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Cryolite primarily used for the production of aluminium — Determination of elements — Wavelength-dispersive X-ray fluorescence spectrometric method using pressed powder tablets

Cryolithe principalement utilisée pour la production de l'aluminium — Dosage des éléments — Méthode par spectrométrie de fluorescence des rayons X à dispersion de longueur d'onde utilisant des pastilles de poudre pressée

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

In the production of aluminium, cryolite is used as a flux in order to lower the melting points of aluminium smelting baths and increase the conductivity of the electrolyte. This use is critical during the start-up and normal operation stages of electrolysis cells.

Cryolite primarily used for the production of aluminium — Determination of elements — Wavelength-dispersive X-ray fluorescence spectrometric method using pressed powder tablets

1 Scope

This document specifies a wavelength-dispersive X-ray fluorescence spectrometric (XRF) method for the determination of cryolite (Na_3AlF_6) from the content of fluorine to the content of trace elements. The calibration reference materials are not specified in this method.

The method is applicable to cryolite, which is primarily used for the production of aluminium. Annex A provides conversion factors for converting elements to compounds. The validity and precision of test results for concentrations outside these ranges has not been determined.

The concentration range of fluorine (given as F) is from 510 g/kg to 560 g/kg. The concentration range of aluminium (given as Al) is from 120 g/kg to 150 g/kg. The concentration range of sodium (given as Na) is from 270 g/kg to 330 g/kg. The concentration range of silicon (given as SiO_2) is from the lowest limit of detection (LLD) to 4,0 g/kg. The concentration range of iron (given as Fe_2O_3) is from LLD to 0,37 g/kg. The concentration range of sulfur (given as SO_4) is from LLD to 5,0 g/kg. The concentration range of phosphorus (given as P_2O_5) is from LLD to 0,40 g/kg. The concentration range of calcium (given as CaO) is from LLD to 0,80 g/kg.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

A representative sample of cryolite is milled. A test portion is packed and pressed on a powder tablet press to make the test tablets.

The test tablets are analysed on an X-ray fluorescence spectrometer instrument that has been calibrated using a series of cryolite reference materials covering the required concentration range of the elements to be determined.

5 Reagents and materials

5.1 Acetone or **ethyl alcohol,** analytical pure, used as dispersing agent.

5.2 Boric acid, analytical pure.

6 Apparatus

6.1 Wavelength-dispersive X-ray fluorescence spectrometer (XRF), with vacuum path and equipped with crystals required as shown in Table 1.

6.2 Vibratory disc mill, with tray, ring and puck made of non-contaminating material. Tungsten-carbide and chrome steel have been found to be satisfactory.

6.3 Tablet press, capable of providing 340 kN for 20 s.

6.4 Balance, with precision ±0,01 g.

6.5 Flat spatula.

7 Test procedure

7.1 Test specimen preparation

See ISO 1619 for guidance.

7.2 Test tablet preparation

7.2.1 Dry the sample to constant mass at (110 ± 2) °C. A typical drying time is 2 h.

7.2.2 Weigh 10,0 g of sample and put it into the mill. Then add 10 drops of acetone or ethyl alcohol and vibrate for 60 s to make the particle size below 45 µm fineness.

7.2.3 Transfer 2,0 g of milled sample to the tablet press, use boric acid backing to prepare the pressed tablet with a pressure of 340 kN and hold for 20 s. Tablet thickness should be a minimum of 4 mm, with a diameter of 40 mm.

7.2.4 Remove the tablets from the tablet press. Touch the edge of the tablets only during measurement. Trim the edges. Avoid polluting the surface during X-ray measurement.

Always use the same mass and proportion of sample and reagents as for the calibration reference materials.

Results are particle-size dependent. Short milling times give larger spread in intralaboratory precision. The particle size should be determined by using a suitable sieving technique. Erroneous data will be collected if analytical samples contain particles varying significantly in size that cause different beam penetration depth and a different surface roughness from those in the calibration reference samples.

The surface of the pressed powder tablet should be smooth and firm and should not drop out power after trimming. The measuring surface should not be mixed with boric acid.

7.3 X-ray fluorescence spectrometer application

7.3.1 Instrumental conditions

Follow the control setting and operation instructions of the spectrometer manufacturer, including monitoring and calibrating angles and monitoring and correcting for X-ray tube intensity.

Suggested conditions of measurement are given in Table 1. All measurements shall be made under vacuum. The Kα analytical lines are preferred. Use spectral lines overlap correction if required. Correct for background, using the lines recommended in Table 1.

Table 1 — Measurement lines and suggested conditions of measurement

Element	Crystal	Angle °2θ	Counter	Time for peak s	Time for background s	Collimator °	Voltage kV	Current mA
Fluorine	XS-55	38,694	Flow	60	30 % of time for peak	0,46	27	111
Aluminium	PET	144,584	Flow	30	30 % of time for peak	0,46	27	60
Sodium	XS-55	24,962	Flow	60	30 % of time for peak	0,46	27	80
Silicon	PET	108,985	Flow	10	30 % of time for peak	0,46	27	111
Iron	LiF200	57,556	Scintilla-tion	2	30 % of time for peak	0,46	60	50
Sulfur	PET	75,73	Flow	10	30 % of time for peak	0,46	27	111
Phosphorus	Ge	141,009	Flow	10	30 % of time for peak	0,46	27	111
Calcium	LiF200	113,135	Flow	2	30 % of time for peak	0,46	50	60

7.3.2 Calibration and calibration reference materials

The calibration reference materials are not specified in this method. The user of this document shall obtain suitable calibration reference materials, such as the China National Set GSB 04-2016-2006 series GFC01 to GFC06 for F, Al, Na, SiO_2, Fe_2O_3, SO_4, P_2O_5, CaO.[1)]

The X-ray fluorescence spectrometer application software is used to make a cryolite application on the XRF instrument and the set of calibration reference materials are analysed. Elemental concentrations in the calibration samples shall bracket the values expected in the analytical samples. The number of calibration reference materials shall be six or more for each element. If six are not available, the number used shall be included in the test report.

Calibration is performed using the XRF instrument control software for application development and is not detailed in this document. If necessary, the instrument manufacturer should be consulted for recommendations on optimal tube anodes, crystal options and any concentration limit restrictions.

7.3.3 Verification of the calibration

Reference sample tablets can be used daily for checking the instrument condition. Limits for acceptable deviation shall be established by the laboratory; if the deviation is unacceptable, the instrument shall be reviewed and, if necessary, recalibrated.

7.4 Monitoring of the sample for correction of instrumental drift

Instrumental drift correction shall be performed regularly in accordance with the instrument manufacturer's instructions to ensure that measured intensities are corrected for any spectrometer

1) The China National Set GSB 04-2016-2006 series GFC01 to GFC06 for F, Al, Na, SiO_2, Fe_2O_3, SO_4, P_2O_5, CaO is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

drift. If monitor samples are measured infrequently, then each batch of analysed samples shall be drift corrected.

7.5 Analyses, calculation and expression of results

The analysis shall be run on three tablets made from the same test portion. The triplicate measurements are averaged to give the concentration to be used in the test report.

However, for any element, if any two results differ by more than twice the intralaboratory repeatability for that element as shown in Table 2, the analysis should be repeated.

8 Precision

8.1 General

The precision given in Table 2 was computed using ASTM E691. For details of the computation of the precision see References [3] and [4]. Annex B provides an example of how to use Table 2.

Table 2 — Precision for elements in cryolite based on average of triplicate measurements

Element	Range	Repeatability	Repeatability standard deviation	Decimals[a]	Reproducibility	Reproducibility standard deviation	Decimals[a]
		r	s_r	D_r	R	s_R	D_R
Fluorine	510 to 560	3	1,1	0	8	2,9	0
Aluminium	120 to 150	1	0,4	0	4	1,6	0
Sodium	270 to 330	3	0,9	0	12	4,4	0
Silicon	LLD to 4,0	0,1	0,03	1	0,3	0,09	1
Iron	LLD to 0,37	0,02	0,007	2	0,03	0,010	2
Sulfur	LLD to 5,0	0,2	0,21	1	0,4	0,14	1
Phosphorus	LLD to 0,40	0,02	0,007	2	0,03	0,010	2
Calcium	LLD to 0,80	0,1	0,02	1	0,3	0,09	1

[a] D_r and D_R are the recommended number of decimals.

8.2 Repeatability

The maximum permissible difference due to test error between two test results obtained by one operator on the same material using the same test method and the same test instrument is given by the repeatability limit (r). The 95 % interval is given in Table 2.

Two test results that do not differ by more than the repeatability limit (r) will be considered to be from the same population; conversely, two test results that differ by more than the repeatability limit (r) will be considered to be from different populations.

More than two test results for which the standard deviation does not differ by more than 1,96 (s_r) (from Table 2) will be considered to be from the same population; conversely, more than two test results for which the standard deviation differs by more than 1,96 (s_r) (from Table 2) will be considered to be from different populations.

8.3 Reproducibility

The maximum permissible difference due to test error between two test results obtained by two operators in different laboratories on the same material using the same test method is given by the reproducibility limit (R). The 95 % interval is given in Table 2.

Two test results that do not differ by more than the reproducibility limit (R) will be considered to be from the same population; conversely, two test results that differ by more than the reproducibility limit (R) will be considered to be from different populations.

More than two laboratories for which the standard deviation does not differ by more than 1,96 (s_R) (from Table 2) will be considered to be from the same population; conversely, more than two laboratories for which the standard deviation differs by more than 1,96 (s_R) (from Table 2) will be considered to be from different populations.

9 Test report

At least the following information shall be included in the test report:

a) identification of the sample;

b) a reference to this document;

c) when the results are from the same population, the arithmetic average with mass per cent unit is taken as the result of the determination;

d) any unusual features noted during the determination;

e) any operation on the sample or test portion or test tablets that is optional, or is not included in this document or in other ISO documents to which reference is made;

f) the date of the test.

Annex A
(informative)

Conversion table

Table A.1 — Conversion table

Element	Atomic mass g/mol	Compound	Molar mass g/mol	Conversion factor
Si	28,085	SiO_2	60,083	2,139
Fe	55,845	Fe_2O_3	159,687	1,430
S	32,06	SO_4	96,056	2,996
P	30,974	P_2O_5	141,943	2,291
Ca	40,078	CaO	56,077	1,399