
**Aluminium fluoride for industrial
use — Determination of trace
elements — Wavelength dispersive
X-ray fluorescence spectrometric
method using pressed powder tablets**

*Fluorure d'aluminium à usage industriel — Détermination d'éléments
traces — Méthode par spectrométrie de fluorescence des rayons X à
dispersion de longueur d'onde utilisant des pastilles de poudre pressée*





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Published in Switzerland

Contents

| | Page |
|---|-----------|
| Foreword | iv |
| Introduction | v |
| 1 Scope | 1 |
| 2 Normative references | 1 |
| 3 Principle | 1 |
| 4 Reagents and materials | 2 |
| 5 Apparatus | 2 |
| 6 Test procedure | 3 |
| 6.1 Test specimen preparation | 3 |
| 6.2 Addition of binder method | 3 |
| 6.3 Backing method | 4 |
| 6.4 X-ray fluorescence spectrometer application | 4 |
| 6.5 Monitor sample for correction of instrumental drift | 6 |
| 6.6 Analysis, calculation and expression of results | 6 |
| 7 Precision | 6 |
| 7.1 General | 6 |
| 7.2 How to use Table 4 using sodium (Na) as an example | 7 |
| 7.3 How to use Table 4 using sulfur (S) as an example | 7 |
| 8 Test report | 8 |
| Annex A (informative) Conversion table | 9 |
| Bibliography | 10 |

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

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.

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 12926 was prepared by Technical Committee ISO/TC 226, *Materials for the production of primary aluminium*.

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Introduction

Aluminium fluoride is used as an electrolyte additive to the aluminium smelting bath to regulate the acidity, or excess aluminium fluoride, level of the electrolyte. This use is critical in the operation of all electrolysis cells used for the production of aluminium. Aluminium fluoride is also used in the cast house as an additive to metal in crucibles in the Treatment of Aluminium in a Crucible process (TAC).

Aluminium fluoride for industrial use — Determination of trace elements — Wavelength dispersive X-ray fluorescence spectrometric method using pressed powder tablets

1 Scope

This International Standard describes an X-ray fluorescence spectrometric (XRF) method for the determination of aluminium fluoride (AlF₃) from the content of fluorine and the content of trace elements in the test specimen. The method does not determine the oxygen content. The calibration reference materials are not specified in this method.

The method is applicable to industrial-grade aluminium fluoride where the concentration range for aluminium fluoride and each trace element is within the concentration range given in Table 1. The validity and precision of test results for concentrations outside these ranges has not been determined (see Note).

Table 1 — Concentration range for aluminium fluoride (from fluorine) and trace elements

| Compound or element | Symbol | Concentration range mass % |
|---------------------|------------------|-------------------------------|
| Aluminium fluoride | AlF ₃ | 86,5 to 95,75 |
| Sodium | Na | 0,05 to 0,25 |
| Silicon | Si | 0,001 to 0,14 |
| Phosphorus | P | 0,001 to 0,02 |
| Sulfur | S | 0,01 to 0,6 |
| Calcium | Ca | 0,001 to 0,10 |
| Iron | Fe | 0,005 to 0,05 |

NOTE The determination of fluorine has an uncertainty due to mineralogical variation among origins of aluminium fluoride. Batches from different origins with the same fluorine contents can give different intensities when determined by this method and pressed tablet preparation does not eliminate this problem. An AlF₃ sample of unusual mineralogical origin should be tested with an absolute method to verify that, when using this test method, the fluorine concentration range reported is valid.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

3 Principle

A representative sample of aluminium fluoride 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 aluminium fluoride reference materials covering the required concentration range of the elements to be determined.

4 Reagents and materials

4.1 **Lithium tetraborate backing**, analytical pure lithium tetraborate.

4.2 **Acetone**, analytical pure.

4.3 **Aluminium tablet dish**, of diameter suitable for the tablet press (5.3) and tapered to hold pressed pellets.

4.4 **Mylar film**, for keeping the test portion separate from press surfaces.

4.5 **Binding agent**, suitable for sample preparation. The following are some examples of materials that have been found satisfactory:

- polyethylene binder, PE-160, PE-190
- mill and press additive, HMPA40 - Herzog mill and press additive¹⁾
- XRF Multi-Mix RXR-250, Premier Lab Supply²⁾
- Retsch - Licowax C micropowder binder (formerly known as Hoechst Wax or Hoechst LICO wax C Micropowder³⁾
- wax, Clairiant Licowax PE-190⁴⁾
- mixture, 9:1 of BASF styrene EMU 120 FD⁵⁾ to Hoechst Ceridust 9615A Wax.

4.6 **Cleaning agent**, if required. Dupont Vertrel XF (MS-782)⁶⁾ has been found suitable.

5 Apparatus

5.1 **Wavelength dispersive X-ray fluorescence spectrometer**, with vacuum path and equipped with crystals required as shown in Table 3.

1) HMPA40 - Herzog mill and press additive is the trade name of a product supplied by Hertzog Automation Corporation www.hertzogautomation.com This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

2) XRF Multi-Mix RXR-250 is the trade name of a product supplied by Premier Lab Supply. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

3) Licowax C micropowder (formerly Hoechst wax) is the trade name of a product supplied by Retsch, Socachim, Spectro. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

4) Clairiant Licowax PE-190 is the trade name of a product supplied by Clariant Ltd www.clariant.com (formerly Hoechst). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5) BASF styrene EMU 120 FD is the trade name of a product supplied by BASF www.basf.com. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

6) Dupont Vertrel XF (MS-782) is the trade name of a product supplied by Dupont www2.dupont.com/vertrel. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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

5.3 Tablet press, capable of providing a 20 ton or up to 400 kN load for 10 s.

5.4 Mould with Mylar film, for forming tablets in press.

5.5 Desiccator, with a non-contaminating desiccant for storing calibration materials and monitor samples.

5.6 Balance, with precision $\pm 0,01$ g.

5.7 Flat spatula.

6 Test procedure

6.1 Test specimen preparation

Two methods of sample preparation are described: the addition of binder method and the backing method. Either method may be used.

NOTE The addition of binder method is most used but the preparation of the precision statement showed that several different methods of sample preparation gave good and sufficient within-laboratory repeatability.

See ISO 1619 for guidance.

6.2 Addition of binder method

6.2.1 Dry the sample to constant mass at (110 to 120) °C.

6.2.2 Take a test portion and weigh it, taking care to always use the same mass as for the calibration reference material. A typical test portion is 10,0 g.

6.2.3 Mix the test portion with binding agent (see the list of examples in 4.5) before grinding in the disc mill (5.2), taking care to always use the same mass and proportion of sample and binding agent as for the calibration reference materials. Some examples of binders in use are given in Table 2.

NOTE The binding agent can decrease the level of segregation in the sample and make it easier to remove the tablet from the grinding vessel.

Table 2 — Some examples of test portion size and binding agents (4.5) in the addition method

| Test portion g | Binder addition ^a |
|--|--|
| 10,0 | 8 pills Hoechst PE-190 amounting to 1,0 g |
| 5,0 | + 4,0 ml Dupont Vertrel XF Cleaning Agent (MS-782) + 0,5 g binder tablet Premier Lab Supply (XRF Multi-Mix RXR-250) |
| 10,0 | 2,5 g of 9:1 BASF styrene EMU 120 FD: Hoechst Ceridust 9615A Wax |
| 4,0 | 2,0 g binder (Lico wax C Micropowder) |
| ^a These materials can be replaced with products with similar properties | |

6.2.4 Mill (5.2) the sample until all particles are below 63 micrometer fineness.

NOTE 1 Examples of milling times are 10 s to 10 min, typical is (1 to 4) min. Short milling times give larger spread in within-laboratory precision. The particle size should be determined by using a suitable sieving technique.

NOTE 2 Results are particle size dependent, and 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.

6.3 Backing method

6.3.1 Pack with 2 mm of lithium tetraborate backing (4.1) in the aluminium tablet dish (4.3) or directly in the die, on fresh Mylar film (4.4).

6.3.2 Transfer a sufficient test portion to produce a cylindrical tablet 4 mm to 7 mm thick. When using an aluminium tablet dish, make a pile of maximum height above the lip of the dish, and hand pack with a flat spatula (5.7) until the ground mix is level with the lip of the dish.

6.3.3 Place fresh Mylar film on top so the press does not touch the tablet surface.

6.3.4 Press to achieve a stable tablet. Use the same time for pressure, pressure load and pressure time for the test portions as for the calibration reference material, i.e. use the same pressure profile for the calibration reference materials and test samples. Example of pressure and time are 20 ton to 40 ton for (10 to 30) s, typical is 25 ton and 20 s with a 40 mm diameter tablet. Release the pressure slowly.

6.3.5 Remove the tablet from the die and inspect the tablet surface to ensure that it is smooth and free from cracks. Mark the pellet for identification.

NOTE Aluminium fluoride tablets can fracture following removal from the press. This problem is described in the literature as a problem of slight deformation of the die or sample cup under high pressure. See Reference[3]: V. Buhrke et al., Preparation of specimen for X-ray fluorescence and X-ray diffraction analysis, Wiley-VCH, 1998, page 41. Laboratories report that a certain level of experience with this sample preparation is needed to reduce this problem of fracture of tablets.

6.4 X-ray fluorescence spectrometer application

6.4.1 Instrumental conditions

Follow the control setting and operation instructions of the spectrometer (5.1) manufacturer including monitoring and calibrating angles and monitoring and correcting for X-ray tube intensity.

Suggested conditions of measurement are given in Table 3. All measurements shall be made under vacuum. The $K\alpha$ analytical lines are preferred. Use spectral lines overlap correction if required; also correct for background; several lines are recommended in the table for this.

NOTE 1 The preparation of the precision statement showed that several choices of measurement lines gave good and sufficient within-laboratory repeatability. For this reason, these lines are included.

NOTE 2 Regarding counting times in Table 3, this gives some guidance but if the XRF is less sensitive than typical these times may be short.

Table 3 — Measurement lines and suggested conditions of measurement

| Element | Crystal | Angle | Counter | Time | Collimator | Voltage | Current | Back-ground |
|---------|------------------|---------------------|---------|-----------|------------------|---------|---------|------------------------|
| | | $^{\circ}2\theta$ | | s | | kV | mA | $^{\circ}2\theta$ |
| F | XS-55 | K α | | 60 | 0,46 $^{\circ}$ | 27 | 111 | |
| F | AX06 | | | | | | | |
| Na | XS-55 | K $\alpha\alpha$ | | 30 to 100 | 0,46 $^{\circ}$ | 27 | 111 | |
| Na | TIAP | 55,1 | Flow | 30 to 100 | > 0,6 $^{\circ}$ | 40 | 60 | $\pm 2^{\circ}2\theta$ |
| Na | PX1 | | | 30 to 100 | | | | |
| Na | AX06 | | | 30 to 100 | | | | |
| Si | PET | K α | | 20 to 30 | 0,46 $^{\circ}$ | 27 | 111 | |
| Si | PET ^a | 109,215 | Flow | 20 to 30 | > 0,6 $^{\circ}$ | 40 | 60 | |
| Si | InSb | 7,52 | Flow | 20 to 30 | > 0,6 $^{\circ}$ | 40 | 60 | |
| Si | InSb | 144,95 | Flow | 20 to 30 | > 0,6 $^{\circ}$ | 40 | 60 | 142,85; 147,05 |
| Si | PX1 | | | | | | | |
| P | PET | K α | | 20 | 0,46 $^{\circ}$ | 27 | 111 | |
| P | PET ^a | 89,56 | Flow | 20 | > 0,6 $^{\circ}$ | 40 | 60 | |
| P | Ge(III) | 141,03 to 141,23 | Flow | 20 | > 0,6 $^{\circ}$ | 40 | 60 | 139,24; 143,24 |
| S | PET | K α | | 10 | 0,46 $^{\circ}$ | 27 | 111 | |
| S | PET ^a | 75,8 | Flow | 10 | 0,6 $^{\circ}$ | 40 | 60 | |
| S | Ge(III) | 110,68 | Flow | 10 | 0,6 $^{\circ}$ | 40 | 60 | 113,18 |
| Ca | LiF (200) | 113,08 to 113,09 | Flow | 10 | 0,2 $^{\circ}$ | 40 | 60 | 116,0 |
| Fe | PET | K α | | 2 to 10 | 0,46 $^{\circ}$ | 60 | 50 | |
| Fe | LiF (200) | 57,49 to 57,52 | Flow | 2 to 10 | 0,2 $^{\circ}$ | 60 | 40 | 59,02 |

^a Use pulse-height selection with PET crystal.

6.4.2 Calibration and calibration reference materials

The calibration reference materials are not specified in this method. The user of this standard shall obtain suitable calibration reference materials. Some certified reference material sets can be obtained⁷⁾.

The X-ray fluorescence spectrometer application software is used to make an aluminium fluoride 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

7) The following sets are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products. — RTA Alcan: Analytical Reference Materials (ARMI) distributes the Rio Tinto Alcan reference materials. The original materials were AIF-01 to AIF-05 and CAA, CAB, CAC, CAN, CAO series for Fe, Si, Na, F, S, P and Ca(F is not used for reporting F/AIF₃ from this set). As of 2010, CAA, CAJ and SAM standards are no longer available. Analytical Reference Materials (ARMI) Golden, Colorado USA info@armi.com. — Do-Fluoride Chemicals Co., Ltd. offers their calibration set: China National Set GSB 04-2194-2008 series GAF-01 to GAF-10 for F, Al, Na, SiO₂, Fe₂O₃, SO₄, P₂O₅, LOI. Do-Fluoride Chemicals Co., Ltd. Zhongzhan District, Jiaozuo 454191 Henan, P.R.China Tel./Fax:0086-391-2802245, Fax:0086-391-2802927, e-mail: sales@dfdchem.com.

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.

NOTE 1 The determination of fluorine has an uncertainty due to mineralogical variation among origins of aluminium fluoride. These calibration sets are made of industrial aluminium fluoride materials commonly in use as raw materials for primary aluminium production. An AlF₃ sample of unusual mineralogical origin should be tested with an absolute method to verify that, when using this test method, the fluorine concentration range reported is valid.

NOTE 2 The preparation of the precision statement showed that the between-laboratory reproducibility was high, while, at the same time, these laboratories analysed to good and sufficient within-laboratory repeatability. This significant and systematic difference between-laboratory reproducibility is due to laboratories using different calibration reference material sets. It is important to be aware of this when using the reproducibility for comparison in a commercial context.

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

6.4.3 Verifying the calibration

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

Repeated irradiation of one tablet can lead to increasing level of intensity for Si and S. If this is observed, a freshly prepared calibration sample set shall be prepared.

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

6.6 Analysis, calculation and expression of results

The analysis is to 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 within-laboratory repeatability for that element as shown in Table 4, the analysis should be repeated.

7 Precision

7.1 General

The precision given in Table 4 was computed using ASTM method E691 and is based on results collected in an interlaboratory study in June 2009. Details of the computation of the precisions given here is available as a technical report: Standard Norge - NS/TR 12590.

Table 4 — Precision for aluminium fluoride and the trace elements (X = Concentration) based on averages of three tablet measurements

| Property | Range | Repeatability r | Standard deviation s_r | Decimals ^a D_r | Reproducibility $y \cdot R$ | Standard deviation s_R | Decimals ^a D_R |
|---|----------------|----------------------|-----------------------------|--------------------------------|--------------------------------|-----------------------------|-----------------------------|
| Aluminium fluoride from fluorine, AlF_3 | 86,5 to 95,75 | 0,6 | 0,2 | 1 | 2,1 | 0,7 | 1 |
| Sodium, Na | 0,05 to 0,25 | 0,010 | 0,004 | 3 | 0,075 | 0,038 | 2 |
| Silicon, Si | 0,001 to 0,14 | 0,001 | 0,0005 | 3 | 0,014 | 0,005 | 3 |
| Phosphorus, P | 0,001 to 0,020 | 0,001 | 0,0002 | 3 | 0,0026 | 0,0009 | 3 |
| Sulfur, S | 0,01 to 0,60 | 0,006 | 0,002 | 2 | 0,38*X | 0,012*X | 2 |
| Calcium, Ca | 0,001 to 0,10 | 0,004 | 0,001 | 3 | 0,011 | 0,004 | 3 |
| Iron, Fe | 0,005 to 0,05 | 0,0014 | 0,0005 | 3 | 0,0022 | 0,0008 | 3 |

^a D is the recommended number of decimals.

NOTE It should be noted that for Na, Si, P, S and Ca the low limit of the concentration range given in Table 1 and Table 4 is smaller than the between-laboratory reproducibility precision R .

7.2 How to use Table 4 using sodium (Na) as an example

7.2.1 This precision statement is valid for sodium in the concentration range (0,05 to 0,25) mass fraction %. The sodium concentration should be reported in mass percent. For within-laboratory reporting, three decimals are significant (D_r), while for between-laboratory comparisons not more than two decimals (D_R) should be used.

7.2.2 Within-laboratory comparison: Given a determination of the concentration of sodium at the same laboratory of two test portions of the same material separately prepared within a short time by the same operator, the difference between the two measurements should be within $r = 0,010$ mass fraction % for 95 out of 100 such comparisons.

7.2.3 Between-laboratory comparison: Given the determination of the concentration of sodium at two different laboratories of a test portion of the same material, the difference should be within $R = 0,075$ mass fraction % for 95 out of 100 such comparisons.

7.2.4 Using the repeatability standard deviation s_r : Given any number of determinations of the concentration of sodium on separately prepared test portions of the same material within a short time by the same operator at the same laboratory, the concentration of sodium should fall within a range of $\pm 1,96 s_r$ for 95 out of 100 such determinations.

7.2.5 Using the reproducibility standard deviation s_R in measurements: Given any number of determinations of the concentration of sodium on test portions of the same material at different laboratories, the concentration of sodium should fall within a range of $\pm 1,96 s_R$ for 95 out of 100 such determinations.

7.3 How to use Table 4 using sulfur (S) as an example

7.3.1 This precision statement is valid for sulfur in the concentration range (0,01 to 0,60) mass fraction %. The sulfur concentration should be reported in mass percent, with two significant decimals (D_R).

7.3.2 Within-laboratory comparison: Given a determination of the concentration of sulfur at the same laboratory of two test portions of the same material separately prepared within a short time by the

same operator, the difference between the two measurements should be within $r = 0,006$ mass fraction % for 95 out of 100 such comparisons.

7.3.3 Between-laboratory comparison: Given the determination of the concentration of sulfur at two different laboratories of a test portion of the same material, for 95 out of 100 such comparisons the difference should be within $R = 0,38X$ where X is the average sulfur concentration of the two laboratories. For $X = 0,10$ mass fraction %, the difference should be within $R = 0,038$ mass fraction % for 95 out of 100 such comparisons.

8 Test report

The test report shall include the following:

- a) identification of the sample;
- b) a reference to this International Standard;
- c) the analysis results with the unit used, i.e. mass percent;
- 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 International Standard or in the International Standards to which reference is made;
- f) the following statement: The method in this International Standard refers to each element as the element, not the oxide, fluoride, sulfate or phosphate. Table A.1 gives conversion factors.

Annex A (informative)

Conversion table

Table A.1 — Conversion factors

| Element | Atomic mass g/mol | Compound | Molar mass g/mol | Conversion factor |
|---------|----------------------|--------------------------------|---------------------|-------------------|
| F | 18,998 | AlF ₃ | 83,976 | 1,473 |
| Na | 22,99 | Na ₂ O | 61,979 | 1,348 |
| Si | 28,086 | SiO ₂ | 60,084 | 2,139 |
| P | 30,974 | P ₂ O ₅ | 141,943 | 2,291 |
| S | 32,064 | SO ₄ ⁻ | 80,061 | 2,497 |
| Ca | 40,08 | CaO | 56,079 | 1,399 |
| Fe | 55,933 | Fe ₂ O ₃ | 159,863 | 1,429 |

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Bibliography

- [1] ISO 5938:1979, *Cryolite, natural and artificial, and aluminium fluoride for industrial use — Determination of sulphur content — X-ray fluorescence spectrometric method*
- [2] ASTM E691, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method*
- [3] BUHRKE. V. *et al. Preparation of specimen for X-ray fluorescence and X-ray diffraction analysis.* Wiley-VCH, 1998, pp. 41.
- [4] Standard Norge - NS/TR 12590, *Aluminium Fluoride Elemental Analysis by XRF – Precision statement for ISO 12926 from an Interlaboratory Study.* - Published November 2011

ICS 71.100.10

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