TECHNICAL REPORT

ISO/TR 4277

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Cryolite, natural and artificial — Conventional test for evaluation of free fluorides content

Cryolithe, naturelle et artificielle — Essai conventionnel pour l'évaluation de la teneur en fluorures libres

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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The main task of technical committees is to prepare International Standards. 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.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 4277 was prepared by Technical Committee ISO/TC 226, *Materials for the production of primary aluminium*.

This first edition cancels and replaces ISO 4277:1977, of which it constitutes a minor revision.

Introduction

This Technical Report was published in order to retain the method specified in ISO 4277:1977 in a publicly available standard.

ISO 4277:1977 was withdrawn in 2004.

Cryolite, natural and artificial — Conventional test for evaluation of free fluorides content

1 Scope

This Technical Report describes a conventional test for the evaluation of the free fluorides content of natural, artificial and recovered cryolite.

This method is applicable to products having free fluorides content greater than 0,15 % (mass fraction) of AlF_3 or 0,4 % (mass fraction) of NaF.

2 Principle

A test portion is sintered with a known quantity of sodium fluoride at 790 ± 20 °C for 20 minutes. Under these conditions, aluminium fluoride in excess of that required for the stoichiometric formula $AlF_3 \cdot 3NaF$ reacts with some of the sodium fluoride to form cryolite.

The ground sintered mass is extracted with boiling water and the solution is acidified with hydrochloric acid solution to a pH less than 3,7, followed by titration of the excess sodium fluoride with standard volumetric thorium nitrate solution in the presence of alizarin-S as indicator.

3 Reagents

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

3.1 Sodium fluoride, anhydrous, dried at about 120 °C to constant mass in a platinum crucible and cooled in a desiccator.

3.2 Gelatine, 3 % freshly prepared solution.

3.3 Hydrochloric acid, approximately 0,1 N solution.

3.4 Sodium fluoride, 4,20 g/l standard solution (corresponding to 0,1 N).

Weigh, to the nearest 0,001 g, 4,20 g of the sodium fluoride (3.1). Transfer quantitatively to a 1 000 ml one-mark volumetric flask containing a little water and, after dissolution, dilute to the mark and mix. Transfer the solution to a suitable plastics bottle.

1 ml of this solution contains 4,20 mg of NaF.

3.5 Thorium nitrate, 0,1 N standard volumetric solution.

Weigh, to the nearest 0,001 g, 13,805 g of thorium nitrate tetrahydrate $[Th(NO_3)_4 \cdot 4H_2O]$, transfer quantitatively to a 1 000 ml one-mark volumetric flask, dissolve in water, dilute to the mark and mix.

3.6 Buffer solution, pH 2,7.

Neutralize a 9,5 % (mass fraction) solution of monochloroacetic acid (CH_2Cl-COOH) with an approximately 10 N sodium hydroxide solution, in the presence of phenolphthalein. Add 50 ml of this solution to 50 ml of the same monochloroacetic acid solution and mix.

3.7 Alizarin-S (sodium alizarinsulfonate), 0,5 g/l solution.

4 Apparatus

Ordinary laboratory apparatus and in particular the following.

4.1 Platinum crucible, diameter approximately 40 mm, height approximately 30 mm.

4.2 Electric furnace, capable of being controlled at 790 ± 20 °C.

5 Procedure

5.1 Test portion

Weigh, to the nearest 0,001 g, 4 g of the dried sample (see ISO 1619:1976, 3.3).

5.2 Preparation of the calibration graph

5.2.1 Preparation of the standard matching solutions

Into a series of seven 100 ml conical plastics flasks, place the volumes of the standard sodium fluoride solution (3.4) shown in the following table.

Table 1 — Volumes of standard sodium fluoride solution

Standard sodium fluoride solution (3.4) ml	**Corresponding mass of NaF** mg
0	0
1,0	4,20
3,0	12,60
5,0	21,00
7,0	29,40
9,0	37,80
10,0	42,00

5.2.2 Titration

Add to each conical flask 40 ml of water, 5 ml of the buffer solution (3.6), 1 ml of the alizarin-S solution (3.7) and 10 ml of the gelatine solution (3.2). Titrate with the standard volumetric thorium nitrate solution (3.5) until the colour of the indicator changes to pink.

5.2.3 Plotting of the calibration graph

Plot a graph having, for example, the masses, in milligrams, of sodium fluoride contained in the standard matching solutions (5.2.1) as abscissa and the volumes, in millilitres, of the standard volumetric thorium nitrate solution (3.5) used for the titrations as ordinates.

In the range of concentrations of sodium fluoride considered, the calibration graph is a straight line, whose ordinate at the origin corresponds approximately to 0,1 ml of the standard volumetric thorium nitrate solution.

5.3 Determination

5.3.1 Preparation of the test solution

Weigh, to the nearest 0,001 g, in the platinum crucible (4.1), 0,800 g of the sodium fluoride (3.1). Add the test portion (5.1) and mix carefully with a small platinum spatula. Place the crucible in the electric furnace (4.2), controlled at 790 ± 20 °C, and maintain at this temperature for 20 min. Remove the crucible from the furnace and allow to cool. Transfer the cooled sintered mass to a small, lipped mortar and grind in the presence of a few millilitres of water. Transfer quantitatively to a beaker of suitable capacity, rinse the crucible and the mortar with a few millilitres of water and add the washings to the beaker. Make up to about 100 ml with water and boil for 1 min. Allow to cool, transfer quantitatively to a 200 ml one-mark volumetric flask, dilute to the mark with water, mix and allow to settle until the supernatant liquid is clear.

5.3.2 Titration

Take 10,0 ml of the clear test solution (5.3.1), place in a 100 ml conical flask and dilute to approximately 40 ml. Add 1 ml of the alizarin-S solution (3.7) and add, from a burette, the hydrochloric acid solution (3.3) until the colour of the indicator changes to yellow. Finally, add 5 ml of the buffer solution (3.6) and 10 ml of the gelatine solution (3.2).

Titrate with the standard volumetric thorium nitrate solution (3.5) until the colour of the indicator changes to a pink identical to that obtained in the calibration (5.2.2).

Read from the calibration graph (5.2.3) the corresponding mass, m_1, of sodium fluoride.

6 Expression of results

The total mass, m_2, in grams, of NaF present in the test solution (5.3.1) is given by the equation

$$m_2 = m_1 \times \frac{1}{1\,000} \times \frac{200}{10}$$

where m_1 is the mass, in milligrams, of NaF found in 10 ml of the test solution (5.3.1) by means of the procedure described in 5.3.2.

If m_2 is greater than 0,800 g, the sample contains free NaF, the content of which, expressed as a percentage by mass, is given by the formula

$$\frac{(m_2 - 0{,}800) \times 100}{m_0}$$

where m_0 is the mass, in grams, of the test portion (5.1).

If m_2 is less than 0,800 g, the sample contains free AlF_3, the content of which, expressed as a percentage by mass, is given by the formula

$$\frac{(0{,}800 - m_2) \times 100}{m_0 \times 1{,}5}$$

where

m_0 is the mass, in grams, of the test portion (5.1);

1,5 is the ratio of three times the relative molar mass of NaF to the relative molar mass of AlF_3 [i.e. $(3 \times 42)/84$] which is the relative molar mass in cryolite.

7 Assessment of results and modified procedure to accommodate special samples

7.1 It is essential that m_2 be greater than 0,15 g for the reaction to go to completion. If m_2 is less than or equal to 0,15 g, repeat the analysis, using a smaller test portion or increasing the amount of the sodium fluoride (3.1) added.

7.2 If the mass m of sodium fluoride to be titrated in 5.3.2 exceeds that which can be accurately read from the calibration graph, carry out the titration with the volume of the test solution (5.3.1) reduced from 10,0 ml to 5,0 ml. Under these conditions, m_2 is given by the equation

$$m_2 = m_1 \times \frac{1}{1\,000} \times \frac{200}{5}$$

8 Test report

The test report shall include at least the following information:

a) a reference to this Technical Report;

b) the date on which the sample was taken;

c) the date of the determinations and calculations;

d) details necessary for the complete identification of the material tested;

e) the results and the method of expression used;

f) any unusual features noted during the determination;

g) any operation not included in this Technical Report or in ISO 1619:1976 to which reference is made, or regarded as optional.

Bibliography

NOTE ISO 4277:1977 contained a Bibliography similar to the following that was relevant in 1977; most of the methods are now out of date and of little use, except for ISO 1619 and ISO 5938.

[1] ISO 1619:1976, *Cryolite, natural and artificial — Preparation and storage of test samples*

[2] ISO 1620:1976, *Cryolite, natural and artificial — Determination of silica content — Reduced molybdosilicate spectrophotometric method*

[3] ISO 1693:1976, *Cryolite, natural and artificial — Determination of fluorine content — Modified Willard-Winter method*

[4] ISO 1694:1976, *Cryolite, natural and artificial — Determination of iron content — 1,10-Phenanthroline photometric method*

[5] ISO 2366:1974, *Cryolite, natural and artificial — Determination of sodium content — Flame emission and atomic absorption spectrophotometric methods*

[6] ISO 2367:1972, *Cryolite (natural and artificial) — Determination of aluminium content — 8-Hydroxyquinoline gravimetric method*

[7] ISO 2830:1973, *Cryolite, natural and artificial — Determination of aluminium content — Atomic absorption method*

[8] ISO 3391:1976, *Cryolite, natural and artificial — Determination of calcium content — Flame atomic absorption method*

[9] ISO 3392:1976, *Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of water content — Electrometric method* (withdrawn)

[10] ISO 3393:1976, *Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of moisture content — Gravimetric method*

[11] ISO 3429:1976, *Sodium fluoride primarily used for the production of aluminium — Determination of iron content — 1,10-Phenanthroline photometric method*

[12] ISO 3430:1976, *Sodium fluoride primarily used for the production of aluminium — Determination of silica content — Reduced molybdosilicate spectrophotometric method*

[13] ISO 3431:1976, *Sodium fluoride primarily used for the production of aluminium — Determination of soluble sulphates content — Turbidimetric method*

[14] ISO 3566:1976, *Sodium fluoride primarily used for the production of aluminium — Determination of chlorides content — Turbidimetric method*

[15] ISO 3699:1976, *Anhydrous hydrogen fluoride for industrial use — Determination of water content — Karl Fischer method*

[16] ISO 4277:1977, *Cryolite, natural and artificial — Conventional test for evaluation of free fluorides content* (withdrawn)

[17] ISO 4280:1977, *Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of sulphate content — Barium sulphate gravimetric method*

[18] ISO 5930:1979, *Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of phosphorus content — Reduced molybdophosphate photometric method*