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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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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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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*.

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.

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 Na_2O, SiO_2, Fe_2O_3, CaO, TiO_2, P_2O_5, V_2O_5, ZnO, MnO, Ga_2O_3, K_2O, CuO, Cr_2O_3, 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_2O	0,10	to	1,00
SiO_2	0,003	to	0,05
Fe_2O_3	0,003	to	0,05
CaO	0,003	to	0,10
TiO_2	0,000 5	to	0,010
P_2O_5	0,000 5	to	0,050
V_2O_5	0,000 5	to	0,010
ZnO	0,000 5	to	0,010
MnO	0,000 5	to	0,010
Ga_2O_3	0,000 5	to	0,020
K2O	0,000 5	to	0,010
CuO	0,000 5	to	0,010
Cr_2O_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 °C± 25 °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** ($Na_2B_4O_7$), nominally 99,99 % $Na_2B_4O_7$.

Prepared by heating to 650 °C ± 25 °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 °C ± 25 °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 °C ± 25 °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 °C ± 5 °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 °C ± 25 °C for a minimum of 1 h and cooling in a desiccator.

4.8 **Ammonium dihydrogen orthophosphate** ($NH_4H_2PO_4$), nominally 99,9 % $NH_4H_2PO_4$.

Prepared by heating to 105 °C ± 5 °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 °C ± 25 °C for 1 h and cooling in a desiccator.

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

Prepared by heating to 1 000 °C ± 25 °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 °C ± 25 °C in a platinum crucible and cool in a dessicator. 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 °C ± 25 °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 °C ± 25 °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 °C ± 25 °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 °C ± 25 °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 °C ± 25 °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 °C ± 10 °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 °C ± 25 °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.

Dimensions in mm (not in scale)

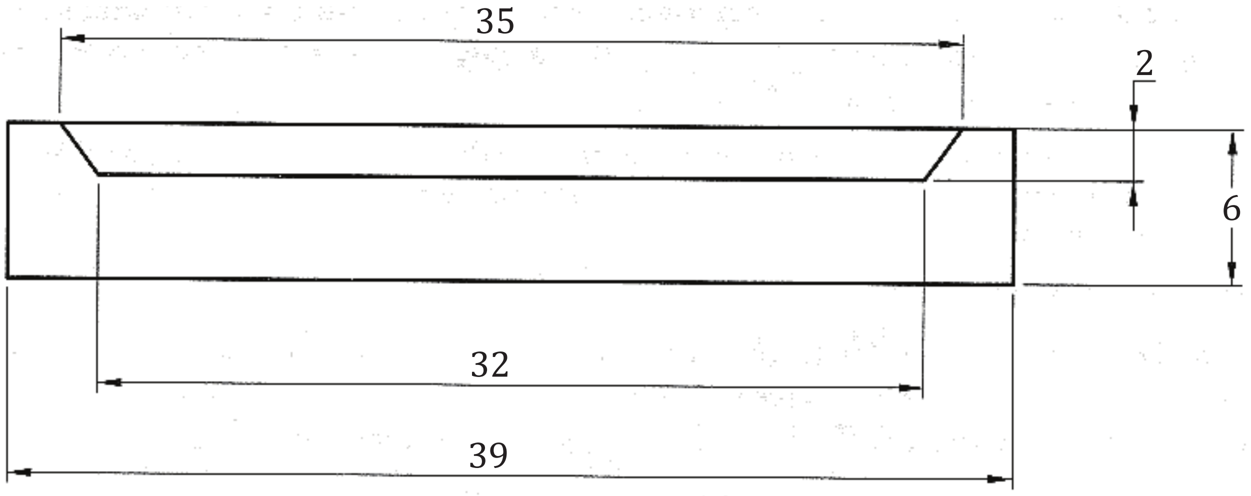

Figure 1 — Drawing of platinum/5 % gold mould

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 °C ± 25 °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 of mass on fusion of flux and flux correction

Determine the loss on fusion as follows:

a) weigh a clean dry platinum crucible (5.1) to the nearest 0,1 mg (m_1);

b) 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 °C ± 10 °C. Slowly increase the temperature to 1 100 °C ± 25 °C over 1 h;

c) after holding at 1 100 °C ± 25 °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);

d) calculate the loss on fusion using Formula (1):

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

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):

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

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:

a) 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;

b) transfer the covered crucible and contents to the electric furnace (5.7), maintained at 300 °C ± 10 °C;

c) slowly increase the furnace temperature to 1 100 °C ± 25 °C over a period of not less than 1 h, at the same heating rate as used in 7.2.1(b);

d) maintain this temperature for 5 min and then swirl the crucible and contents to mix the molten mass;

e) after a further 15 min at 1 100 °C ± 25 °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;

f) 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
$Na_2B_4O_7$	5,191 3	0,308 2	1,600 0 Na2O 3,591 3 B4O6 reports to flux
SiO_2	0,080 0	1,000 0	0,080 0
Fe_2O_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
$NH_4H_2PO_4$	0,129 6	0,617 0	0,080 0
V_2O_5	0,016 0	1,000 0	0,016 0
ZnO	0,016 0	1,000 0	0,016 0
Mn_3O_4	0,017 2	0,930 1	0,016 0 MnO 0,001 2 oxygen reports to flux
Ga_2O_3	0,032 0	1,000 0	0,032 0
K_2CO_3	0,023 5	0,681 2	0,016 0
CuO	0,016 0	1,000 0	0,016 0
Cr_2O_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[a][b]	3,902 0	5,853 0
High purity Al_2O_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.

Prepare the SCD as follows:

a) add the weighed reagents (to the nearest 0,5 mg) reagents to the crucible (5.1) and mix thoroughly, ensuring that no contamination or loss of material occurs. To facilitate dissolution, intimate mixing is essential;

b) transfer the crucible and contents to the furnace (5.7), which is maintained at 1 100 °C ± 25 °C;

c) maintain this temperature for 5 min, and then swirl the crucible to assist dissolution;

d) after a further 15 min at 1 100 °C ± 25 °C, swirl the crucible once more. Repeat the swirling at 5 min intervals until all alumina is fully dissolved. Place the mould (5.4) next to the crucible in the furnace at least two minutes before casting, and then pour the crucible contents into the mould. Care should be taken to maximize the transfer of the melt to the mould;

e) remove the mould and allow it to cool on a heat sink (5.7) in a contamination-free environment. After approximately 2 min, the glass will pull away from the mould and may be tapped out when cool;

f) when the glass disc is at ambient temperature, transfer it to an airtight container and store in the desiccator (5.2).

Alternatively these discs may be made using an automatic fusion machine (5.7), in this case steps 7.2.3 b to e are performed by such a device.

Prior to storage, inspect discs visually, paying particular attention to the analytical surface. The discs shall not contain un-dissolved material, and should be whole and free from crystallization, cracks and bubbles. Defective discs shall be re-fused in the crucible, or discarded and substitute discs prepared.

When not being measured, discs should be stored in a clean desiccator.

To avoid contamination of the analytical surface, handle the specimen by its edges and do not touch the surface by hand or treat in any way. Specifically, do not grind, polish or wash with water or other solvents.

If paper labels are used on the backs of discs, take great care to ensure that labels do not contact the analytical surfaces of other discs. Do not use paper envelopes to store the discs.

NOTE Paper labels and envelopes are clay coated and readily cause contamination by silicon and aluminium.

The composition of the synthetic calibration disc is given in Table 4.

Table 4 — Composition of synthetic calibration disc

Component	Concentration, %
Na_2O	1,000
SiO_2	0,050
Fe_2O_3	0,050
CaO	0,100
TiO_2	0,010
P_2O_5	0,050
V_2O_5	0,010
ZnO	0,010
MnO	0,010
Ga_2O_3	0,020
K_2O	0,010
CuO	0,010
Cr_2O_3	0,010
NiO	0,010

7.2.4 Preparation of the blank calibration discs

The masses of reagents required to prepare each blank calibration disc are given in Table 5. They may be reduced or increased proportionally to suit any other size mould.

Prepare at least two blank discs in the same manner as in 7.2.3, however weighing to within 1 mg is acceptable for these discs.

Table 5 — Reagent masses for blank calibration disc

Reagent	Mass for 35 mm mould g	Mass for 40 mm mould g
Flux[a][b]	4,000	6,000
High purity Al_2O_3 [b]	2,000	3,000

[a] This flux mass shall be corrected for loss of mass on fusion.

[b] If a flux-to-sample ratio higher than 2:1 is used, Annex C should be used to calculate new masses for Table 5.

7.3 Preparation of the sample discs

The mass of sample and the mass of flux required to prepare a test disc are given in Table 6. They may be reduced or increased proportionally to suit any other size mould. Discs are prepared in the same manner as in 7.2.3.

Flux shall be weighed to within 2 mg and the sample to within 1 mg of the tabled mass.

Table 6 — Sample and flux masses for test sample preparation

	Mass for 35 mm mould g	Mass for 40 mm mould g
Flux [a][b]	4,000	6,000
Test sample[b]	2,000	3,000

[a] This flux mass shall be corrected for loss of mass on fusion.

[b] If a flux-to-sample ratio higher than 2:1 is used, Annex C should be used to calculate new masses for Table 5.

7.4 X-ray fluorescence measurement

7.4.1 General instrumental conditions

The *Kα* analytical lines are preferred, suggested measurement conditions are given in Table 7.

All measurements shall be made under vacuum. Appropriate X-ray tube anode materials for the elements to be determined shall be used. Rhodium, scandium and scandium / molybdenum anode X-ray tubes have been found to be satisfactory for the elements specified in this International Standard. Chromium tubes are also satisfactory, unless chromium is being determined.

It is preferable, where possible to use off-peak background measurements as more reliable determinations for test samples are expected. Where the background is sloping measure two off-peak background intensities on either side of the peak position. Making a single off-peak measurement is acceptable if the background is flat.

It is recommended that X-ray detector pulse-height selection be used. If the PE crystal is used for P Kα, the X-ray flow counter detector must use a suitable pulse-height selection to exclude second order CaKβ radiation signals and its associated escape peak. The use of a Ge crystal for P Kα is recommended as it does not diffract the interfering second order CaKβ radiation.

A counting time strategy shall be used so that, for the test specimens, the relative standard deviations for counting statistical error indicated in 7.4.6 are achieved. Using these counting times, the X-ray intensity of each line shall be recorded. If required, the background intensity shall also be recorded.

If vanadium and / or chromium are being determined, spectral line overlap correction is mandatory for the effect of Ti Kβ on V Kα and V Kβ on Cr Kα

Table 7 — Suggested conditions of measurement

Kα **Line**	**Crystal**	**Theoretical peak 2θ angle, degrees**
Na	TlAP or	55,1
	Multilayer	Depends on “d” spacing
Si	PE or	109,215
	InSb or	144,6
	Multilayer	Depends on “d” spacing
Fe	LiF (200)	57,49
Ca	LiF (200)	113,09
Ti	LiF (200)	86,14
P	PET or	89,56
	Ge(III)	141,03
V	LiF (200)	76,94
Zn	LiF (200)	41,80
Mn	LiF (200)	62,97
Ga	LiF (200)	38,92
K	LiF (200)	136,76
Cu	LiF (200)	45,14
Cr	LiF (200)	69,54
Ni	LiF (200)	48,81

7.4.2 Guidelines for instrument optimization

It is recommended that correct operation of the instrument is assessed in accordance with AS 2563. Additionally, carry out X-ray intensity scans for each element to be determined (this is not possible for simultaneous instruments). This shall be done for a minimum of 1,5° either side of the theoretical 2θ peak position. Suggested counting conditions are 10 s count time per step, and 2θ angle step increments of 0,05°. The scans shall be carried out at least once prior to calibration and do not need to be repeated until a future calibration. The scans are run on prepared discs of the blank, the synthetic calibration disc, and at least one disc of the test alumina type to be analysed. They allow checking for the presence of peak and background interferences, correction of the theoretical 2θ peak positions and observation of peak-to-background ratios. If required, the choice of background correction positions shall be based on these scans. Channel setting options (e.g. tube power, crystal and collimator type) shall be set to optimize sensitivity and, if required reduce overlap effects. The presence of contamination in the blank or spectrometer shall be checked as described in B.3. Annex B further explains instrument optimization.

7.4.3 Sample loading

Present the flat analytical surface of the disc to the X-ray beam for analysis.

7.4.4 Monitor disc: correction for instrumental drift

To compensate for drift in X-ray tube output intensity, ensure all X-ray measurements are drift corrected by reference to a monitor measurement. The initial monitor measurement is made immediately prior to measuring the calibration discs. Subsequent batches of test sample disc measurements are corrected to the equivalent intensities that would have been measured had they been made at the same time as the calibration discs. This is called drift correction.

Update the monitor disc intensities regularly enough to ensure that any spectrometer drift is corrected. If samples are measured less often than on a daily basis, re-measure the monitor disc intensities with each batch of test samples analysed.

Counting times for each element measured in the monitor shall be long enough to ensure that the contribution from counting statistical error to the drift correction factor (see Formula (4) is no larger than 0,2 % relative (at one standard deviation). In practice, this means that at least 500 kilocounts in total have to be measured for each monitor-corrected element each time the monitor disc count rates are updated. The monitor disc shall be measured in the same sample cup each time it is measured. Care must be taken to ensure the monitor surface is not contaminated.

The requirements of a monitor disc used for drift correction are that it is stable with respect to intensity output and that it gives intensities for the various analytes significantly greater than intensities from the test discs. Drift correction using a monitor is only viable if the monitor being used remains stable. The stability of monitors shall be determined by normal quality control techniques, i.e. by charting control sample or reference sample results, observing statistically significant variations and correcting problems observed.

Monitor discs may contain high concentrations of silicon, ensure that the monitor's countrate for silica does not exceed the saturation threshold of the flow–proportional detector.

A method for making suitable monitor discs is given in Annex D. Commercially supplied monitors are available and have been found to be suitable1).

7.4.5 Measurements for calibration

Measure at least duplicate synthetic calibration discs (i.e. two SCD's made from the same batch of ICG) and high purity Al_2O_3 blank discs to create a calibration. The maximum allowable counting statistical errors (at one standard deviation) for the SCDs are given in Table 8.

Calculate measurement times for the SCD's (using Formula (B.1), Formula (B.2), and Formula (B.3) to achieve the counting relative standard deviations given in Table 8. For the blank discs, use the same total time as calculated for the SCD. Longer times may be used, in which case lower counting statistical errors will be achieved. Table B.1 gives examples of counting time calculations based on some real measurements. Some elements require very short times to achieve the counting statistical errors given in Table 8. For these elements counting times could easily be quadrupled with a consequent halving in counting statistical error (e.g. Ga only requires a total time of two seconds to achieve a counting statistical error of 0,000 3 %, if this time is increased to eight seconds counting statistical error will reduce to 0,000 15 %).

The measuring requirement for calibration is as follows:

a) a monitor disc. (7.4.4);

b) at least two synthetic calibration discs. (7.2.3);

c) at least two blank calibration discs. (7.2.4).

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[1] Known successful application of this method has used monitor discs supplied by Coltide (www.coltide.com.au) and Breitlander (www.breitlander.com). Mention of these suppliers is done for completeness of the method and does not imply endorsement by ISO. Others suppliers may also be appropriate.

Table 8 — Standard deviations for counting statistical errors for the measurement of the SCD’s

Analyte	Standard deviation, absolute %	Relative standard deviation (E) %
Na_2O	0,003 0	0,3
SiO_2	0,000 5	1,0
Fe_2O_3	0,000 5	1,0
CaO	0,000 5	0,5
TiO_2	0,000 3	3,0
P_2O_5	0,000 3	0,6
V_2O_5	0,000 3	3,0
ZnO	0,000 3	3,0
MnO	0,000 3	3,0
Ga_2O_3	0,000 3	1,5
K_2O	0,000 3	3,0
CuO	0,000 3	3,0
Cr_2O_3	0,000 3	3,0
NiO	0,000 3	3,0

7.4.6 Measurement of test discs

Measure test discs to counting statistical errors of ≤1 % relative standard deviation for Na_2O, SiO_2, Fe_2O_3 and CaO, and ≤3 % for all other analytes, as calculated from count rates measured on an SCD (see Annex B for calculation method).

8 Calculations

8.1 Calculation of net intensity

If background-corrected intensities are required, calculate the net intensity for each component using Formula (3):

$$l_\mathrm{n} = l_\mathrm{p} - 1_\mathrm{b} \tag{3}$$

where

l_n is the net intensity, in counts per second;

l_p is the measured intensity, in counts per second;

1_b is the intensity at the off-peak background position. Where high and low angle backgrounds are measured, refer to B.4 for the calculation method.

8.2 Comparison of duplicate measurements for the Al_2O_3 blanks and Synthetic Calibration Discs (SCDs)

8.2.1 SCDs criteria for the acceptability of duplicate measurements

Differences in intensities for duplicate SCDs shall be within a range corresponding to 3E, where E refers to the relative counting statistical error as outlined in Table 8. If this criterion is not met, identify and correct the reason for the error and repeat the measurements.

8.2.2 Al_2O_3 blanks criteria for the acceptability of duplicate measurement

8.2.2.1 Peak only measurements

The counting statistical error σ for measuring the peak only intensity for a blank disc is

$$\sigma = \left(l_\mathrm{p} / t_\mathrm{p}\right)^{1/2} \quad (4)$$

where

l_p is the measured peak intensity, in counts per second;

t_p is the the counting time on the peak, in counts per second.

Differences in peak intensities for duplicate blanks shall be within a range corresponding to 3σ [Formula (4)]. If this criterion is not met, identify and correct the reason for the error and repeat the measurements.

8.2.2.2 Net intensity measurements

The counting statistical error σ' for measuring the net intensity for a blank disc is

$$\sigma' = \left(l_\mathrm{p} / t_\mathrm{p} + l_\mathrm{b} / t_\mathrm{b}\right)^{1/2} \quad (5)$$

where

l_p is the measured peak intensity, in counts per second;

l_b is the intensity at the off-peak background position, in counts per second, or where a high and low angle background is measured, refer to B.4 for calculation of this figure;

t_p is the counting time on the peak in seconds;

t_b is the the counting time on the background in seconds.

Differences in net intensities for duplicate blanks shall be within a range corresponding to $3\sigma'$ [Formula (5)]. If this criterion is not met, identify and correct the reason for the error and repeat the measurements.

8.3 Drift correction of measured intensities

Calculate monitor-corrected intensities from the measured intensities using Formula (6):

$$I' = I \times M_0 / M \tag{6}$$

where

I' is the monitor-corrected intensity, in counts per second;

I is the measured on-peak intensity, or if using background-corrected intensities the net intensity calculated using Formula (3);

M_0 is the initial monitor intensity obtained during calibration, in counts per second;

M is the updated monitor intensity, in counts per second.

M_0 /M is referred to as the monitor drift correction factor.

8.4 Calculation of the calibration parameters

The drift-corrected intensities C are converted to concentration using Formula (7):

$$C = E \times I' - D \tag{7}$$

where

C is the concentration, in percent;

E is the calibration slope constant, in percent per counts per second;

I' is the monitor-corrected net intensity;

D is the residual background equivalent concentration below the peak.

The *D* and *E* factors are explained and determined as follows.

The *D* factor is derived from the Al_2O_3 blank measurements for each analyte. *D* represents the sum of the equivalent background concentration contributions from contaminants in the flux, the Al_2O_3 blank and from the spectrometer. If off-peak background intensities are not subtracted from peak intensities then the D value will be much larger because background from tube scattered X-rays are included in an on-peak only measurement. Subtracting the off-peak background from the peak intensity eliminates most of the scattered tube radiation background component.

Additionally if the Al_2O_3 blank contains impurities of a measured analyte, the *D* factor will be too large, biasing the test result low. Impurity analyte contamination in a batch of flux must be homogenous in order to achieve consistent test results but different batches of flux will contain different impurity concentrations. When a different batch of flux is used, changes to the D value must be determined and applied to compensate for these changes. The *D* factor can also be used to indicate variations in flux purity from batch to batch. (See Annex F).

E and *D* parameters are determined as follows:

$$E = C_0 / \left(I'_s - I'_b\right) \tag{8}$$

$$D = I'_{\mathrm{b}} \times E \tag{9}$$

where

C_0 is the percent concentration in the synthetic calibration disc of the analyte being considered (Table 3);

I'_{s} is the average monitor corrected on-peak intensity of duplicate calibration discs, or if background correction is required, the average monitor corrected net intensity calculated using Formula (3);

I'_{b} is the average monitor corrected on-peak intensity of duplicate calibration blanks, or if background correction is required, the average monitor corrected net intensity calculated using Formula (3).

Modern spectrometers incorporate software calibration packages and with some systems the calculation methodology is not disclosed. Where the methodology is disclosed and acceptable, the packages may be used provided the accuracy criteria in Clause 11 are achieved.

9 Consistency checks and reporting results

If replicate discs of a test sample are made and averages of multiple analyses reported, replicate analyses shall agree within the “r” repeatability statistic 95 % of the time. If replicate determinations fall outside this range exclude them from the average calculation. Repeatability values are given in Table 9.

Report averages to two decimal places for sodium oxide and three decimal places for all other oxides with concentrations greater than 0,005 %. Lower level traces (less than 0,005 %) may be reported to four decimal places if precision performance at one standard deviation is 0,000 2 % absolute or less. If averages fall below the lower concentration range stated in Table 1, report the result as being less than this lower concentration limit. Results shall be rounded in accordance with AS 2706.

10 Precision

The values for within-laboratory precision (i.e. repeatability, *r*) and between-laboratory precision (reproducibility, *R*) should not exceed the values given in Table 9. These values were derived from an inter-laboratory test program conducted according to AS 2850. Eight samples of different compositions and sourced from several refineries were analysed in quadruplicate. Eight laboratories participated in the test program.

Note: the repeatability, *r*, given in Table 9 is for a single sample analysis. The quadruplicate analysis used in the test program was necessary to calculate this statistic.

Table 9 — Precision results (absolute) of XRF analyses for the sample test program(at 95 % confidence level)

Analyte	**Repeatability, *r*** %	**Reproducibility, *R*** %
Na_2O^2	0,011 8c + 0,007	0,052 1c + 0,005
SiO_2	0,006 3	0,007 7
Fe_2O_3	0,002 4	0,003 2

NOTE 1 The inter-laboratory test program results for ASCRM 27 and NIST 699 are given in Annex E.

NOTE 2 The *r* and *R* values for Na_2O are expressed as a function of the mean analysis value (c) because of the inter-laboratory test program data showed this to be the case. Over the range of samples tested, similar function could not be derived for the other elements; for these the fixed values calculated are given.

Table 9 *(continued)*

Analyte	**Repeatability, *r*** %	**Reproducibility, *R*** %
CaO	0,001 4	0,002 2
TiO_2	0,001 2	0,001 3
P_2O_5	0,000 7	0,000 9
V_2O_5	0,000 9	0,001 0
ZnO	0,000 7	0,000 8
MnO	0,000 4	0,000 5
Ga_2O_3	0,000 7	0,001 0
K_2O	0,000 6	0,000 9
CuO	0,000 7	0,000 8
Cr_2O_3	0,000 6	0,000 7
NiO	0,000 7	0,000 9

NOTE 1 The inter-laboratory test program results for ASCRM 27 and NIST 699 are given in Annex E.

NOTE 2 The *r* and *R* values for Na_2O are expressed as a function of the mean analysis value (c) because of the inter-laboratory test program data showed this to be the case. Over the range of samples tested, similar function could not be derived for the other elements; for these the fixed values calculated are given.

11 Accuracy

Prior to test sample analysis the calibrations shall be verified by analysing the certified reference materials ASCRM 027 and/or NIST 699 (4.17). Average values for triplicate determinations shall lay within the "*R*" reproducibility statistic of the certified value (see Tables E.1 and E.2). If they are not, investigate the reasons and correct the cause

Results consistently biased low may be due to contamination by that element of the high purity aluminium oxide (4.2) used in the production of calibration discs. This problem can be remedied by sourcing and testing higher purity aluminium oxide as explained in 4.2.

12 Quality assurance and control

A suitable homogenous control sample shall be analysed with each batch of test samples, or at least on each day samples are analysed. Control analyses shall be charted and statistically signifiant trends and deviations from average values investigated and their causes addressed.

A useful diagnostic tool is to measure the same disc numerous times in succession on the XRF spectrometer. The standard deviation for repeat measurement for each analyte should be very close to the expected counting statistical error and this can be calculated using Formula (4), or Annex B [Formula (B.3)]. If the variability is significantly greater than counting statistical error, investigate and correct the cause. This variability is most often a consequence of instrument problems.

13 Test report

The test report shall contain the following information:

a) identification of the sample;

b) a reference to this International Standard, i.e. ISO 23201;

c) the date on which the test was carried out;

d) the sodium, silicon, iron, calcium, titanium, phosphorus, vanadium, zinc, manganese, gallium, potassium, copper, chromium, and nickel contents, expressed as oxides, and the basis on which they are reported, i.e. dried or un-dried. If samples are dried, the drying conditions used shall be stated;

e) in any case, whether the analyses were performed on a dried or un-dried sample, the drying conditions shall be included in the report;

f) any unusual observations made during the course of the test which may have had an effect on the result.

Annex A
(informative)

Contamination issues and care of platinum ware

A.1 General

Spectral interference may occur from analyte elements present in X-ray instruments, the sample preparation environment and reagents, including the flux and the high-purity alumina used for the blank. It is essential that contamination sources be identified. If the contaminant is in the blank or a variable source, it has to be eliminated. Constant sources, e.g. impurities in the X-ray tube, are compensated by the blank correction.

A.2 Platinum ware

Contamination of calibration and test sample fused glass discs can result from silica in the platinum ware and from the laboratory environment transferring to the fused glass during preparation of the disc. New platinum ware is likely to contain silica as an impurity. Platinum ware that has been used for other purposes may have taken up silica, iron and other elements in these applications. For example, if high-silica materials are prepared for XRF analysis in the platinum ware, silica contamination is likely. Steps shall be taken to eliminate all sources of contamination in sample preparation. For this purpose, platinum ware shall be fumed with hydrofluoric acid to remove silica. This conditioning need be done only once, provided that contamination does not recur. A final wash in hot 20 % hydrochloric acid, followed by rinsing with de-ionized water, completes the process and will also remove other contaminants such as iron.

If the platinum ware is exposed to high-silica materials at fusion temperatures, it may be necessary to repeat the hydrofluoric acid treatment.

An alumina of known analysis can be analysed using the treated platinum ware to check for contamination of discs made using this platinum ware.

WARNING — EXTREME CARE SHALL BE TAKEN WHEN HANDLING HYDROFLUORIC ACID. APPROPRIATE SAFETY EQUIPMENT AND HANDLING TECHNIQUES SHALL BE FOLLOWED (SEE Material Safety Data Sheet). A WASH-DOWN FUME HOOD SHALL BE USED FOR THE FUMING STEP.

General cleanliness of the sample preparation area and elimination of specific sources of contaminants are essential. It is good practice to store platinum moulds face down to avoid dust falling onto the polished face of the mould.

In routine use, crucibles and moulds should be cleaned between each fusion. Immersion in hot dilute (5 % to 10 % weight/volume) hydrochloric acid, nitric acid, citric acid, or acetic acid for about 1 h is usually sufficient, inspect to ensure that all residual glass has been removed.

A rapid method of cleaning is to put the crucible or mould into a beaker containing hydrochloric acid. This is placed in a small ultrasonic bath for about 20 min or until all residual glass is removed. Rinse in de-ionized water and dry before using.

An alternative method of cleaning is to fuse several grams of flux in the crucible, moving the melt around to clean the entire inner surface. The molten flux is then poured from the crucible. If a droplet adheres to the crucible, this can easily be flaked off when the crucible is cold.

A.3 Blank

If silica contamination of the high purity Al_2O_3 used to make the blank is suspected, treatment of the Al_2O_3 with hydrofluoric acid which volatilizes and removes the silica is effective. In a platinum vessel, slowly heat 10 g of alumina, 20 ml of water and 1 ml of 50 % hydrofluoric acid to 150 °C ± 10 °C and fume to dryness. Calcine the alumina for 2 h at 1 200 °C ± 25 °C.

WARNING — SEE A.2.

Annex B
(normative)

Example of instrument optimization

B.1 General

This Annex gives some examples of counting strategies, background correction positions and strategies in relation to contamination in the blank or the spectrometer.

B.2 Counting strategy

B.2.1 Sequential instruments

As an example of the development of a counting strategy, the case of titanium is described using off-peak background correction. All intensities used for calculating counting times and counting statistical error must not be monitor drift corrected. The following formulae are used:

$$t = t_{\mathrm{p}} + t_{\mathrm{b}} \tag{B.1}$$

$$t_{\mathrm{p}} / t_{\mathrm{b}} = \left(l_{\mathrm{p}} / l_{\mathrm{b}}\right)^{1/2} \tag{B.2}$$

$$t = \left\langle \left[\left(100 / E\right)\right] \times 1 / \left(l_{\mathrm{p}}^{1/2} - l_{\mathrm{b}}^{1/2}\right) \right\rangle^{2} \tag{B.3}$$

where

t is the total counting time, in seconds;

t_{p} is the counting time on the peak;

t_{b} is the counting time on the background;

l_{p} is the measured peak intensity, in counts per second;

l_{b} is the measured background intensity, in counts per second;

E is the percent relative standard deviation required from the analysis.

The denominator term in Formula (B.3): $\left(l_{\mathrm{p}}^{1/2} - l_{\mathrm{b}}^{1/2}\right)$ is a “figure of merit” value that can be used to compare the suitability of different spectrometer settings for measuring a particular line. The larger this factor the better will be the peak to background discrimination. An example of using this factor is collimator selection. Measure peak and background (the background either as off-peak on the same disc or on-peak on a blank disc) for the same disc(s). Use the same conditions with the exception of the collimators, where a coarse and fine collimator is used. Whichever collimator gives the greater figure of merit value will be the preferred one to use (all other factors being equal, e.g. spectral overlaps do not preclude the use of a coarse collimater). Similarly, x-ray tube power settings and crystal selection can be optimised.

The following X-ray intensities were measured for a typical test specimen:

- 86,70° 2θ 163 cps = I_b;
- 86,21° 2θ 197 cps = I_p.

Hence, for a standard deviation of 0,000 2 % TiO_2 at the 0,003 % TiO_2 level, E = 6,7 % and t = 140 s.

From Formula (B.1) and Formula (B.2), it follows that:

- t_p = 73 s;
- t_b = 67 s

B.2.2 Fixed-channel instruments

The formulae presented in B.2.1 can be used but I_b is measured instead on the alumina blank. Should the alumina blank contain a small amount of impurity, this will give a small increase in the overall count time.

B.3 Spectral interference

B.3.1 Sample - related

Titanium is typically present in alumina in much higher concentrations than vanadium, the peak for Ti Kβ will spectrally overlap the V Kα peak. In order to correct for such an interference, a blank calibration glass was made which was doped with a small amount of TiO_2. The X-ray intensity measurements in Table B.1 were made at the vanadium peak and background positions, and at the titanium peak position.

Table B.1 — Example of overlap correction

	Intensities (Counts per second)			
	V Kα	**V KαBG1**	**V KαBG2**	**Ti Kα**
Blank calibration glass	237	233	214	162
Spiked blank calibration glass	268	237	219	904
Effect	**31**	**4**	**5**	**Net 742**

From these results, the following calculations were made.

a) Effect of Ti on V Kα = 31/742 = 0,041 8.

b) Effect of Ti on V KαBG1 = 4/742 = 0,005 4.

c) Effect of Ti on V KαBG2 = 5/742 = 0,006 7.

Hence the spectral overlap correction can be made on measured vanadium X-ray intensities, i.e.

V Kα corrected = V Kα uncorrected - (Ti Kα × 0,041 8).

This is referred to as an intensity based line overlap correction.

Concentration based spectral overlap corrections are more commonly used. In this case, factors are determined to express the concentration effect on an overlapped element by a given concentration of an overlapping element. To use this approach make up a blank disc with a known concentration of the interfering element .

For the necessary example of V Kβ overlapping Cr Kα;

Make a blank disc with a weighed mass of V_2O_5 (4.9) and assuming masses as per Table 5. For a 40 mm mould, if 0,150 0 g of V_2O_5 is added to a blank composition disc, this will produce a 5,00 % V_2O_5 disc [(0,15/3,0) × 100 = 5,00 %]. If this disc is measured for % Cr_2O_3 it will have an "apparent concentration" of Cr_2O_3 from the V Kβ overlap. If this apparent concentration was 0.25 % then the concentration based overlap correction for V Kβ overlapping CrKα would be:

0,25 % Cr_2O_3 for 5 00 % V_2O_5 that is 0 050 % Cr_2O_3 for 1 00 % V_2O_5

So, 0,05 × % V_2O_5 must be subtracted from the Cr_2O_3 concentration as determined by Formula (7).

The concentration based overlap correction factor for V Kβ overlapping CrKα is −0,05 in this example.

% Cr_2O_3 corrected = % Cr_2O_3 uncorrected - (% V_2O_5 × 0,05).

These factors are readily calculated using commercially available software packages. Discs that contain independent and variable amounts of overlapping/overlapped elements can be measured and concentration based overlap corrections calculated by linear regressions.

B.3.2 Spectrometer-related

Spectral interference from anode impurities in the X-ray tube or from other parts of the spectrometer are constant and are compensated for in the blank correction.

B.4 Calculating beneath peak background from off peak background measurements

Net intensities are calculated from peak and background measurements using Formula (B.4):

$$l_{\mathrm{n}} = l_{\mathrm{p}} - l_{\mathrm{b}} \tag{B.4}$$

where

l_{n} is the net intensity, in counts per second;

l_{p} is the measured intensity, in counts per second;

l_{b} is the intensity of the "background below peak", in counts per second.

In this method, the term, l_b can be determined in three ways.

a) One single off-peak background is measured and used directly as l_{b}. This approach is valid for non-sloping backgrounds.

b) Two off-peak backgrounds are measured, one on either side of the peak and both being the same angular distance from the peak. In this case take the average of the off-peak intensities and use this as l_{b}.

c) Two off-peak backgrounds are measured, one on either side of the peak and each being at different angular distances from the peak. In this case calculate l_{b} as follows:

$$1_b = \left[\left(l_{b1} \times d\right) + \left(l_{b2} \times f\right)\right] / \left(d + f\right) \tag{B.5}$$

where

l_{b1} is the lower angle off peak background intensity, in counts per second;

l_{b2} is thehigher angle off peak background intensity, in counts per second;

d is the ($b2$-P) degrees;

f is the (P-$b1$) degrees.

where

$b2$ is the higher angle off-peak background °2θ position;

P is the peak °2θ position;

$b1$ is the lower angle off-peak background °2θ position.

Annex C
(informative)

Calculation of reagent masses for different sample/flux combinations and synthetic calibration discs when omitting some elements

C.1 General

This Annex explains how to modify the ICG to exclude analytes that are not required and how to make SCDs with different flux to sample ratios that have concentrations of analytes at values as per Table 4.

The reagent masses in Table 2 produce a total mass of 10 g of intermediate calibration glass (ICG). If certain elements are not to be measured, they may be omitted from the ICG and be replaced by the equivalent mass of flux to ensure that the total mass of ICG remains 10 g after fusion. For example, if phosphorus is to be omitted, 0,129 6 g of $NH_4H_2PO_4$ in the ICG (see Table 2) is replaced by 0,080 0 g of loss-corrected flux. This replaces the mass of P_2O_5 that remains in the SCD from $NH_4H_2PO_4$.

From: $2NH_4H_2PO_4 \rightarrow 2NH_3\uparrow + 3H_2O\uparrow + P_2O_5$ on fusion.

Also, the masses given in Table 3 are for a flux to sample ratio of 2:1. If a different flux to sample ratio is to be used, the mass of reagents required to make a synthetic calibration disc (SCD) must be re-calculated. As an example, the case of discs containing 5 g of flux and 1 g of sample (i.e. a flux to sample ratio of 5:1) is discussed. This 6 g disc would be cast in a 35 mm mould (see Table 3).

C.2 Example of calculation

The general calculation method is as follows:

a) Using a total SCD mass of 6,00 g, express the flux/sample combination as W grams of sample and therefore $(6 - W)$ grams of flux.

The mass of ICG required is

$$\text{Mass}_{\text{ICG}} = 0{,}0625 \times W \text{ grams} \tag{C.1}$$

This mass of ICG will result in analyte concentrations as per Table 4.

b) From Table 2 and knowing the mass of each of the components in the ICG, the total mass of analyte oxides in the 10 g of ICG, Ox_{ICG}, is calculated.

The total mass of flux in 10 g of ICG is

$$\text{F}_{\text{ICG}} = 10 - \text{Ox}_{\text{ICG}} \tag{C.2}$$

where

F_{ICG} is the mass of flux in the ICG;

Ox_{ICG} is the summed mass of analyte oxides in the ICG.

c) The mass of Al_2O_3 required to make up the SCD, Al_{SCD} is then

$$\mathrm{Al}_{\mathrm{SCD}} = W\left(1 - 0{,}0625 \times \mathrm{Ox}_{\mathrm{ICG}} / 10\right) \quad \text{(C.3)}$$

d) And the mass of flux F_{SCD} required to make up the SCD, is then

$$\mathrm{F}_{\mathrm{SCD}} = 6 - W\left(1 + 0{,}0625 \times \mathrm{F}_{\mathrm{ICG}} / 10\right) \quad \text{(C.4)}$$

C.3 Example

As an example, consider a 5:1 ratio (6 g) disc that does not include phosphorus:

- the mass of sample in the disc, W = 1 g;
- hence the mass of ICG required [Formula (C.1)], $\mathrm{Mass}_{\mathrm{ICG}}$ = 0,062 5 × W = 0,062 5 g;
- from Table 2, the total mass of oxide components, excluding P_2O_5, in 10 g of ICG, $\mathrm{Ox}_{\mathrm{ICG}}$ = 2,080 0 g;
- therefore, the total mass of flux in 10 g of ICG [Formula (C.2)],

$$\mathrm{F}_{\mathrm{ICG}} = 10 - \mathrm{Ox}_{\mathrm{ICG}} = 10 - 2{,}0800 = 7{,}9200 \text{ g}$$

NOTE There are three components of this flux, 3,591 3 g of B_4O_6 from the 5,191 3 g of $Na_2B_4O_7$ plus 0,001 2 g of “O” from the 0,017 2 g of Mn_3O_4 and 4,327 5 g of loss-adjusted 12:22 flux.

The mass of Al_2O_3 required to make up the SCD [(Formula (C.3)], $\mathrm{Al}_{\mathrm{SCD}}$ is then

$$\mathrm{Al}_{\mathrm{SCD}} = W\left(1 - 0{,}0625 \times \mathrm{Ox}_{\mathrm{ICG}} / 10\right) = 1\left(1 - 0{,}0625 \times 2{,}08 / 10\right) = 0{,}9870 \text{ g}$$

The mass of flux required to make up the SCD [Formula (C.4)], $\mathrm{F}_{\mathrm{SCD}}$ is then

$$\mathrm{F}_{\mathrm{SCD}} = 6 - W\left(1 + 0{,}0625 \times \mathrm{F}_{\mathrm{ICG}} / 10\right) = 6\left(1 + 0{,}0625 \times 7{,}9200 / 10\right) = 4{,}9505 \text{ g}$$

For test samples and high purity alumina calibration discs, 1 000 g of sample and 5 000 g of loss adjusted flux is used [Formula (2)].

Annex D
(informative)

Preparation of monitor disc

A suggested method for preparing a monitor disc suitable for smelter grade alumina analysis is as follows.

a) Weigh out the masses of dried reagents in Table D.1. If some weighed materials are lumpy, grind the combined weighed reagent materials in a mortar; otherwise mix reagents thoroughly with a spatula.

b) Transfer the reagents into a large (e.g. 70 ml) platinum crucible and place in a furnace at 500 °C ± 10 °C. Cover the crucible with a platinum lid. Over a period of at least 2 h, bring the temperature up to 1 200 °C ± 25 °C. Swirl the crucible thoroughly (using titanium or platinum-tipped steel furnace tongs) when the temperature reaches 1 200 °C.

c) Clean three platinum moulds and highly polish them to ensure the monitor discs release from the moulds without breaking. Place the three moulds in the furnace to pre-heat for 5 min. Prior to pouring the molten glass a small mass (0,1 g to 0,2 g) of a non-wetting agent (NH_4I or LiBr) may be added to the melt to assist pouring and reduce the possibility of the glass cracking while cooling. Swirl the crucible and pour the melt into the three moulds. Remove moulds from the furnace and cool on a ceramic tile.

d) When cooled to room temperature, tap the discs out of the moulds. Sharp disc edges may be ground down with a sharpening stone. Any visible contaminants on the surface of the monitor disc should be removed using petroleum ether. Discs are now ready for measurement.

Producing monitor discs that are not cracked and do not contain bubbles or un-dissolved reagents requires patience and often several trials. Varying cooling conditions to reduce disc cracking may be required. The monitor melt also has a higher tendency to stick to moulds and crucibles and can damage them. For these reasons, commercial monitors are often preferred.

Table D.1 — Components of monitor glass

Reagent	**Mass,** g
$Li_2B_4O_7$	8,44
Li_2CO_3	6,58
SiO_2	10,00
Al_2O_3	5,6
MgO	5,6
Fe_2O_3	1,12
TiO_2	0,56
$CaCO_3$	0,96
Ga_2O_3	0,20
Na_2CO_3	4,79
$NH_4H_2PO_4$	1,84
V_2O_5	0,56
ZnO	0,20
Mn_3O_4	0,60
K_2CO_3	1,00

Table D.1 *(continued)*

Reagent	**Mass,** g
NiO	0,40
CuO	0,20
Cr_2O_3	0,56

Annex E
(informative)

Interlaboratory test program analysis of NIST 699 and ASCRM 27 smelter grade alumina, certified reference materials

E.1 General

NIST 699 and ASCRM 27 may be used as verification materials to check the accuracy of calibrations made using this method.

NIST 699 is available from the US. National Institute of Standards and Technology.

http://ts.nist.gov/MeasurementServices/ReferenceMaterials Search for: “699”

The ASCRM 27 test report is available from SAI Global. ASCRM027 is available in limited quantities only and on a non-commercial basis from the laboratories of the following refineries; Alcoa (Kwinana), BHP (Worsley) and QAL (Gladstone) - these laboratories have representation on the Australian MN/9 committee.”

http://www.saiglobal.com/shop Search for: “alumina reference material”

This method, ISO/WD 23201, is based on method AS 2879.7–1997. Shortly after the development of the AS method eight Australian alumina industry laboratories analysed NIST 699 in quadruplicate using the AS method. Later, during 2006/7 22 international laboratories (including the original Australian participants) analysed ASCRM 27. The certified values and precision data obtained from these test programs are given in Tables E.1 and E.2 respectively.

For NIST 699, five of the analyte’s average values were lower than the method’s lower concentration range limit of 0,000 5 %. These averages are therefore included as indicative only and should be considered with reference to the calculated reproducibility (*R*) values. The values are not appropriate for checking the accuracy of analytes present at very low concentrations in alumina i.e. <0,000 5 %.

ASCRM 27 was developed between 2005 and 2010 by the AS MN/9 committee (developers of the base AS 2879.7 method) to improve the number of analyte calibrations able to be checked at levels commonly found in the alumina industry. This material contains levels measurable by this method for all but one (Ni) of the listed elements. The ASCRM 27 test report is available from SAI Global. ASCRM027 is available in limited quantities only and on a non-commercial basis from the laboratories of the following refineries; Alcoa (Kwinana), BHP (Worsley) and QAL (Gladstone) — these laboratories have representation on the Standards Australia MN/9 committee.

E.2 Procedure

The samples were dried for 2 h at 300 °C ± 10 °C and cooled in a desiccator prior to analysis, as specified on the analysis certificate. Additional significant figures to those required by Clause 9 are quoted for the “average analysis”, to enhance the usefulness of the data. The data in the average analysis column is from the original test program for AS 2879.7–1997.

Table E.1 — NIST 699 analysis and precision results. NIST certified value is included

Component	Average Analysis, %	Certificate Value, %	Repeatability r[a]	Reproducibility R[a]
Na_2O	0,61	0,59	0,013 7	0,037 7
SiO_2	0,012	0,012	0,002 9	0,004 9
Fe_2O_3	0,013	0,013	0,002 0	0,002 7
CaO	0,037	0,036	0,000 7	0,001 5
TiO_2	0,000 7	0,001[b]	0,001 0	0,001 2
P_2O_5	0,000 4	0,000 2	0,000 5	0,000 6
V_2O_5	0,000 1	0,000 5	0,000 7	0,001 0
ZnO	0,013 6	0,013	0,000 8	0,001 1
MnO	0,000 5	0,000 5	0,000 4	0,000 6
Ga_2O_3	0,010 7	0,010	0,000 7	0,000 7
K_2O	0,007 1	0,005[b]	0,000 6	0,001 2
CuO	0,000 2	0,000 5[b]	0,000 6	0,000 6
Cr_2O_3	0,000 1	0,000 2	0,000 3	0,000 6
NiO	0,000 0		0,000 6	0,000 9

[a] At the 95 % confidence level.

[b] These values are indicative, not certified.

Table E.2 — ASCRM 027 analysis and precision results

Component	Certificate Value, %	Repeatability r[a]	Reproducibility R[a]
Na_2O	0,395	0,010	0,035
SiO_2	0,013 8	0,001 3	0,002 6
Fe_2O_3	0,015 3	0,001 0	0,002 7
CaO	0,046 2	0,001 5	0,004 9
TiO_2	0,003 2	0,000 8	0,001 3
P_2O_5	0,001 2	0,000 27	0,000 57
V_2O_5	0,001 8	0,000 46	0,000 62
ZnO	0,009 0	0,000 35	0,000 89
MnO	0,001 5	0,000 24	0,001 02
Ga_2O_3	0,005 3	0,000 3	0,000 9
K_2O	0,000 7	0,000 29	0,001 14
CuO	0,001 6	0,000 28	0,000 32
Cr_2O_3	0,001 0	0,000 21	0,000 49
NiO	0,000 3	0,000 33	0,000 47

[a] At the 95 % confidence level.

Annex F
(informative)

Comments on flux purity

Due to the difficulty in obtaining reliable concentrations of impurities in X-Ray fluxes used for the analysis of smelter grade alumina, a different approach can be made using the D parameter (see 8.4). D values include intensity contributions from the flux, spectrometer and high purity alumina blank. This approach provides a useful means of monitoring implied flux impurity levels and variation between flux batches.

This approach is valid where D values are determined for off-peak background correction intensities. If the background is not subtracted, D values will be larger due to the contribution of X-ray tube continuum background and other constant instrument related sources

Since flux impurities vary between batches, the “blank” concentration must be checked and the calibration updated for each batch either by adjustment of the D parameter or recalibration. Typical acceptable concentrations calculated from D values are presented in Table F1 below. These data were obtained from 19 flux batches used by three Australian laboratories. The need for re-calibration of the D values can be minimised by purchasing larger quantities of a given batch, if usage makes this appropriate.

Table F1 — Impurity concentrations calculated from D values for X-ray flux

Analyte	**Concentration Range (ppm) over 19 batches**	**Average concentration (ppm)**
Na_2O	−150 to 70	20
SiO_2	18 to 60	35
Fe_2O_3	18 to 55	25
CaO	2 to 15	10
TiO_2	−2 to 3	1
P_2O_5	1 to 3	2
V_2O_5	−2 to 0	0
ZnO	1 to 15	4
MnO	2 to 5	3
Ga_2O_3	−2 to 2	1
K_2O	0 to 2	1
CuO	10 to 16	11
Cr_2O_3	4 to 5	5
NiO	3 to 50	18

NOTE 1 The ppm concentration of an analyte in the flux is assumed to be close to:

−10 000 X D / (ratio of flux to sample).

where: ratio of flux to sample = mass of flux / mass of sample.

NOTE 2 As seen in the table for Na_2O, it is possible to get negative D values due to sloping or curved backgrounds. Small negative values can also result from acceptable variability in the calibration process as seen for TiO_2, Ga_2O_3 and V_2O_5 where the flux has been assumed to contain near zero impurities.

NOTE 3 Higher D values can also occur from interference in the spectrometer or from the X-ray tube. For example in the table above NiO has shown a D value of 50 ppm for one instrument whereas it is typically 10 ppm on another. Since however this interference is constant and common to all measurements, it may be ignored.

Bibliography

[1] ISO 806, *Aluminium oxide primarily used for the production of aluminium — Determination of loss of mass at 300 °C and 1 000 °C*

International Organization for Standardization

ICS 71.100.10

Price based on 32 pages