

INTERNATIONAL
STANDARD

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9061

Second edition
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**Acid-grade and ceramic-grade fluorspar —
Determination of iron content —
1,10-Phenanthroline spectrometric method**

*Spaths fluor pour la fabrication de l'acide fluorhydrique et spaths fluor
utilisables dans l'industrie céramique — Dosage du fer — Méthode
spectrométrique à la phénanthroline-1,10*



Reference number
ISO 9061:1993(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 9061 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

This second edition cancels and replaces the first edition (ISO 9061:1988), 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 iron content — 1,10-Phenanthroline spectrometric method

1 Scope

This International Standard specifies a 1,10-phenanthroline spectrometric method for the determination of the iron content of acid-grade and ceramic-grade fluorspar.

The method is applicable to products having iron contents, expressed as Fe_2O_3 , in the range 0,1 % (m/m) to 2,0 % (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

Alkaline fusion of a test portion with a mixture of sodium carbonate and boric acid. Dissolution of the melt in excess hydrochloric acid. Reduction of the iron(III) with hydroxylammonium chloride. Formation of the iron(II)-1,10-phenanthroline complex in a buffered medium (pH between 3 and 5).

Spectrometric measurement of the coloured complex at a wavelength of about 510 nm, corresponding to the absorption maximum.

4 Reagents

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

4.1 Sodium carbonate, anhydrous.

4.2 Boric acid (H_3BO_3).

4.3 Hydrochloric acid, diluted 1 + 1.

Dilute one volume of hydrochloric acid (ρ approximately 1,18 g/ml) with an equal volume of water.

4.4 Hydroxylammonium chloride (HONH_2Cl), 10 g/l solution.

4.5 1,10-Phenanthroline monohydrate ($\text{C}_{12}\text{H}_8\text{N}_2\cdot\text{H}_2\text{O}$), 2 g/l solution.

4.6 Sodium acetate trihydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$), 500 g/l solution.

4.7 Iron, standard solution corresponding to 0,100 g of Fe_2O_3 per litre.

Weigh 0,605 g of ammonium iron(III) sulfate 24-hydrate [$\text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4\cdot 24\text{H}_2\text{O}$] to the nearest 1 mg, place in a beaker and dissolve in water.

Add 10 ml of sulfuric acid (ρ approximately 1,84 g/ml), allow to cool, transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,100 mg of Fe_2O_3 .

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Electric oven, capable of being maintained at a temperature of $105\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$.

5.2 Platinum dish, flat bottomed, of diameter approximately 80 mm and depth approximately 35 mm, fitted with a platinum lid.

5.3 Muffle furnace, capable of being maintained at a temperature of approximately $1\ 000\text{ }^{\circ}\text{C}$.

5.4 Spectrometer, with a radiation selector for continuous variation, fitted with cells of optical path length 2 cm.

5.5 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 510 nm.

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) in an agate mortar until it passes through a $63\ \mu\text{m}$ mesh sieve (see ISO 565). Dry the sieved material for 2 h in the oven (5.1) maintained at $105\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, allow to cool in a desiccator and weigh, to the nearest 1 mg, about 0,5 g of this sample into a platinum dish (5.2).

Add 6 g of the boric acid (4.2) and 4 g of the anhydrous sodium carbonate (4.1) and mix carefully, preferably using a platinum spatula. Cover the dish with its lid, place it on a heat-resistant and thermally insulating plate, heat gently at first and then increase the heat gradually until the reaction slows down. Transfer the dish to the muffle furnace (5.3) maintained at approximately $1\ 000\text{ }^{\circ}\text{C}$ and heat to complete fusion.

Remove the dish from the muffle furnace and allow to cool in air. Add hot water to the dish, heat in a water bath until the melt has dissolved, acidify by slowly adding 20 ml of hydrochloric acid (4.3) and transfer quantitatively to a 250 ml one-mark volumetric flask. Allow to cool, dilute to the mark with water and mix.

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 reagents as used for the determination, but omitting the test portion.

7.3 Preparation of the calibration graph

7.3.1 Preparation of the calibration solutions

Into each of a series of seven 250 ml one-mark volumetric flasks, place the volumes of standard iron solution (4.7) shown in table 1.

Table 1 — Calibration solutions

Volume of standard iron solution (4.7) ml	Corresponding mass of Fe_2O_3 mg
0 ¹⁾	0
1,0	0,1
2,0	0,2
3,0	0,3
4,0	0,4
5,0	0,5
6,0	0,6

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

7.3.2 Formation of the absorbing compound

Add to the contents of each volumetric flask an amount of water sufficient to dilute it to approximately 200 ml, then add 5 ml of the hydroxylammonium chloride solution (4.4), mix and allow to stand for 1 min. Add 10 ml of the sodium acetate solution (4.6) and 5 ml of the 1,10-phenanthroline solution (4.5), dilute with water to the mark and mix.

7.3.3 Spectrometric measurements

After 15 min, measure the absorbance of each calibration solution (7.3.1) using the spectrometer (5.4) adjusted to a wavelength of about 510 nm or the spectrometer (5.5) fitted with the appropriate filters, after having adjusted the instrument to zero absorbance against water.

7.3.4 Plotting the calibration graph

Subtract the absorbance of the zero calibration solution from the absorbance of each of the other calibration solutions (see table 1) to yield the net absorbance.

Plot a calibration graph showing, for example, the mass, in milligrams, of the iron(III) oxide (Fe_2O_3) contained in the calibration solutions on the abscissa and

the corresponding values of net absorbance on the ordinate.

7.4 Determination

7.4.1 Aliquot portion of the test solution

In accordance with the estimated iron content, place an aliquot portion, as shown in table 2, of the test solution prepared in 7.1 in a 250 ml one-mark volumetric flask.

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

Fe ₂ O ₃ content % (m/m)	Aliquot portion to be taken ml
0,1 to 0,5	50
0,5 to 1,0	20
1,0 to 2,0	10

7.4.2 Formation of the absorbing compound

To the aliquot portion of the test solution placed in the 250 ml one-mark volumetric flask (7.4.1), add the same quantities of all reagents as used for the standard iron solution (see 7.3.2), dilute to the mark with water and mix.

7.4.3 Spectrometric measurement

After 15 min, carry out the spectrometric measurements of the test solution (7.4.2) and the blank test solution (7.2), following the procedure specified in 7.3.3, after having adjusted the instrument to zero absorbance against water.

8 Expression of results

8.1 Method of calculation

By reference to the calibration graph (7.3.4), determine the mass of iron(III) oxide (Fe₂O₃) corresponding to the values of the net absorbances of the test solution and the blank test solution.

The iron content, expressed as a percentage by mass of Fe₂O₃, is given by the formula

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

where

- m_0 is the mass, in grams, of the test portion (7.1);
- m_1 is the mass, in milligrams, of iron(III) oxide (Fe₂O₃) determined in the aliquot portion of the test solution (see 7.1) used for formation of the absorbing compound;
- m_2 is the mass, in milligrams, of iron(III) oxide (Fe₂O₃) determined in the aliquot portion of the blank test solution (7.2);
- r_D is the ratio of the volume of the test solution to the volume of the aliquot portion taken for the formation of the absorbing compound (7.4.2).

8.2 Precision

See annex A for information.

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.

Annex A (informative)

Precision of the method

Comparative analyses carried out in five laboratories on the three samples gave the statistical information shown in table A.1.

The test samples for the comparative analyses carried out in the five laboratories were distributed to the laboratories after being ground until all the sample passed through a 63 μm mesh sieve.

Table A.1 — Results of interlaboratory tests

Sample	1	2	3
Mean of Fe₂O₃ content [% (m/m)]	0,133	0,064	2,07
Standard deviation	of repeatability, σ_r	0,006	0,03
	of reproducibility, σ_R	0,008	0,08