175

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Acid-grade and ceramic-grade fluorspar — Determination of manganese content — Periodate spectrometric method

Spaths fluor pour la fabrication de l'acide fluorhydrique et spaths fluor utilisables dans l'industrie céramique — Dosage du manganèse — Méthode spectrométrique au periodate

Reference number
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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 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.

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International Organization for Standardization
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Acid-grade and ceramic-grade fluorspar — Determination of manganese content — Periodate spectrometric method

1 Scope

This International Standard specifies a periodate spectrometric method for the determination of the manganese content of acid-grade and ceramic-grade fluorspar.

The method is applicable to products having manganese contents, expressed as Mn, in the range 0,006 % (m/m) to 0,4 % (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 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

Decomposition of the test portion in a platinum dish using nitric and perchloric acids. After dilution, oxidation of the manganese in an aliquot portion of the solution to permanganate ion using sodium metaperiodate, and spectrometric measurement of the absorbance at a wavelength of 545 nm.

4 Reagents

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

4.1 Nitric acid, ϱ approximately 1,40 g/ml, about 68 % (m/m) solution.

4.2 Perchloric acid, about 70 % (m/m) solution.

4.3 Phosphoric acid, about 85 % (m/m) solution.

4.4 Sodium metaperiodate, 50 g/l solution.

4.5 Manganese, standard stock solution A corresponding to 1 000 mg of Mn per litre.

Dissolve 0,5 g of pure metallic manganese (> 99,5 % purity) in 20 ml of water and 20 ml of nitric acid (4.1). Add 50 ml of water and boil for 10 min. Leave to cool. Transfer the solution quantitatively to a 500 ml volumetric flask, dilute to the mark with water and mix.

1 ml of this standard stock solution contains 1 000 µg of Mn.

4.6 Manganese, standard solution B corresponding to 100 mg of Mn per litre.

Into a 250 ml volumetric flask, introduce 25,0 ml of the manganese standard stock solution A (4.5), dilute to the mark with water and mix.

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

4.7 Manganese, standard solution C corresponding to 20 mg of Mn per litre.

Into a 250 ml volumetric flask, introduce 50,0 ml of the manganese standard solution B (4.6), dilute to the mark with water and mix.

1 ml of this standard solution contains 20 µg of Mn.

5 Apparatus

Ordinary laboratory apparatus, and

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

5.2 Platinum dish, of approximately 100 ml capacity.

5.3 Platinum crucible, of 30 ml capacity.

5.4 Molecular absorption spectrometer, capable of measuring absorbance to within 0,001 absorbance units at approximately 545 nm.

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.

7 Procedure

WARNING — Perchloric acid vapour may cause explosions in the presence of ammonia, nitrous fumes or organic matter in general.

7.1 Test portion and preparation of the test solution

Grind several grams of the test sample (clause 6) in an agate or similar mortar until it passes through a 63 µm mesh sieve (see ISO 565). Dry the sieved material for 2 h in the oven (5.1) maintained at 105 °C ± 2 °C, allow to cool in a desiccator and weigh, to the nearest 0,2 mg, about 1 g of this sample into the platinum dish (5.2).

Add 2 ml to 3 ml of water and agitate slightly to suspend the sample in the water. Add 10 ml of nitric acid (4.1) and 10 ml of perchloric acid (4.2). Heat carefully until fumes of perchloric acid are evolved and maintain gentle fume development for 5 min. Allow to cool and add 2 ml to 3 ml of water. Heat again until fumes of perchloric acid are again evolved and again maintain gentle fume development for 5 min. Allow to cool.

Add 10 ml of water and 5 ml of nitric acid and warm to dissolve the salts. Transfer the solution quantitatively to a 150 ml beaker. Place a glass cover on the beaker and heat until fumes of perchloric acid are evolved and the perchloric acid refluxes down the sides of the beaker. Allow to reflux for 5 min. Do not allow the volume of perchloric acid to decrease to less than 3 ml. Add further perchloric acid if necessary. Allow to cool.

Add 20 ml of water and 5 ml of nitric acid. Heat to boiling and boil gently for 5 min. Allow to cool. Transfer quantitatively to a 100 ml volumetric flask, dilute with water to the mark and mix.

NOTE — If there is an appreciable amount of insoluble material, treat the solution as follows.

Quantitatively transfer the solution and insoluble material on to a small close-textured filter paper, collecting the filtrate in a 100 ml volumetric flask. Wash the filter paper three times with hot water. Transfer the filter paper and contents to the platinum crucible (5.3), dry and then incinerate at 500 °C to 600 °C. Fuse the residue with 1 g of anhydrous sodium carbonate. Dissolve in 10 ml of water and 3 ml of nitric acid (4.1) and boil to remove carbon dioxide. Add this solution to the filtrate in the 100 ml volumetric flask. Allow to cool, and dilute with water to the mark.

7.2 Blank test

Carry out a reagent blank test concurrently with the determination using the same procedure and the same quantities of all the 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

7.3.1.1 Range 0,03 % (*m*/*m*) to 0,4 % (*m*/*m*) of Mn

a) Into each of a series of seven 150 ml beakers, place the volumes of the manganese standard solution B (4.6) shown in table 1.

Table 1

Volume of manganese standard solution B (4.6) ml	**Corresponding mass of Mn** µg
0*)	0
0,5	50
1,0	100
2,0	200
4,0	400
6,0	600
8,0	800

*) Calibration compensation solution.

b) Add to the contents of each beaker 4 ml of nitric acid (4.1), 4 ml of phosphoric acid (4.3), and 10 ml of sodium metaperiodate solution (4.4). Dilute each solution to 40 ml with water. Place glass covers on the beakers and heat the solutions to incipient boiling. Allow them to simmer for 30 min and maintain the volumes at between 30 and 40 ml by addition of water. Allow the solutions to cool, transfer them quantitatively to 50 ml volumetric flasks, dilute to the marks with water and mix.

7.3.1.2 Range 0,006 % (*m*/*m*) to 0,08 % (*m*/*m*) of Mn

a) Into each of a series of seven 150 ml beakers, place the volumes of the manganese standard solution C (4.7) shown in table 2.

Table 2

Volume of manganese standard solution C (4.7) ml	**Corresponding mass of Mn** µg
0*)	0
0,5	10
1,0	20
2,0	40
4,0	80
6,0	120
8,0	160

*) Calibration compensation solution.

b) Continue in accordance with the method specified in 7.3.1.1 b).

7.3.2 Spectrometric measurements

7.3.2.1 Range 0,03 % (*m*/*m*) to 0,4 % (*m*/*m*) of Mn

Carry out the spectrometric measurements on the calibration solutions prepared in 7.3.1.1, using the spectrometer (5.4) at a wavelength of 545 nm, and using optical cells of 10 mm optical path length after having adjusted the instrument to zero absorbance against water.

7.3.2.2 Range 0,006 % (m/m) to 0,08 % (m/m) of Mn

Carry out the spectrometric measurements of the calibration solutions prepared in 7.3.1.2 in accordance with the method specified in 7.3.2.1, but using optical cells of 50 mm optical path length in place of optical cells of 10 mm optical path length.

7.3.3 Plotting the calibration graph

Subtract the absorbance of the calibration compensation solution (see tables 1 and 2) from the absorbance of each of the calibration solutions to yield the net absorbance. Plot a calibration graph showing, for example, the mass, in micrograms, of manganese contained in 50 ml of the calibration solutions as the abscissa and the corresponding net absorbance values as the ordinate.

7.4 Determination

7.4.1 Formation of the permanganate ion and the compensation solution for the determination

Using a pipette, transfer from the test solution prepared in 7.1 two 20 ml aliquot portions into two 150 ml beakers. To the contents of each beaker add 4 ml of nitric acid (4.1) and 4 ml of phosphoric acid (4.3). To the contents of one of the beakers, add 10 ml of the sodium metaperiodate solution (4.4) and to the contents of the other beaker (compensation solution for the determination) add 10 ml of water. Place glass covers on the beakers and heat the solutions to incipient boiling. Allow them to simmer for 30 min and maintain the volumes at between 30 ml and 40 ml by the addition of water. Allow the solutions to cool, transfer quantitatively to two 50 ml volumetric flasks, dilute to the marks with water and mix.

7.4.2 Spectrometric measurements

Carry out the spectrometric measurements on the test solution and the compensation solution for the determination in accordance with the method specified in 7.3.2, using optical cells of 10 mm or 50 mm optical path length.

Subtract the absorbance of the compensation solution for the determination from the absorbance of the test solution to yield the corrected absorbance of the test solution.

Repeat the same procedure using two 20 ml aliquot portions of the blank test solution and making a similar correction to the absorbances thus obtained.

Subtract the corrected absorbance of the blank test solution from the corrected absorbance of the test solution to obtain the net absorbance of the test solution.

8 Expression of results

Using the calibration graph plotted in 7.3.3, determine the mass of manganese corresponding to the net absorbance value of the test solution.

The manganese content, expressed as a percentage by mass of Mn, is given by the formula

$$\frac{m_1 \times 100 \times 100}{m_0 \times 20 \times 10^6}$$

$$= \frac{m_1 \times 5}{m_0 \times 10^4}$$

where

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

m_1 is the mass, in micrograms, of manganese determined in the aliquot portion of the test solution.

9 Test report

The test report shall include the following information:

a) an identification of the sample;

b) a reference to this International Standard;

c) the results and the units in which they are expressed;

d) any unusual features noted during the determination;

e) any operating details not included in this International Standard, or in the International Standards to which reference is made, as well as any operations regarded as optional.