INTERNATIONAL STANDARD

ISO 6676

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Acid-grade and ceramic-grade fluorspar — Determination of total phosphorus content — Reduced-molybdophosphate spectrometric method

Spaths fluor pour la fabrication de l'acide fluorhydrique et spaths fluor utilisables dans l'industrie céramique — Dosage du phosphore total — Méthode spectrométrique au molybdophosphate réduit

Reference number
ISO 6676:1993(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 6676 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

This third edition cancels and replaces the second edition (ISO 6676:1990), which has been updated.

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Acid-grade and ceramic-grade fluorspar — Determination of total phosphorus content — Reduced-molybdophosphate spectrometric method

1 Scope

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

The method is applicable to products having total phosphorus contents, expressed as PO_4^{3-}, 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

Dissolution of a test portion by fusion with a mixture of sodium carbonate, boric acid and sodium nitrate, and subsequent acidification with nitric acid. Formation of the molybdophosphate complex and extraction with a mixture of ethyl acetate and butyl acetate, followed by selective reduction of the complex to molybdenum blue by means of tin(II) chloride added to the organic phase.

Spectrometric measurement of the absorbance of the coloured complex at the wavelength of maximum absorption (about 710 nm).

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/boric acid, mixture.

Mix 100 g of sodium carbonate and 50 g of boric acid.

4.2 Sodium nitrate.

4.3 Nitric acid, ρ approximately 1,38 g/ml.

4.4 Methanol, ρ approximately 0,794 g/ml.

4.5 Ethyl acetate/butyl acetate, solvent mixture.

Mix 7 volumes of ethyl acetate and 3 volumes of butyl acetate.

4.6 Ammonium molybdate, 30 g/l solution.

Dissolve 30 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ and 10 g of ammonium amidosulfate ($NH_4OSO_2NH_2$) in about 500 ml of water, dilute to 1 000 ml and mix.

4.7 Tin(II) chloride, 20 g/l solution.

Weigh 20 g of tin(II) chloride dihydrate ($SnCl_2.2H_2O$) into a 1 000 ml volumetric flask. Add 200 ml of hydrochloric acid (ρ approximately 1,18 g/ml). Swirl the contents from time to time until dissolution is complete. Dilute to the mark with water and mix.

4.8 Phosphorus, standard solution corresponding to 0,100 g of PO_4^{3-} per litre.

Dry a little potassium dihydrogen orthophosphate (KH_2PO_4) by heating in the oven (5.1), maintained at 105 °C ± 2 °C, for 2 h. Allow to cool in a desiccator. Weigh, to the nearest 0,2 mg, 0,143 3 g of the dried material, and transfer it quantitatively to a 1 000 ml one-mark volumetric flask. Dissolve in water, dilute to the mark and mix.

1 ml of this standard solution contains 100 µg of PO_4^{3-}.

4.9 Phosphorus, standard solution corresponding to 0,010 g of PO_4^{3-} per litre.

Transfer 100,0 ml of standard phosphorus solution (4.8) to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 10 µg of PO_4^{3-}.

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 diameter approximately 45 mm and depth about 25 mm.

5.3 Separating funnels, of capacity 100 ml, with a mark at 60 ml.

5.4 Spectrometer, with a radiation selector for continuous variation of wavelength, fitted with cells of optical path length 1 cm.

5.5 Spectrometer, with a radiation selector for discontinuous variation of wavelength, fitted with the same cells and with filters providing maximum transmission at a wavelength of about 710 nm.

5.6 Optical cells, of optical path length 1 cm.

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 (see clause 6) in an agate 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, and allow to cool in a desiccator. Weigh, to the nearest 0,2 mg, about 0,2 g of this sample into a platinum dish (5.2) containing 2 g of the sodium carbonate/boric acid mixture (4.1) and 0,2 g of the sodium nitrate (4.2) and mix well, preferably with a platinum spatula.

If the fluorspar has a total phosphorus content, expressed as PO_4^{3-}, of more than 0,1 % (*m/m*), take a test portion of about 0,1 g, weighed to the nearest 0,2 mg.

Cover with a further 2 g of the sodium carbonate/boric acid mixture (4.1). Heat with a gas flame, gently at first and then to a dull red heat for 3 min. If the fusion is carried out in an electric furnace, heat for 10 min at 900 °C. Swirl the contents of the dish for a few seconds once the contents have become molten.

Allow the dish to cool and put it into a 250 ml beaker made of materials free from phosphorus, e.g. silica. Add about 20 ml of water and 8,8 ml of the nitric acid (4.3). Heat gently until the contents of the dish are completely dissolved. Allow to cool, and then transfer quantitatively to a 100 ml separating funnel (5.3), rinsing the beaker with about 10 ml of water.

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 eight 100 ml separating funnels (5.3), place one of the volumes of standard phosphorus solution (4.9) shown in table 1.

Table 1 — Calibration solutions

Volume of standard phosphorus solution (4.9) ml	Corresponding mass of PO_4^{3-} µg
0[1]	0
2,0	20
5,0	50
8,0	80
11,0	110
14,0	140
17,0	170
20,0	200

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

7.3.2 Formation of the absorbing compound

Treat each of the calibration solutions prepared in 7.3.1 as follows.

Add about 20 ml of water, 5 ml of nitric acid (4.3) and 10 ml of ammonium molybdate solution (4.6). Dilute to the 60 ml mark with water and swirl. Add 10 ml of the solvent mixture (4.5) and shake for about 60 s. Allow the layers to separate and discard the lower layer completely. Remove any water remaining inside the outlet tube of the separating funnel with a piece of filter paper, and then transfer the solvent mixture layer into a 50 ml volumetric flask. Add 20 ml of tin(II) chloride solution (4.7) and dilute to the mark with methanol (4.4). Shake for 20 s to develop the blue colour of the reduced-molybdophosphate complex.

7.3.3 Spectrometric measurements

Within 10 min after the formation of the absorbing compound (7.3.2), measure the absorbance of each of the organic phases obtained in 7.3.2, using the spectrometer (5.4) set at a wavelength of about 710 nm, or the spectrometer (5.5) fitted with the appropriate filters, after having adjusted the instrument to zero absorbance against the solvent mixture (4.5).

7.3.4 Plotting the calibration graph

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

Plot a calibration graph having, for example, the masses, in micrograms, of PO_4^{3-} contained in 60 ml of the calibration solutions as abscissae, and the corresponding values of net absorbance as ordinates.

7.4 Determination

7.4.1 Formation of the absorbing compound

Carry out, at a temperature between 20 °C and 30 °C, the following procedure to form the molybdophosphate complex and to extract it.

To the test solution in the separating funnel (see 7.1) add 10 ml of ammonium molybdate solution (4.6), dilute to the 60 ml mark with water and swirl. Add 10 ml of the solvent mixture (4.5) and carry out the extraction procedure specified in 7.3.2.

If the fluorspar has a total phosphorus content, expressed as PO_4^{3-}, of more than 0,1 % (*m/m*), use the following procedure.

Transfer the test solution to a 100 ml one-mark volumetric flask instead of the separating funnel (5.3), dilute to the mark with water and mix well. Transfer a 20 ml aliquot portion of this solution to the separating funnel (5.3).

Add 4,0 ml of nitric acid (4.3) and 10 ml of ammonium molybdate solution (4.6), dilute to the 60 ml mark with water and carry out the extraction procedure specified in 7.3.2.

7.4.2 Spectrometric measurements

Measure the absorbances of the organic phases obtained from the test solution (see 7.4.1) and the blank test solution (see 7.2), following the procedure specified in 7.3.3, after having first adjusted the instrument to zero absorbance against the solvent mixture (4.5).

8 Expression of results

By reference to the calibration graph (see 7.3.4), determine the masses of PO_4^{3-} corresponding to the net absorbances of the test solution and the blank test solution.

The total phosphorus content, expressed as a percentage by mass of PO_4^{3-}, is given by the formula

$$\frac{r_D(m_1 - m_2)}{10^6} \times \frac{100}{m_0} = \frac{m_1 - m_2}{m_0} \times r_D \times 10^{-4}$$

where

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

m_1 is the mass, in micrograms, of PO_4^{3-} corresponding to the absorbance of the test solution (see 7.1);

m_2 is the mass, in micrograms, of PO_4^{3-} corresponding to the absorbance of the blank test solution (see 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 (see 7.4.1).

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

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