

# INTERNATIONAL STANDARD

# ISO 6676

Second edition  
1990-04-01

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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*

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Reference number  
ISO 6676 : 1990 (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 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 6676 was prepared by Technical Committee ISO/TC 175, *Fluorspar*.

This second edition cancels and replaces the first edition (ISO 6676 : 1981), of which it constitutes a technical revision.

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International Organization for Standardization  
Case postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

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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  $\text{PO}_4^{3-}$ , 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 : 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

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 ( $\rho$ approximately 1,38 g/ml).

### 4.4 Methanol ( $\rho$ 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  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$  and 10 g of ammonium amidosulfate  $(\text{NH}_4\text{OSO}_2\text{NH}_2)$  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  $(\text{SnCl}_2\cdot 2\text{H}_2\text{O})$  into a 1 000 ml volumetric flask. Add 200 ml of hydrochloric acid ( $\rho$  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 $\text{PO}_4^{3-}$ per litre.

Dry a little potassium dihydrogen orthophosphate  $(\text{KH}_2\text{PO}_4)$  by heating in the oven (5.1), maintained at  $105\text{ °C} \pm 2\text{ °C}$ , for 2 h. Allow to cool in a desiccator. Weigh, to the nearest 0,2 mg, 0,1433 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  $\mu\text{g}$  of  $\text{PO}_4^{3-}$ .

### 4.9 Phosphorus, standard solution corresponding to 0,010 g of $\text{PO}_4^{3-}$ 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  $\mu\text{g}$  of  $\text{PO}_4^{3-}$ .

## 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**, 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 selector for continuous variation of wavelength**

or

**spectrometer with selector for discontinuous variation of wavelength**, fitted with filters providing maximum transmission at a wavelength of about 710 nm.

**5.5 Optical cells**, of optical path length 1 cm.

## 6 Test sample

Use as the test sample the residue obtained in the determination of the loss in mass at  $105\text{ }^{\circ}\text{C}$  (see ISO 4282).

NOTE — ISO 4282, although specified for acid-grade fluorspar, is equally applicable to ceramic-grade fluorspar.

## 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 all passes through a  $63\text{ }\mu\text{m}$  mesh sieve (see ISO 565). Dry the sieved material for 2 h in the oven (5.1), maintained at  $105\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ , 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  $\text{PO}_4^{3-}$ , 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  $900\text{ }^{\circ}\text{C}$ . 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, 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 $\text{PO}_4^{3-}$ $\mu\text{g}$
0 <sup>*)</sup>	0
2,0	20,0
5,0	50,0
8,0	80,0
11,0	110,0
14,0	140,0
17,0	170,0
20,0	200,0

<sup>\*)</sup> Compensation solution (blank test).

#### 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 blue colour has developed, 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, 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 calibration compensation solution (see table 1) from the absorbance of each of the calibration solutions to give the net absorbance.