
**Aluminium oxide primarily used
for production of aluminium —
Determination of trace elements
— Wavelength dispersive X-ray
fluorescence spectrometric method**

*Oxyde d'aluminium utilisé pour la production d'aluminium —
Détermination d'éléments traces — Spectrométrie de fluorescence des
rayons X par dispersion en longueur d'onde*

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Contents

	Page
Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Principle	2
4 Reagents and materials	2
5 Apparatus	3
6 Sampling and samples	5
7 Procedure	5
7.1 General.....	5
7.2 Preparation of calibration specimens.....	6
7.2.1 Determination of loss of mass on fusion of flux and flux correction.....	6
7.2.2 Preparation of intermediate calibration glass (ICG).....	6
7.2.3 Preparation of the synthetic calibration disk (SCD).....	7
7.2.4 Preparation of the blank calibration discs.....	9
7.3 Preparation of the sample discs.....	9
7.4 X-ray fluorescence measurement.....	10
7.4.1 General instrumental conditions.....	10
7.4.2 Guidelines for instrument optimization.....	11
7.4.3 Sample loading.....	11
7.4.4 Monitor disc: correction for instrumental drift.....	11
7.4.5 Measurements for calibration.....	12
7.4.6 Measurement of test discs.....	13
8 Calculations	13
8.1 Calculation of net intensity.....	13
8.2 Comparison of duplicate measurements for the Al ₂ O ₃ blanks and Synthetic Calibration Discs (SCDs).....	14
8.2.1 SCDs criteria for the acceptability of duplicate measurements.....	14
8.2.2 Al ₂ O ₃ blanks criteria for the acceptability of duplicate measurement.....	14
8.3 Drift correction of measured intensities.....	15
8.4 Calculation of the calibration parameters.....	15
9 Consistency checks and reporting results	16
10 Precision	16
11 Accuracy	17
12 Quality assurance and control	17
13 Test report	17
Annex A (informative) Contamination issues and care of platinum ware	19
Annex B (normative) Example of instrument optimization	21
Annex C (informative) Calculation of reagent masses for different sample/flux combinations and synthetic calibration discs when omitting some elements	25
Annex D (informative) Preparation of monitor disc	27
Annex E (informative) Interlaboratory test program analysis of NIST 699 and ASCRM 27 smelter grade alumina, certified reference materials	29
Annex F (informative) Comments on flux purity	31
Bibliography	32

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.

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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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: [Foreword - Supplementary information](#)

The committee responsible for this document is ISO/TC 226, *Materials for the production of primary aluminium*.

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Introduction

This International Standard is based on Australian Standard AS 2879.7-1997, *Alumina — Determination of trace elements — Wavelength dispersive X-ray fluorescence spectrometric method*, developed by the Standards Australia Committee on Alumina and Materials used in Aluminium Production to provide an XRF method for the analysis of alumina.

The objective of this International Standard is to provide those responsible for the analysis of smelting-grade alumina with a standardized, validated procedure that will ensure the integrity of the analysis.

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Aluminium oxide primarily used for production of aluminium — Determination of trace elements — Wavelength dispersive X-ray fluorescence spectrometric method

1 Scope

This International Standard sets out a wavelength dispersive X-ray fluorescence spectrometric method for the analysis of aluminium oxide for trace amounts of any or all of the following elements: sodium, silicon, iron, calcium, titanium, phosphorus, vanadium, zinc, manganese, gallium, potassium, copper, chromium and nickel. These elements are expressed as the oxides Na₂O, SiO₂, Fe₂O₃, CaO, TiO₂, P₂O₅, V₂O₅, ZnO, MnO, Ga₂O₃, K₂O, CuO, Cr₂O₃, and NiO on an un-dried sample basis.

The method is applicable to smelting-grade aluminium oxide. The concentration range covered for each of the components is given in [Table 1](#).

Table 1 — Applicable concentration range

Component	Concentration range %	
Na ₂ O	0,10	to 1,00
SiO ₂	0,003	to 0,05
Fe ₂ O ₃	0,003	to 0,05
CaO	0,003	to 0,10
TiO ₂	0,000 5	to 0,010
P ₂ O ₅	0,000 5	to 0,050
V ₂ O ₅	0,000 5	to 0,010
ZnO	0,000 5	to 0,010
MnO	0,000 5	to 0,010
Ga ₂ O ₃	0,000 5	to 0,020
K ₂ O	0,000 5	to 0,010
CuO	0,000 5	to 0,010
Cr ₂ O ₃	0,000 5	to 0,010
NiO	0,000 5	to 0,010

2 Normative references

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

AS 2563, *Wavelength dispersive X-ray fluorescence spectrometers — Determination of precision*

AS 2706, *Numeric values — Rounding and interpretation of limiting values*

AS 4538.1-1999 (R2013), *Guide to the sampling of alumina — Sampling procedures*

AS 4538.2-2000 (R2013), *Guide to the sampling of alumina — Preparation of samples*

3 Principle

A portion of the aluminium oxide test sample is incorporated, via fusion, into a borate glass disc using a casting technique. X-ray fluorescence measurements are made on this disc.

Calibration is carried out using synthetic standards prepared from pure chemicals using a two-point regression. Matrix corrections may be employed but, because of the low levels at which the analytes are present in the Al_2O_3 matrix, will have negligible effect within the scope of the method.

Intensity measurements are corrected for spectrometer drift.

A certified reference material, (see [Annex E](#)) is used to verify the calibration.

4 Reagents and materials

4.1 Flux, mixture of 12 parts lithium tetraborate to 22 parts lithium metaborate, pre-fused.

This flux is available commercially. Flux will absorb atmospheric moisture when exposed to air. Minimize water uptake by storing flux in an airtight container.

See [Annex F](#) for comments on flux purity.

4.2 Aluminium oxide (Al_2O_3), high purity, nominally 99,999 % Al_2O_3 .

Prepared by heating to $1\ 200\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ for 2 h and cooling in a desiccator.

To ensure the high purity Al_2O_3 is not contaminated with analyte elements, analyse it before use by preparing a disc made from the aluminium oxide (referred to as a "blank disc") and measuring net intensities for each analyte element.

The method for the measurement of blank discs is given in [7.4.5](#). If a number of differently sourced high purity aluminium oxides are tested select the one with the lowest countrates for impurities for use in calibration and blank discs. [A.3](#) gives instructions for reducing silica contamination in high purity aluminium oxide and may be employed if required.

4.3 Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$), nominally 99,99 % $\text{Na}_2\text{B}_4\text{O}_7$.

Prepared by heating to $650\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ for 4 h minimum and cooling in a desiccator.

4.4 Silicon dioxide (SiO_2), nominally 99,9 % SiO_2 .

Prepared by heating to $1\ 200\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ for 2 h and cooling in a desiccator.

4.5 Iron(III) oxide (Fe_2O_3), nominally 99,9 % Fe_2O_3 .

Prepared by heating to $1\ 000\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ for a minimum of 1 h and cooling in a desiccator.

4.6 Calcium carbonate (CaCO_3), nominally 99,9 % CaCO_3 .

Prepared by heating to $105\ ^\circ\text{C} \pm 5\ ^\circ\text{C}$ for 1 h and cooling in a desiccator.

4.7 Titanium dioxide (TiO_2), nominally 99,9 % TiO_2 .

Prepared by heating to $1\ 000\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$ for a minimum of 1 h and cooling in a desiccator.

4.8 Ammonium dihydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), nominally 99,9 % $\text{NH}_4\text{H}_2\text{PO}_4$.

Prepared by heating to $105\ ^\circ\text{C} \pm 5\ ^\circ\text{C}$ for 1 h and cooling in a desiccator.

4.9 Vanadium pentoxide (V_2O_5), nominally 99,9 % V_2O_5 .

Prepared by heating to $600\text{ °C} \pm 25\text{ °C}$ for 1 h and cooling in a desiccator.

4.10 Zinc oxide (ZnO), nominally 99,9 % ZnO .

Prepared by heating to $1\ 000\text{ °C} \pm 25\text{ °C}$ for a minimum of 1 h and cooling in a desiccator.

4.11 Manganese oxide (Mn_3O_4), nominally 99,9 % pure.

Heat manganese dioxide (99,9 % pure, MnO_2) for 24 h at $1\ 000\text{ °C} \pm 25\text{ °C}$ in a platinum crucible and cool in a desiccator. Crush the resultant lumpy material to a fine powder. The product material is Mn_3O_4 .

4.12 Gallium oxide (Ga_2O_3), nominally 99,9 % Ga_2O_3 .

Prepared by heating to $1\ 000\text{ °C} \pm 25\text{ °C}$ for a minimum of 1 h and cooling in a desiccator.

4.13 Potassium carbonate (K_2CO_3), nominally 99,9 % K_2CO_3 .

Prepared by heating to $600\text{ °C} \pm 25\text{ °C}$ for a minimum of 2 h and cooling in a desiccator.

4.14 Copper oxide (CuO), nominally 99,9 % CuO .

Prepared by heating to $1\ 000\text{ °C} \pm 25\text{ °C}$ for a minimum of 1 h and cooling in a desiccator.

4.15 Chromium(III) oxide (Cr_2O_3), nominally 99,9 % Cr_2O_3 .

Prepared by heating to $1\ 000\text{ °C} \pm 25\text{ °C}$ for a minimum of 1 h and cooling in a desiccator.

4.16 Nickel(II) oxide (NiO), nominally 99,9 % NiO .

Prepared by heating to $1\ 000\text{ °C} \pm 25\text{ °C}$ for a minimum of 1 h and cooling in a desiccator.

4.17 Certified Reference Material (CRM), one or both of the alumina materials NIST699 and ASCRM027.

Prepared by heating to $300\text{ °C} \pm 10\text{ °C}$ for a minimum of 2 h and cooling in a desiccator. Details for NIST699 can be found at www.nist.gov. A test report for ASCRM027 is available from SAI-Global, www.saiglobal.com, details of availability can be found within this International Standard.

5 Apparatus

5.1 Platinum crucible, non-wetting, platinum-alloy with a platinum lid and having a capacity compatible with the bead requirements.

Typical crucibles have a volume of 25 mL to 40 mL.

Crucibles shall be free of all elements to be determined.

NOTE Silica has been found to be a common contaminant of platinum metal alloys, and a suggested method for cleaning platinum ware to remove silica is given in [A.2](#).

5.2 Desiccator, provided with an effective, non-contaminating desiccant.

All heat treated reagents ([4.2](#) to [4.17](#)) shall be stored in a desiccator.

NOTE Pelletized molecular sieves and phosphorous pentoxide have been found to be satisfactory desiccants. Silica gel is not suitable.

5.3 Electric furnace, fitted with an automatic temperature controller and capable of maintaining a temperature of $1\ 200\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$.

5.4 Platinum mould, non-wetting, platinum or platinum-alloy, circular-shaped of the type shown in [Figure 1](#) and with dimensions compatible with sample holders employed in the particular spectrometer used.

An example of a 35 mm mould is given in [Figure 1](#).

The surfaces of moulds shall be free of all elements to be determined, flat and polished to a mirror finish.

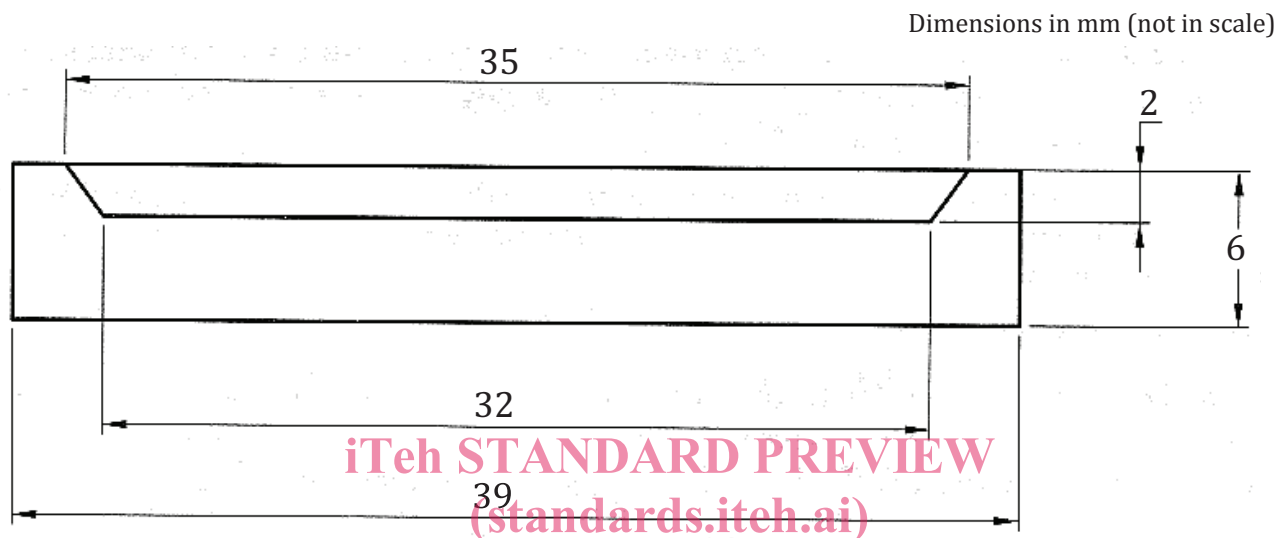


Figure 1 — Drawing of platinum/5 % gold mould
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NOTE Silica has been found to be a common contaminant, and a suggested method for cleaning platinum ware and to remove silica is given in [A.2](#).

5.5 X-ray fluorescence spectrometer, wavelength dispersive, vacuum path X-ray fluorescence spectrometer, provided that the performance of the instrument has been verified and found to comply with the manufacture’s specifications or the performance requirements given in AS 2563, “Wavelength dispersive X — ray fluorescence spectrometers — Determination of precision.”

5.6 Vibratory mill, having grinding components that do not contaminate the intermediate calibration glass (ICG) with analyte elements.

Take care to ensure that contaminants from the grinding equipment do not affect the analysis.

NOTE Alumina, tungsten carbide and zirconia grinding components have been found to be satisfactory.

5.7 Fusion equipment, an electric furnace capable of maintaining a temperature of $1\ 100\ ^\circ\text{C} \pm 25\ ^\circ\text{C}$.

A flat, level heat sink is required to cool hot charged moulds. Using both an aluminium and ceramic heat sink is effective, where initial cooling is achieved on the ceramic heat sink and quicker cooling to ambient temperature is achieved on the aluminium heat sink.

Alternatively, commercially available automatic fusion machines may be used since the development of modern automated fusion equipment has made bead preparation faster and significantly less operator-dependent. Most of these machines use similar sized crucibles and moulds to those described in the manual method and simulate the action required to ensure complete dissolution of the sample in the molten flux. The use of these devices to prepare fused beads is acceptable as long as the agitation

provided is sufficient to ensure complete dissolution of the samples and that it can be demonstrated that the results so generated achieve the accuracy and precision criteria outlined in [Clauses 11](#) and [12](#).

WARNING — Warning: certain flame fusion devices have been found to reduce reported Fe_2O_3 levels by up to 0,002 % due to reduction and subsequent alloying with the Pt crucible. Other elements may also be affected. For burner type fusion devices an oxidizing flame shall be used.

5.8 Balance, analytical balance capable of weighing up to 100 g, to the nearest 0,1 mg.

5.9 Platinum tipped stainless steel tongs, for transferring crucibles ([5.1](#)) and their lids in and out of the furnace ([5.3](#)) and, where applicable, fusion equipment ([5.7](#)) of a length and construction suitable for safely performing this task.

A heat shield fitted to the front of the tongs' handles is advisable. Titanium tongs may also be used but titanium contamination must be avoided.

5.10 Stainless steel mould tongs for transferring moulds ([5.4](#)) in and out of the furnace ([5.3](#)) and, where applicable, fusion equipment ([5.7](#)) of a length and construction suitable for safely performing this task.

They are typically of a two pronged forked design, the prongs fit the mould's underside, securely supporting it. A heat shield fitted to the front of the tongs' handle is advisable.

5.11 Monitor disc, described in [7.4.4](#).

6 Sampling and samples

Bulk samples shall be taken in accordance with AS 4538.1 and test samples prepared in accordance with AS 4538.2 Weighed test portions are extracted from test samples and may be dried or analysed as-received. As-received samples often contain up to 3 % moisture and proper drying requires a 300 °C treatment. Procedures for this are contained in ISO 806.

It is possible to fuse and produce borate discs from as-received test samples. However alumina used for aluminium production typically contains a few mass per cent of particles greater than 150 micron, consequently better repeatability is often achieved by grinding in a vibratory mill ([5.6](#)). Grinding is recommended if coarse impurities are present from the manufacturing process. Examples of these contaminants are refractory fragments from the calcination process or quartz particles not removed during refining.

7 Procedure

7.1 General

Calibration is performed using a two-point regression. Determine the zero concentration point from a blank calibration disc of flux and high purity Al_2O_3 , and the high concentration point from a synthetic calibration disc (SCD) derived from flux and an intermediate calibration glass (ICG). Make a correction for the loss of mass on fusion of the flux, by establishing a value for the loss on fusion of each batch of flux.

Test sample discs are produced using a specified flux-to-sample ratio of 2:1 and the masses given in [Table 3](#), [Table 5](#), and [Table 6](#) are calculated for this ratio. Other ratios have been found to be satisfactory but require re-calculation of the masses in these tables (see [Annex C](#)). Higher ratios than the specified 2:1 substantially improve dissolution and ease of disc preparation but count rates for analytes will decrease. Ratios up to 5:1 are successfully used on modern spectrometers.

Also, different mould sizes may be used. This only requires that fusion masses in [Table 3](#), [Table 5](#), and [Table 6](#) be adjusted proportionately to the mould's volume.

7.2 Preparation of calibration specimens

7.2.1 Determination of loss on fusion of flux and flux correction

Determine the loss on fusion as follows:

- weigh a clean dry platinum crucible (5.1) to the nearest 0,1 mg (m_1);
- add approximately 4 g of the flux (4.1), weighed to the nearest 0,1 mg (m_2), to the crucible and place in a furnace at $300\text{ °C} \pm 10\text{ °C}$. Slowly increase the temperature to $1\ 100\text{ °C} \pm 25\text{ °C}$ over 1 h;
- after holding at $1\ 100\text{ °C} \pm 25\text{ °C}$ for 20 min, remove from the furnace, allow to cool in a desiccator and then re-weigh to the nearest 0,1 mg (m_3);
- calculate the loss on fusion using Formula (1):

$$\text{Loss on fusion (LOF)} = \frac{m_1 + m_2 - m_3}{m_2} \quad (1)$$

where

m_1 is the mass of clean dry crucible, in grams;

m_2 is the mass of flux before heating, in grams;

m_3 is the mass of crucible plus flux after heating, in grams.

To determine the mass of flux to be taken in 7.2.2, 7.2.3, 7.2.4 and 7.3, use Formula (2):

$$\text{Corrected mass} = \text{mass given} / (1 - \text{LOF}) \quad (2)$$

7.2.2 Preparation of intermediate calibration glass (ICG)

Prepare the reagents by heating and cooling as shown in [Clause 4](#).

Select the masses of reagents used to prepare the ICG in accordance with [Table 2](#).

If any elements in [Table 2](#) are not required, they may be omitted from the ICG. In this case, increase the mass of flux in [Table 2](#) by the equivalent mass of that reagent after fusion. (See [Annex C](#)).

Where reagents are omitted, the addition of extra flux will change the masses of flux and Al_2O_3 from those shown in [Table 3](#). Use the information given in [Annex C](#) to calculate the new masses required.

Prepare the ICG as follows:

- add the weighed reagents (as per [Table 2](#), weighed to within 0,1 mg) to the crucible (5.1) and mix thoroughly, ensuring that no contamination or loss of material occurs. Cover the crucible with its lid and keep the crucible covered for the rest of the procedure, except while stirring the contents;
- transfer the covered crucible and contents to the electric furnace (5.7), maintained at $300\text{ °C} \pm 10\text{ °C}$;
- slowly increase the furnace temperature to $1\ 100\text{ °C} \pm 25\text{ °C}$ over a period of not less than 1 h, at the same heating rate as used in 7.2.1(b);
- maintain this temperature for 5 min and then swirl the crucible and contents to mix the molten mass;
- after a further 15 min at $1\ 100\text{ °C} \pm 25\text{ °C}$, remove the crucible and allow it to cool on a heat sink (described in 5.7). When cool, the glass may be tapped from the crucible;
- grind the glass in a vibratory mill (5.6).

Transfer the ground glass to an airtight container and store in the desiccator (5.2).

Table 2 — Reagent masses for intermediate calibration glass

Reagent	Mass g	Conversion factor to mass of equivalent oxide	Equivalent mass of reagent after fusion g
Flux	4,247 5 ^a		4,247 5
Na ₂ B ₄ O ₇	5,191 3	0,308 2	1,600 0 Na ₂ O 3,591 3 B ₄ O ₆ reports to flux
SiO ₂	0,080 0	1,000 0	0,080 0
Fe ₂ O ₃	0,080 0	1,000 0	0,080 0
CaCO ₃	0,285 5	0,560 4	0,160 0
TiO ₂	0,016 0	1,000 0	0,016 0
NH ₄ H ₂ PO ₄	0,129 6	0,617 0	0,080 0
V ₂ O ₅	0,016 0	1,000 0	0,016 0
ZnO	0,016 0	1,000 0	0,016 0
Mn ₃ O ₄	0,017 2	0,930 1	0,016 0 MnO 0,001 2 oxygen reports to flux
Ga ₂ O ₃	0,032 0	1,000 0	0,032 0
K ₂ CO ₃	0,023 5	0,681 2	0,016 0
CuO	0,016 0	1,000 0	0,016 0
Cr ₂ O ₃	0,016 0	1,000 0	0,016 0
NiO	0,016 0	1,000 0	0,016 0
Total mass of ICG			10,000

^a This flux mass shall be loss corrected as per Formula (2).

7.2.3 Preparation of the synthetic calibration disk (SCD)

The masses of SCD reagents suitable for 35 mm and 40 mm moulds are given in Table 3. These masses may be reduced or increased proportionally to suit any other size mould.

Table 3 — Reagent masses for synthetic calibration disc

Reagent	Mass for 35 mm mould g	Mass for 40 mm mould g
Intermediate calibration glass	0,125 0	0,187 5
Flux ^{ab}	3,902 0	5,853 0
High purity Al ₂ O ₃ ^b	1,973 0	2,959 5
Total mass	6,00	9,00

^a This flux mass shall be loss corrected as per Formula (2).
^b If elements in Table 2 are omitted and/or a flux-to-sample ratio higher than 2:1 is used, Annex C should be used to calculate new masses for Table 3.