International Standard 5938

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

Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of sulphur content — X-ray fluorescence spectrometric method

Cryolithe, naturelle et artificielle, et fluorure d'aluminium à usage industriel — Dosage du soufre — Méthode par spectrométrie de fluorescence X

First edition — 1979-07-15

UDC 553.634 + 661.862.36 : 543.845

Ref. No. ISO 5938-1979 (E)

Descriptors : cryolite, aluminium fluoride, chemical analysis, determination of content, sulphur, X-ray analysis, spectrophotometric analysis, atomic fluorescence spectrometry.

Price based on 4 pages

Foreword

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International Standard 5938 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in September 1977.

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

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The member body of the following country expressed disapproval of the document on technical grounds :

United Kingdom

Printed in Switzerland

Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of sulphur content — X-ray fluorescence spectrometric method

1 Scope

This International Standard specifies an X-ray fluorescence spectrometric method for the determination of the sulphur content of natural and artificial cryolite and of aluminium fluoride for industrial use.

2 Field of application

The method is applicable to products having sulphur contents, expressed as SO_4^{2-}, between 0,01 and 2 % (*m/m*).

3 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.*

4 Principle

Preparation of tablets from a mixture of the test portion and a binder. Measurement of the intensity of the K_α line emitted by the sulphur at a wavelength of 0,537 3 nm by means of a vacuum X-ray fluorescence spectrometer fitted with a tube having a rhodium, chromium or tungsten anticathode.

Comparison of the measured intensity with the intensity of emission of standard tablets of known SO_4^{2-} content.

5 Reagents

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

5.1 Binder.

Crystalline cellulose for use in chromatography, or other equivalent binder.

5.2 Aluminium fluoride.

Use either :

a) very pure (96,4 %) aluminium fluoride, containing only traces of SO_4^{2-}; or

b) the sublimate obtained by subliming technical grade aluminium fluoride in the electric vacuum furnace (6.4), controlled at 860 ± 20 °C, under a vacuum of 0,01 to 0,1 Pa*.

5.3 Sodium fluoride, prepared by calcination, at about 600 °C, of sodium fluoride obtained by crystallization from an aqueous solution.

5.4 Cryolite, prepared by fusing, in the nickel crucible (6.1), a stoichiometric mixture of the aluminium fluoride (5.2) and the sodium fluoride (5.3), in the electric furnace (6.3), controlled at 1 000 ± 20 °C, for 2 h.

In order to prevent evaporation of fluorides during fusion, place the nickel crucible in the iron container (6.2), and close the latter hermetically with its lid.

5.5 Acetone.

5.6 Sodium sulphate, anhydrous.

5.7 Sodium sulphate, standard solution corresponding to 20,0 g of Na_2SO_4 per litre.

Weigh, to the nearest 0,000 1 g, 20,0 g of the anhydrous sodium sulphate (5.5) and dissolve in 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 20,0 mg of Na_2SO_4, corresponding to 0,013 52 g of SO_4^{2-}.

5.8 Sodium sulphate, standard solution corresponding to 100,0 g of Na_2SO_4 per litre.

* 1 Pa = 1 N/m^2 = 10 µbar;

133 Pa ≈ 1 torr

Weigh, to nearest 0,001 g, 100,0 g of the anhydrous sodium sulphate (5.5) and dissolve in 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 100,0 mg of Na_2SO_4, corresponding to 0,067 6 g of SO_4^{2-}.

6 Apparatus

Ordinary laboratory apparatus and

6.1 Nickel crucible.

6.2 Iron container, having a threaded lid with which it may be hermetically sealed, and capable of containing the crucible (6.1).

6.3 Electric furnace, capable of being controlled at 1 000 ± 20 °C.

6.4 Electric vacuum furnace, capable of being controlled at 860 ± 20 °C.

6.5 Laboratory mixer.

6.6 Grinder, capable of grinding the powders used for tablet preparation to a particle size smaller than 20 µm.

6.7 Press, for preparing tablets of thickness at least 8 mm and diameter 40 mm.

6.8 Electric oven, capable of being controlled at 110 ± 5 °C.

6.9 Vacuum X-ray fluorescence spectrometer, fitted with a tube having a rhodium, chromium or tungsten anticathode, a sodium chloride or pentaerythritol crystal analyser, a physical pulse height analyser and a proportional gas flow detector.

7 Procedure

7.1 Test portion

Weigh, to the nearest 0,10 g, 15 g of the dried test sample, prepared as specified in ISO 1619 for cryolite, or in ISO 2925 for aluminium fluoride.

7.2 Grinding and preparation of tablets

Carefully mix the binder (5.1) with the test portion (7.1) in the proportion of 1,5 g of binder to 5 g of cryolite or aluminium fluoride, using the mixer (6.5) in order to obtain a homogeneous mixture. Add 10 to 15 drops of the acetone (5.5) to prevent compacting of the product and grind for 1 min in the grinder (6.6). Then press the powder into tablets using the press (6.7) for 15 s at 250 MPa.*

7.3 Calibration

7.3.1 Preparation of the standard tablets

Into a series of seven watch-glasses of suitable size, place 20 g of the ground aluminium fluoride (5.2) or cryolite (5.4). Add the volumes of the standard sodium sulphate solution (5.7 or 5.8) specified in table 1.

Table 1

Standard sodium sulphate solution	Volume added	Corresponding mass of SO_4^{2-}	Corresponding SO_4^{2-} content
	ml	g	% (*m*/*m*)
5.7	0	0	0
	0,5	0,006 76	0,033 8
	1,0	0,013 52	0,067 6
	1,5	0,020 28	0,101 4
5.8	0,5	0,033 80	0,169 0
	1,0	0,067 60	0,338 0
	1,5	0,101 40	0,507 0

Add the standard solution, drop by drop, onto the centre of the surface of the powder, taking care not to wet the surface of the glass. Dry for about 12 h in the electric oven (6.8), controlled at 110 ± 5 °C. Allow to cool in a desiccator. Mix each powder carefully in an agate mortar.

Prepare tablets by the procedure specified in 7.2, using 15 g of powder from each dried and mixed standard.

NOTE — In the special case of aluminium fluoride having a high SO_4^{2-} content, the sodium sulphate may be added directly in the form of the solid sodium sulphate (5.6).

7.3.2 Spectrometric measurements

Switch on the current to the apparatus (6.9) and allow to stabilize. Adjust the current according to the type of anticathode (see table 2). Place the standard tablets in position

* 1 MPa = 10^6 N/m^2

and adjust the vacuum to a value equal to or less than 1,33 Pa. Then, under the operating conditions specified, for example, in table 2, measure the intensity of the sulphur K_α line emitted for each standard tablet.

Table 2

Characteristic or element of apparatus	Specification
Tube voltage	50 kV[1)]
Current :	
— rhodium anticathode	40 mA[1)]
— tungsten anticathode	50 mA[1)]
— chromium anticathode	20 mA[1)]
Vacuum	⩽ 1,33 Pa
Sulphur K_α wavelength	0,537 3 nm
Analyser	NaCl or pentaerythritol crystal
Detector	Proportional gas type

1) These are typical conditions, but account must be taken of the characteristics of the instrument in establishing the exact operating conditions. These shall be such as to give a statistically acceptable count, for example 100 000. If the pulse height analyser does not have an automatic setting, it is important to adjust it to give best discrimination from background radiation.

7.3.3 Plotting the graph

Plot a graph having, for example, the intensities (number of pulses per second) of the K_α line emitted by the sulphur present in the standards as ordinates, and the corresponding sulphur contents, expressed directly as percentages by mass of SO_4^{2-}, as abscissae.

NOTE — For high concentrations of sulphur, it is recommended that the ordinate be expressed as the ratio of the measured intensity to the measured intensity of one of the standards, so as eliminate errors caused by day-to-day variations in the instrument. This is particularly necessary for older types of instruments.

7.4 Determination

Carry out the measurement on the test portion (7.1), crushed and pressed into a tablet as specified in 7.2, by placing the tablet in the apparatus (6.9) and following the procedure specified in 7.3.2.

7.5 Blank test

The blank test corresponds to the zero term used for the calibration.

8 Expression of results

By means of the calibration graph (7.3.3), determine the percentage by means of SO_4^{2-} corresponding to the intensity of the K_α line emitted by the sulphur present in the test portion, taking into account the value of the blank test.

9 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.

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.

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.