# International Standard ISO 6374

G-01-33

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

# Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of phosphorus content — Atomic absorption spectrometric method after extraction

*Cryolithe, naturelle et artificielle, et fluorure d'aluminium à usage industriel — Dosage du phosphore — Méthode par spectrométrie d'absorption atomique après extraction*

**First edition — 1981-10-15**

**UDC 661.862 + 553.634 : 543.422 : 546.18** **Ref. No. ISO 6374-1981 (E)**

**Descriptors :** metal industry, aluminium ores, tests, determination of content, phosphorus, atomic absorption spectroscopic analysis.

ISO 6374-1981 (E)

Price based on 4 pages

COPYRIGHT 2000 International Organization For Standardization
Information Handling Services, 2000

## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

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.

International Standard ISO 6374 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in May 1980.

It has been approved by the member bodies of the following countries :

Australia
Austria
Belgium
Brazil
China
Czechoslovakia
Egypt, Arab Rep. of
France
Germany, F. R.
Hungary
India
Ireland
Italy
Korea, Rep. of
Mexico
Netherlands
Philippines
Poland
Romania
South Africa, Rep. of
Switzerland
United Kingdom
USSR

No member body expressed disapproval of the document.

© **International Organization for Standardization, 1981** ●

Printed in Switzerland

COPYRIGHT 2000 International Organization For Standardization
Information Handling Services, 2000

# Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of phosphorus content — Atomic absorption spectrometric method after extraction

## 1 Scope and field of application

This International Standard specifies an atomic absorption spectrometric method, after extraction, for the determination of the phosphorus content of natural and artificial cryolite and of aluminium fluoride for industrial use.

The method is applicable to products having phosphorus contents, expressed as $P_2O_5$, in the range 5 to 60 mg/kg.

## 2 References

ISO 1619, *Cryolite, natural and artificial — Preparation and storage of test samples.*

ISO 2925, *Aluminium fluoride for industrial use — Preparation and storage of test samples.*

## 3 Principle

Fusion of a test portion with sodium carbonate and boric acid and dissolution in perchloric acid solution. Formation of the ammonium molybdophosphate complex and extraction of the complex with *iso*butyl acetate.

Aspiration of the solution into an acetylene/dinitrogen monoxide flame and determination of the molybdenum, and hence the phosphorus, by measurement of the absorbance of the 379,8 nm line emitted by a molybdenum hollow-cathode lamp.

## 4 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and double-distilled water.

**4.1 Sodium carbonate decahydrate.**

**4.2 Boric acid.**

**4.3 *Iso*butyl acetate** $[CH_3CO_2CH_2CH(CH_3)_2]$.

**4.4 Ammonium molybdate tetrahydrate** $[(NH_4)_6Mo_7O_{24}.4H_2O]$, 10,7 g/l solution.

**4.5 Perchloric acid,** approximately 500 g/l solution.

Dilute 215 ml of perchloric acid, $\varrho$ 1,68 g/ml, approximately 70 % (*m*/*m*) solution, to 500 ml.

**4.6 Perchloric acid,** approximately 200 g/l solution.

Dilute 87 ml of perchloric acid, $\varrho$ 1,68 g/ml, approximately 70 % (*m*/*m*) solution, to 500 ml.

**4.7 Phosphorus,** standard solution corresponding to 1,000 g of P per litre.

Weigh, to the nearest 0,000 1 g, 4,393 6 g of potassium dihydrogenorthophosphate ($KH_2PO_4$) and dissolve in a little water. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 1 mg of P.

**4.8 Phosphorus,** standard solution corresponding to 0,050 g of P per litre.

Place 50,0 ml of the standard phosphorus solution (4.7) in a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 50 µg of P.

Store this solution in a suitable plastics flask.

**4.9 Phosphorus,** standard solution corresponding to 0,002 g of P per litre.

Place 20,0 ml of the standard phosphorus solution (4.8) in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 2 µg of P.

Prepare this solution immediately before use.

## 5 Apparatus

Ordinary laboratory apparatus, and

**5.1 Platinum crucible,** of capacity about 40 ml.

**5.2 Separating funnels,** of capacity 100 ml.

**5.3 Atomic absorption spectrometer,** fitted with a burner fed from cylinders of acetylene and dinitrogen monoxide.

**5.4 Hollow-cathode lamp for molybdenum.**

**5.5 Shaker,** for the separating funnels.

COPYRIGHT 2000 International Organization For Standardization
Information Handling Services, 2000

## 6 Procedure

### 6.1 Test portion

Weigh, to the nearest 0,001 g, about 1 g of the dried test sample, prepared as specified in ISO 1619 for cryolite, or in ISO 2925 for aluminium fluoride.

NOTE — According to the expected phosphorus content of the sample, the mass of the test portion may be increased to about 2 g or reduced, as appropriate.

### 6.2 Preparation of calibration graph

Prepare a calibration graph each time a series of samples is analysed.

#### 6.2.1 Preparation of calibration solutions

**6.2.1.1** Formation of the ammonium molybdophosphate complex

Place the quantities of reagents shown in the table into a series of six of the separating funnels (5.2). When dissolution is complete, treat the solutions (total volume 20 ml) in each of the funnels as follows. Add 10 ml of the ammonium molybdate solution (4.4) and mix. Allow to stand for 15 min so as to ensure that the molybdophosphate complexing reaction is complete.

**6.2.1.2** Extraction of the complex

Add to each separating funnel 20,0 ml of the *iso*butyl acetate (4.3) and, using the shaker (5.5), shake for 5 min. Allow to stand for 10 min and discard the aqueous lower layer. Add 10 ml of the perchloric acid solution (4.6), shake for 5 min and allow to stand for 10 min. Run off and discard the aqueous lower layer.

Use the organic layer for the spectrometric measurements.

NOTES

1 The added sodium carbonate and boric acid are readily soluble in water and perchloric acid solution.

2 The calibration graph is linear in the range 0,1 to 2,0 µg of P per millilitre. Within this range, other calibration solutions, more concentrated than those specified in the table, may be used to facilitate the determination of higher phosphorus contents.

3 The acidity (1,8 to 2,4 mol of $H^+$ per litre), the initial volume (20 ml) of the calibration solutions (6.2.1) and of the aliquot portion of the test solution (6.3.1), have been selected to give maximum and constant absorbances.

4 The solutions may be shaken manually if a mechanical shaker is not available.

5 Take the organic layer from the separating funnel by means of a pipette in order to avoid contact with the inner surface of the funnel outlet on which traces of molybdenum may adhere.

#### 6.2.2 Spectrometric measurements

**6.2.2.1** Adjustment of the apparatus

Fit the hollow-cathode lamp for molybdenum (5.4) to the apparatus (5.3), switch on the current and allow to stabilize. Adjust the instrument to give maximum absorption at a wavelength of about 379,8 nm, and adjust the sensitivity and the slit according to the characteristics of the instrument. Adjust the pressure of the acetylene and the dinitrogen monoxide according to the characteristics of the nebulizer/burner so as to obtain a clear oxidizing flame.

Aspirate the *iso*butyl acetate (4.3) and reset the fuel supply.

**6.2.2.2** Measurements

Aspirate the series of calibration solutions (6.2.1) into the flame and measure the absorbance of each. Take care to keep the aspiration rate constant throughout this series of measurements.

NOTE — The absorbance of the solution for the blank test on the reagents for calibration should not exceed 50 % of that of calibration solution No. 1.

#### 6.2.3 Plotting the graph

Plot a graph having, for example, the masses of P, expressed in micrograms in 20 ml of calibration solution, as abscissae and the corresponding values of the measured absorbance, less the measured value for the solution for the blank test on the reagents for calibration, as ordinates.

| Calibration solution | Sodium carbonate (4.1) | Boric acid (4.2) | Water | Perchloric acid solution (4.5) | Standard phosphorus solution (4.9) | Mass of P in 20 ml |
|---|---|---|---|---|---|---|
| No. | mg | mg | ml | ml | ml | µg |
| 0 * | 360 | 280 | 12 | 8 | 0 | 0 |
| 1 | 360 | 280 | 11 | 8 | 1,00 | 2 |
| 2 | 360 | 280 | 10 | 8 | 2,00 | 4 |
| 3 | 360 | 280 | 9 | 8 | 3,00 | 6 |
| 4 | 360 | 280 | 8 | 8 | 4,00 | 8 |
| 5 | 360 | 280 | 7 | 8 | 5,00 | 10 |

* Blank test on the reagents for the calibration.

COPYRIGHT 2000 International Organization For Standardization
Information Handling Services, 2000

### 6.3 Determination

#### 6.3.1 Preparation of the test solution

Place the test portion (6.1) in the platinum crucible (5.1); add 0,9 g of the sodium carbonate (4.1) and 0,7 g of the boric acid (4.2) and mix with a platinum spatula. Heat the crucible and its contents gently for 5 min over a small flame, gradually increasing it, until the mixture melts, giving a clear molten mass. Allow to cool, add 20 ml of the perchloric acid solution (4.5) to the crucible and heat gently to dissolve the solidified mass. Transfer the solution quantitatively into a 50 ml one-mark volumetric flask and, after cooling to room temperature, dilute to the mark and mix.

Transfer 20,0 ml of this solution to one of the separating funnels (5.2). Add 10 ml of the ammonium molybdate solution (4.4), mix and allow to stand for 15 min.

Continue as specified in 6.2.1.2.

#### 6.3.2 Spectrometric measurements

Following the procedure specified in 6.2.2.2, in order to ensure that the conditions for the calibration, test and blank are as similar as possible, especially with respect to the rate of aspiration, determine, in the given order, the absorbances of

a) one of the calibration solutions (6.2.1);

b) the test solution (6.3.1);

c) the blank test solution (6.4).

### 6.4 Blank test

Carry out a blank test at the same time as the determination and following the same procedure, using the same quantities of all the reagents as for the determination, but omitting the test portion (6.1).

## 7 Expression of results

From the calibration graph (6.2.3), determine the masses of P corresponding to the values of the measured absorbances of the test solution and the blank test solution.

The phosphorus content, expressed in milligrams of $P_2O_5$ per kilogram, is given by the formula

$$\frac{m_1 - m_2}{1\,000} \times \frac{50}{20} \times \frac{1\,000}{m_0} \times 2{,}29$$

$$= 5{,}725 \times \frac{(m_1 - m_2)}{m_0}$$

where

$m_0$ is the mass, in grams, of the test portion (6.1);

$m_1$ is the mass, in micrograms, of P found in the test solution (6.3.1);

$m_2$ is the mass, in micrograms, of P found in the blank test solution (6.4);

2,29 is the factor for conversion from P to $P_2O_5$.

## 8 Test report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

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.

COPYRIGHT 2000 International Organization For Standardization
Information Handling Services, 2000

# Annex

## ISO publications relating to cryolite, natural and artificial, and aluminium fluoride for industrial use

### Cryolite, natural and artificial

ISO 1619 — Preparation and storage of test samples.

ISO 1620 — Determination of silica content — Reduced molybdosilicate spectrophotometric method.

ISO 1693 — Determination of fluorine content — Modified Willard-Winter method.

ISO 1694 — Determination of iron content — 1,10-Phenanthroline photometric method.

ISO 2366 — Determination of sodium content — Flame emission and atomic absorption spectrophotometric methods.

ISO 2367 — Determination of aluminium content — 8-Hydroxyquinoline gravimetric method.

ISO 2830 — Determination of aluminium content — Atomic absorption method.

ISO 3391 — Determination of calcium content — Flame atomic absorption method.

ISO 3392 — Determination of water content — Electrometric method.

ISO 3393 — Determination of moisture content — Gravimetric method.

ISO 4277 — Evaluation of free fluorides content — Conventional titrimetric method.

ISO 4280 — Determination of sulphates content — Barium sulphate gravimetric method.

ISO 5930 — Determination of phosphorus content — Reduced molybdophosphate photometric method.

ISO 5938 — Determination of sulphur content — X-ray fluorescence spectrometric method.

ISO 6374 — Determination of phosphorus content — Atomic absorption spectrometric method after extraction.

### Aluminium fluoride for industrial use

ISO 2362 — Determination of fluorine content — Modified Willard-Winter method.

ISO 2368 — Determination of iron content — 1,10-Phenanthroline photometric method.

ISO 2369 — Determination of silica content — Spectrophotometric method using the reduced silicomolybdic complex.

ISO 2925 — Preparation and storage of test samples.

ISO 3392 — Determination of water content — Electrometric method.

ISO 3393 — Determination of moisture content — Gravimetric method.

ISO 4279 — Determination of sodium content — Flame emission spectrophotometric method.

ISO 4280 — Determination of sulphates content — Barium sulphate gravimetric method.

ISO 5930 — Determination of phosphorus content — Reduced molybdophosphate photometric method.

ISO 5938 — Determination of sulphur content — X-ray fluorescence spectrometric method.

ISO 6374 — Determination of phosphorus content — Atomic absorption spectrometric method after extraction.

COPYRIGHT 2000 International Organization For Standardization
Information Handling Services, 2000