

Analysis of aluminium ores —

Part 3: Method for multi-element analysis by wavelength dispersive X-ray fluorescence

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by the Non-ferrous Metals Standards Policy Committee to Technical Committee NFM/31, upon which the following bodies were represented:

- Aluminium Federation
- British Ceramic Research Ltd.
- British Geological Survey
- Department of Trade and Industry (Laboratory of the Government Chemist)
- Imperial College of Science and Technology

This British Standard, having been prepared under the direction of the Non-ferrous Metals Standards Policy Committee, was published under the authority of the Board of BSI and comes into effect on 29 September 1989

© BSI 12-1999

The following BSI references relate to the work on this standard:
Committee reference NFM/31
Draft for comment 87/40315 DC

ISBN 0 580 17094 2

Amendments issued since publication

Amd. No.	Date of issue	Comments

Contents

	Page
Committees responsible	Inside front cover
Foreword	ii
1 Scope	1
2 Principle	1
3 Preparation of the analysis sample	1
4 Reagents	1
5 Apparatus	2
6 Preparation of beads	3
7 Presentation of beads	5
8 XRF spectrometer	5
9 Ratio standard beads	6
10 Calibration standard beads	7
11 Alpha correction standard beads	8
12 Calibration	8
13 Line interference and background effects	9
14 Alpha corrections	10
15 Analysis	10
16 Correction for tungsten carbide contamination and loss on ignition	11
17 Reporting of results	11
18 Test report	11
Appendix A Tungsten carbide corrections with cobalt or nickel binder	13
Appendix B Monitoring of background and sensitivity	13
Appendix C Typical alpha corrections for rhodium end window X-ray tubes	14
Appendix D Computation of third order equations	14
Figure 1 — Example of a fusion mould	12
Table 1 — Ranges of content on the ignited basis	1
Table 2 — Maximum allowable detection limits	6
Table 3 — Composition of ratio standard beads	7
Table 4 — Silicon dioxide/aluminium oxide binaries	8
Table 5 — Minor constituents and silicon dioxide	9
Table 6 — Iron (III) oxide and minor constituents	9
Table 7 — Rhodium end window tube empirical alpha corrections ($\times 10^5$)	14
Publications referred to	Inside back cover

Foreword

This Part of BS 6870 has been prepared under the direction of the Non-ferrous Metals Standards Policy Committee. It is one of a series of Parts and Sections covering methods for the analysis of aluminium ores. General information, together with a list of contents, is given in Part 1 and chemical methods of analysis are described in Part 2.

The method described in this Part of BS 6870 is based on the fused, cast bead technique. The flux used is of low melting point, which greatly assists mixing and dissolution. Binary standard beads are used for calibration and for line interference and background corrections, and binary or tertiary standard beads for inter-element (alpha) corrections; this ensures that each of these parameters is determined separately. An ignited sample and an ignited-basis flux are used, so that dilution of sample in the melt is constant, hence simplifying calibration and analysis.

A similar technique is described in BS 1902-9.1, which uses many of the same calibration standards.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 16, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope

This Part of BS 6870 describes a method for the analysis of aluminium ores using wavelength dispersive X-ray fluorescence.

It is applicable to materials containing not more than 40 % of iron (III) oxide (Fe_2O_3) on the ignited basis. The ranges of content of constituents covered by this standard are given in Table 1.

Table 1 — Ranges of content on the ignited basis

Oxide	Range
	% (m/m)
Silicon dioxide (SiO_2)	0.5 to 30
Aluminium oxide (Al_2O_3)	20 to 100
Iron (III) oxide (Fe_2O_3)	0.05 to 40
Titanium oxide (TiO_2)	0.05 to 8
Calcium oxide (CaO)	0.05 to 2
Magnesium oxide (MgO)	0.05 to 2
Phosphorus pentoxide (P_2O_5)	0.05 to 5
Gallium oxide (Ga_2O_3)	0.005 to 0.2
NOTE Other elements may be added as necessary, and in particular tungsten oxide (WO_3) [0.02 % to 5 % (m/m)] where a material containing tungsten carbide is used for sample preparation.	

NOTE The titles of the publications referred to in this standard are listed on the inside back cover.

2 Principle

The powdered sample of aluminium ore is fused with a flux to destroy its mineralogical and particulate composition. The resultant melt is cast into a glass bead which is introduced into an X-ray fluorescence spectrometer. The intensities of the fluorescent X-rays of the required elements in the bead are measured and the chemical composition of the sample is determined by reference to calibration graphs or equations.

3 Preparation of the analysis samples

First check the sample with a magnet for adventitious iron, which may have been introduced during the crushing/grinding of the bulk sample.

Then finely grind the sample (the bulk to be finer than 150 μm equivalent spherical diameter), using equipment made from a material which will not contaminate the sample, for example an agate pestle and mortar. When tungsten carbide equipment, for example a swing mill or percussion mortar, is used for the preparation of very hard aluminium ores, such as diaspore-types or those containing free quartz, monitor any contamination and apply appropriate corrections to the analysis and loss on ignition figure (see clause 16).

NOTE Further corrections resulting from the binder in the tungsten carbide are shown in Appendix A.

4 Reagents

4.1 Flux.¹⁾ The flux shall be a mixture of one part by mass lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) to four parts by mass lithium metaborate (LiBO_2), the ratio being of the dry reagents. Both flux reagents shall be of an analytical quality.

In practice the flux will contain moisture which shall be corrected for in one of the following two ways.

- Immediately before it is to be used for the analysis, ignite the required quantity of flux overnight at 700 °C and then store in a desiccator.

¹⁾ For information on the availability of suitable premixed fluxes, apply to the Enquiry Section, BSI, Linford Wood, Milton Keynes MK14 6LE, enclosing a stamped addressed envelope for reply.

b) Determine duplicate losses on ignition on 1 g portions of the well-mixed contents of each kilogram of flux used: this shall be either at 700 °C for 1 h or at 1 200 °C for 10 min. Keep the flux tightly sealed except when in use. Determine the loss on ignition weekly, or for each kilogram of flux used, whichever is the more frequent. The loss on ignition is then used to calculate the mass of the unignited flux m_u (in g) needed to produce the required mass of flux on the ignited basis [see equation (1)].

$$m_u = \frac{100m_i}{100 - L} \quad (1)$$

where

m_i is the required mass of the flux on the ignited basis (in g);

L is the loss on ignition (in %).

Recheck calibrations when batches of flux are changed.

4.2 Oxides or carbonates for glass beads. The reagents used to prepare the standard beads shall be pure oxides or carbonates of at least 99.95 % purity (excluding moisture or CO₂) for minor constituents and of at least 99.99 % purity for silicon dioxide, aluminium oxide and iron (III) oxide. The Ga₂O₃ content in all oxides and carbonates shall be less than 0.001 % (m/m).

In order to obtain the reagents in a known stoichiometry in terms of content they shall be treated before use as follows.

a) *Silicon dioxide, aluminium oxide and magnesium oxide.* Immediately before use, determine the loss on ignition by igniting a known mass at 1 200 °C for 30 min. Cool in a desiccator to room temperature, reweigh and calculate the loss in mass. After allowing for this loss, weigh the appropriate amount of the unignited material to prepare the standard bead.

NOTE 1 A granular form of silicon dioxide and aluminium oxide is preferable, since finely powdered or flaky forms have been shown to yield inconsistent loss on ignition results. It is advisable to use phosphorus pentoxide as desiccant for these reagents.

b) *Titanium oxide.* Ignite at 1 000 °C for 30 min before use. Cool in a desiccator to room temperature.

c) *Iron (III) oxide and lithium orthophosphate.* Ignite at 700 °C for 30 min before use. Cool in a desiccator to room temperature.

d) *Calcium carbonate, gallium oxide and tungsten oxide.* Dry at 220 °C to constant mass before use. Cool in a desiccator to room temperature.

NOTE 2 A 2 h treatment is usually sufficient for drying.

NOTE 3 If very hard aluminium ores have been prepared using tungsten carbide equipment (see clause 3), tungsten may have been introduced as a contaminant. Laboratories using tungsten carbide for sample grinding should therefore calibrate for WO₃ in order to monitor its presence in samples. If necessary the analysis and the loss on ignition should be corrected for tungsten carbide contamination (see clause 16).

5 Apparatus

5.1 Fusion dishes, made from a platinum alloy that is not wetted by the melt. They shall be of sufficient capacity to hold the quantity of unfused flux and sample required by the size of the casting mould.

NOTE 1 An alloy consisting of 95 % platinum and 5 % gold is suitable.

NOTE 2 For a 35 mm diameter bead, where 1.5 g sample and 7.5 g flux are used, a fusion dish of 50 mL capacity is suitable.

5.2 Casting moulds,²⁾ made from a platinum alloy that is not wetted by the melt (see note 1 to 5.1). The moulds shall be designed to give a circular bead of a diameter within the range 25 mm to 40 mm and of thickness to exceed the critical depth for the element lines used in analysis. The sides shall be set at a suitable angle to the vertical to ensure that the beads are readily released. If the top surface of the bead is to be used for analysis, there shall be a horizontal rim to the casting mould and the mass of melt shall be sufficient to fill the mould and give a reproducible curved top surface.

NOTE Calibration and analysis should be carried out using the same pattern and size of casting mould throughout. If any changes in moulds are made, recalibration is required for top surfaces. For flat-bottomed surfaces recalibration is necessary if the change in diameter of the mould requires a different aperture of the spectrometer sample holder.

²⁾ For information on the availability of suitable casting and fusion moulds, apply to the Enquiry Section, BSI, Linford Wood, Milton Keynes MK14 6LE, enclosing a stamped addressed envelope for reply.

5.3 Fusion moulds,³⁾ made from a platinum alloy that is not wetted by the melt (see note 1 to 5.1). This is an optional alternative to 5.1 and 5.2, allowing both fusion and casting to be carried out in the same vessel (see Figure 1).

The volume of the dish shall be sufficient to hold the amount of unfused sample and flux required to fill the mould part of the vessel when fused. The mould part of the vessel shall comply with 5.2. In particular, if the top surface of the bead is to be used for analysis, a horizontal rim shall be interposed between the top of the mould and the sides of the dish.

NOTE 1 If the rim is not present, concave top surfaces will be produced on the beads, which, if used, would not be conducive to accurate analysis.

NOTE 2 Once a size and type of mould has been selected it should be used throughout; if it is changed, recalibration is required.

5.4 Lids for dishes and fusion moulds, large enough to cover the vessels completely and made from an alloy of platinum, although not necessarily a non-wetted alloy.

NOTE Platinum itself is suitable.

5.5 Heat reservoir for casting mould (optional)

NOTE A heat reservoir is usually required, especially when using moulds of small sizes, so that the mould does not cool too rapidly when removed from the furnace. A small piece of flat refractory material is suitable, e.g. a piece of sillimanite batt with approximate dimensions 10 mm thick by 50 mm square.

5.6 Air jet (optional)

NOTE An air jet helps to free the melt from the dish and cool the former rapidly. This can be any device whereby a narrow jet of air can be directed to the centre of the base of the casting dish. A convenient way to do this is to use the base of a Bunsen burner without a barrel.

6 Preparation of beads

6.1 Loss on ignition

The mass of sample resulting after the loss on ignition determination shall be sufficient to produce an adequate mass of sample for the fusion procedure. In practice the mass required will be 2 g to 3 g weighed to ± 0.0005 g.

Dry the ground sample at 110 ± 5 °C for at least 4 h or to constant mass. Store the samples in a desiccator containing phosphorus pentoxide while cooling.

Weigh accurately 2 g to 3 g into a suitable fusion dish (5.1) or fusion mould (5.3) of known mass. Almost completely cover the vessel with a lid. Then either place the vessel in a muffle furnace and slowly increase the temperature to $1\ 075 \pm 25$ °C, or start the ignition over a low flame, taking care to ensure oxidizing conditions, and slowly increase the temperature to a dull red heat over a period of 20 min, then transfer the vessel to a furnace at $1\ 075 \pm 25$ °C.

NOTE 1 A tunnel kiln programmed to meet the above requirements may be used to carry out the slow increase in temperature and subsequent ignition.

Ignite to constant mass at this temperature.

NOTE 2 Ignition for 60 min is usually sufficient.

Remove the vessel from the furnace, completely cover with the lid, cool to room temperature in a desiccator and reweigh immediately.

Correct the recorded loss on ignition figure for the effect of any tungsten carbide introduced into the sample being oxidized to WO_3 (see clause 16).

6.2 Fusion of samples and casting of beads

NOTE At several of the stages, a choice of procedures is given. Once a choice has been made, the procedure should be adhered to throughout, unless a recalibration is carried out.

6.2.1 General. Before fusing the samples and casting the beads, the following requirements shall be satisfied.

- a) Duplicate or single beads may be prepared; the method used shall be stated in the test report (see clause 18).

NOTE Duplicate beads are preferable to single beads.

³⁾ For information on the availability of suitable casting and fusion moulds, apply to the Enquiry Section, BSI, Linford Wood, Milton Keynes MK14 6LE, enclosing a stamped addressed envelope for reply.