combustion tube inlet bung and then replacing it to restore the nitrogen flow through the apparatus. Finally, titrate the solution to a slightly blue end point and record the volume V_1 , in millilitres, of the potassium iodate solution used.

Record also the volume V_2 , in millilitres, of the potassium iodate solution used in the blank test (see 7.2).

8 Expression of results

8.1 Method of calculation

By means of the calibration graph plotted in 7.3, determine the mass of sulfur in the test solution (m_1) and in the blank test solution (m_2) corresponding to the volume of potassium iodate solution (4.6) consumed in the respective tests.

The total sulfur content, expressed as a percentage by mass of sulfur, is given by the formula

$$\frac{m_1 - m_2}{m_0} \times \frac{1}{10}$$

where

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

m_1 is the mass, in milligrams, of sulfur found in the test solution;

m_2 is the mass, in milligrams, of sulfur found in the blank test solution.

8.2 Precision

The results of a series of inter-laboratory tests are presented in annex A, and a statistical analysis of these results in annex B.

9 Test report

The test report shall include the following particulars:

- identification of the sample;
- reference to this International Standard;
- the results and way 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.

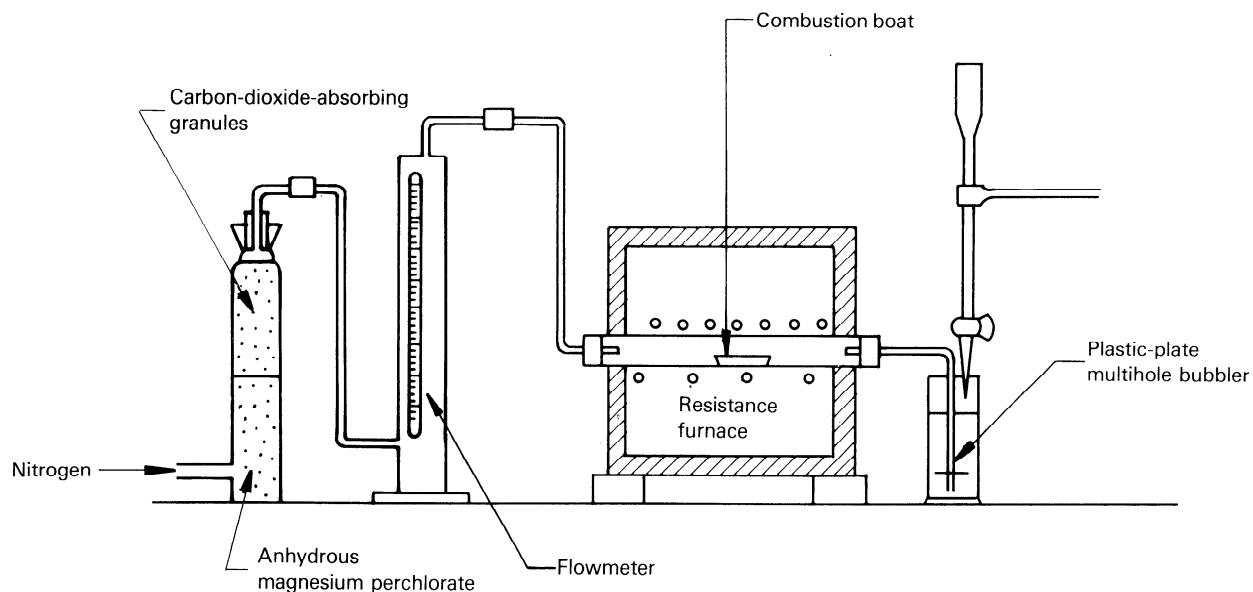
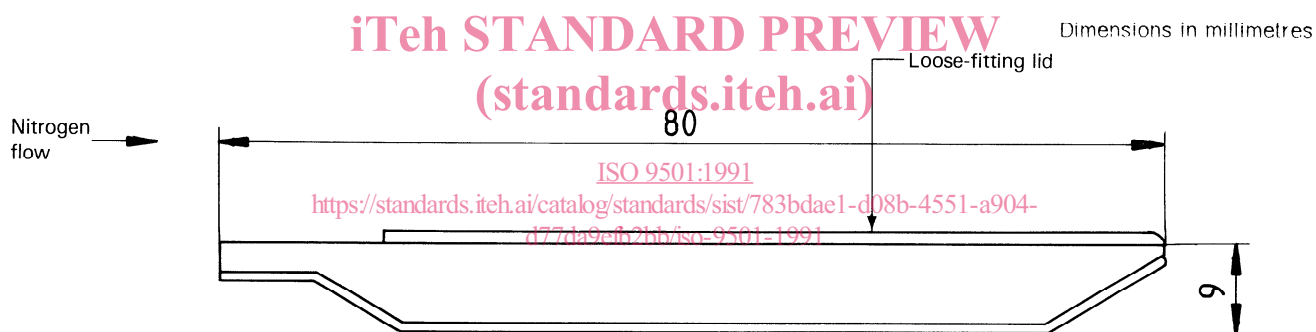
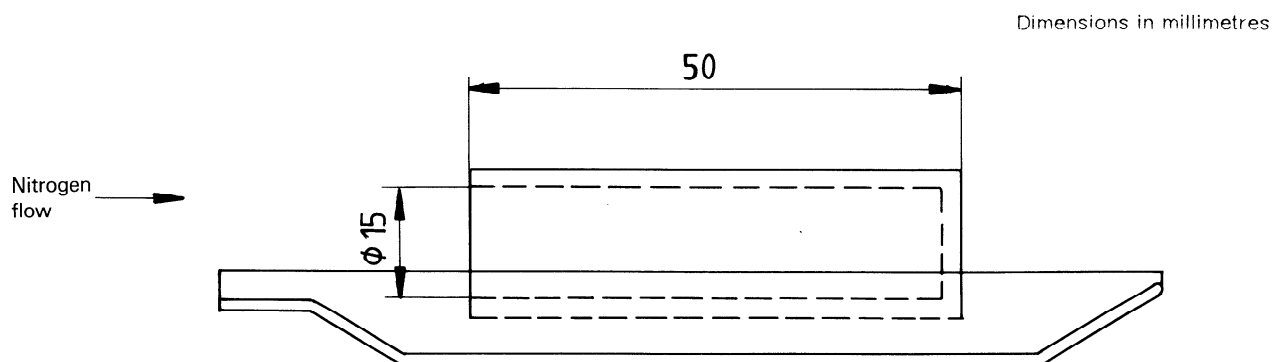


Figure 1 — Combustion and titration apparatus



NOTE — The dimensions shown are intended as guidelines only.

Figure 2 — Combustion boat with loose-fitting lid



NOTE — The dimensions shown are intended as guidelines only.

Figure 3 — Combustion boat with cartridge

Annex A
(informative)

Values of total sulfur content of metallurgical grade fluorspars obtained in inter-laboratory trials using the iodometric method after combustion specified in this International Standard

Table A.1

S[% (m/m)]

Laboratory	Sample					
	China-1	Mexico-1	Mexico-2	China-2	China-3	Korea, Dem. P. Rep. of
A	0,011 0,011	0,128 0,127	0,433 0,436	0,321 0,321	0,400 0,402	0,840 0,845
B	0,006 0,006	0,123 0,119	0,405 0,407	0,295 0,301	0,384 0,392	0,815 0,824
C	0,011 0,013	0,116 0,115	0,403 0,404	0,307 0,308	0,377 0,389	0,837 0,855
D	0,010 0,010	0,125 0,120	0,440 0,435	0,326 0,315	0,406 0,408	0,800 0,801
E	0,010 0,008	0,116 0,118	0,407 0,411	0,308 0,306	0,379 0,381	0,828 0,829
F	0,008 0,007	0,105 0,107	0,411 0,411	0,294 0,287	0,392 0,392	0,804 0,813
G	0,015 0,012	0,120 0,123	0,406 0,411	0,303 0,306	0,386 0,391	0,817 0,821
H	0,008 0,009	0,125 0,124	0,425 0,419	0,315 0,313	0,391 0,391	0,845 0,837

Annex B
(informative)

Results of statistical analysis of the total sulfur content values in annex A

Table B.1

S [% (m/m)]

Laboratory	Sample											
	China-1		Mexico-1		Mexico-2		China-2		China-3		Korea, Dem. P. Rep. of	
	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x	\bar{x}	σ_x
A	0,0110	0	0,127 5	0,000 7	0,434 5	0,002 1	0,321 0	0	0,401 0	0,001 4	0,842 5	0,003 5
B	0,006 0	0	0,121 0	0,002 8	0,406 0	0,001 4	0,298 0	0,004 2	0,388 0	0,005 6	0,819 5	0,006 3
C	0,012 0	0,001 4	0,115 5	0,000 7	0,403 5	0,000 7	0,307 5	0,000 7	0,383 0	0,008 4	0,846 0	0,012 7
D	0,010 0	0	0,122 5	0,003 5	0,437 5	0,003 5	0,320 5	0,007 7	0,407 0	0,001 4	0,800 5	0,000 7
E	0,009 0	0,001 4	0,117 0	0,001 4	0,409 0	0,002 8	0,307 0	0,001 4	0,380 0	0,001 4	0,828 5	0,000 7
F	0,007 5	0,000 7	0,106 0	0,001 4	0,411 0	0	0,290 5	0,004 9	0,392 0	0	0,808 5	0,006 3
G	0,013 5	0,002 1	0,121 5	0,002 1	0,408 5	0,003 5	0,304 5	0,002 1	0,388 5	0,003 5	0,819 0	0,002 8
H	0,008 5	0,000 7	0,124 5	0,000 7	0,422 0	0,004 2	0,314 0	0,001 4	0,391 0	0	0,841 0	0,005 6
$\bar{\bar{x}}$	0,009 68		0,119 43		0,416 50		0,307 87		0,391 31		0,825 68	
σ_r	0,001 07		0,001 93		0,002 66		0,003 70		0,003 87		0,006 052	
σ_R	0,002 56		0,006 77		0,013 36		0,010 87		0,009 32		0,017 23	
CV	26,4		5,66		3,20		3,53		2,38		2,08	

where

x is the result of a determination;

\bar{x} is the mean of the determinations made by a particular laboratory on a particular sample;

σ_x is the standard deviation for these determinations, given by the equation:

$$\sigma_x = \sqrt{\frac{1}{n-1} \sum (x - \bar{x})^2}$$

in which n is the number of determinations;

$\bar{\bar{x}}$ is the overall mean, for a particular sample, of the means \bar{x} , given by the equation:

$$\bar{\bar{x}} = \frac{1}{p} \sum \bar{x}$$

in which p is the number of laboratories involved;

σ_r is the repeatability standard deviation, given by the equation:

$$\sigma_r = \sqrt{\frac{1}{p} \sum \sigma_x^2}$$

σ_R is the reproducibility standard deviation, given by the equation:

$$\sigma_R = \sqrt{\frac{1}{p-1} \sum (\bar{x} - \bar{\bar{x}})^2 - \frac{\sigma_r^2}{n} + \sigma_r^2}$$

CV is the coefficient of variation, given by the equation:

$$CV = \frac{\sigma_R}{\bar{\bar{x}}} \times 100$$

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