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Analysis of aluminium ores —

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

Committees responsible for this British Standard

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Aluminium Federation
British Ceramic Research Ltd.
British Geological Survey
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Imperial College of Science and Technology

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Contents

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.

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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 ($Li_2B_4O_7$) 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.

a) 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)].

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

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 CO_2) for minor constituents and of at least 99.99 % purity for silicon dioxide, aluminium oxide and iron (III) oxide. The Ga_2O_3 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 WO_3 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 ± 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 ± 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.

b) The total mass of sample and flux shall be chosen for the particular casting mould type used, and this mass shall always be the same.

c) The ratio by mass of the flux to the sample shall be 5 : 1.

d) The melts produced shall be homogeneous.

e) There shall be no measurable loss of any component from the sample during fusion, e.g. loss of Fe_2O_3 by reduction or loss of volatile oxides due to evaporation (excessive temperature).

f) Any loss of flux during fusion shall be reproducible.

g) The process shall not contaminate the sample in any way that affects the analysis.

h) Beads produced shall be free from blemishes on the chosen analytical surface.

i) If the top surface of the bead is to be used for analysis, it shall be either convex or flat and be symmetrical across any diameter.

j) Standard beads of known composition shall be prepared in the same way as sample beads.

6.2.2 *Fusion*. Weigh an amount designated m (in g) [see **6.2.1** b)] of the ignited sample (or sufficient of the sample dried at 110 °C to yield m on the ignited basis) into the fusion dish (see **5.1**). Then weigh an amount equal to $5m$ of the ignited flux (or mass of the flux on the as-received basis to yield $5m$ on ignition) into the dish. Thoroughly mix the sample and flux and cover the dish with the lid.

Fuse the sample and flux together, with occasional swirling until the sample is seen to be dissolved and the melt homogeneous.

NOTE Although a 1 200 °C furnace can be used for this purpose, losses of flux can occur and it is more satisfactory and convenient to use a gas burner for the fusion process.

After the decomposition is complete, transfer the fusion dish, together with its lid, and the casting mould (**5.2**), on its heat reservoir (see **5.5**) if used, into a 1 200 °C furnace.

6.2.3 ***Casting of beads***

6.2.3.1 *General.* Cast the beads using one of the following methods.

a) *Outside the furnace*. After 5 min at 1 200 °C, remove the casting mould and heat reservoir from the furnace and place on a horizontal surface. Remove the lid from the fusion dish, then remove the dish from the furnace and immediately pour the melt into the mould.

Proceed in accordance with **6.2.3.2**.

NOTE When the top surface of the bead is used for subsequent analysis, a rippled surface produced in the casting process can lead to erroneous results. In order to avoid this effect the melt should be poured into the mould, at a point nearer to the edge of the mould than the centre.

NOTE When using top surfaces, in order to maintain a uniform curvature on the top surface, it is necessary to get as much of the melt into the casting mould as possible so as to achieve consistent bead masses.

b) *In the furnace*. After 5 min at 1 200 °C, remove the lid from the fusion dish and pour the melt into the mould inside the furnace, ensuring that as much of the melt is transferred to the mould as possible. Remove the mould from the furnace and place on a horizontal surface.

Proceed in accordance with **6.2.3.2**.

c) *Combined fusion mould*. After 5 min at 1 200 °C, remove the fusion mould from the furnace and by swirling ensure the transfer of the whole of the melt into the mould part of the dish.

Proceed in accordance with **6.2.3.2**.

d) *Mould heated over a burner*. Heat the casting mould to red heat over a Meker (or similar) burner. After heating the fusion dish at 1 200 °C for 5 min, remove it from the furnace, take off the lid and pour the melt into the mould. Turn the burner off and allow the melt to solidify. Alternatively, an air jet can be used to assist cooling as described in **6.2.3.2**.

NOTE Small amounts of lithium iodide or iodate may be added to assist in releasing the beads from the mould, hence preventing their cracking on cooling.

6.2.3.2 *Cooling of beads*. Allow the mould to cool on a horizontal surface. If the air jet (see **5.6**) is used, transfer the mould to it when the melt has cooled from red heat. The melt may be molten or solid at this stage; if it is molten and top surfaces are to be measured, ensure that the support over the air jet is horizontal.

Hold the dish in a horizontal position above the air jet so that the air is directed on to the centre of the base of the mould. When the bead has solidified and released itself, turn off the air jet.

NOTE It may be necessary to encourage the release of the beads at this stage by gently tapping the casting mould on to a solid surface.

6.2.4 *Automatic bead preparation*. Automatic bead equipment may be used provided that it complies with **6.2.1**.

7 Presentation of beads

Either the top (curved) or bottom (flat) surface may be presented to the instrument. Whichever surface is chosen, however, it shall be used for all beads, otherwise recalibration will be required.

The bead surface to be analysed shall be inspected for blemishes and if they are present a fresh bead shall be fused.

If the bottom surface is used, the moulds shall be kept in condition by frequent polishing. On any sign of bowing the dish shall be reformed.

The beads shall be introduced into the instrument so that the chosen surface is irradiated by the X-ray tube.

8 XRF spectrometer

8.1 General requirements

NOTE Because of the inherent differences in commercial XRF spectrometers, it is not possible to specify conditions too closely. It is better to define the requirements of the spectrometer to meet the needs of the analysis.

The XRF spectrometer shall comply with the following.

a) It shall be used and maintained in accordance with any limitations imposed by the manufacturer.

b) It shall be able to achieve the detection limits given in **8.3**.

c) The X-ray lines, crystals, collimators, detectors, use of off-peak backgrounds and pulse height analysis shall be chosen wherever possible to avoid line overlap. Any line overlap occurring shall be minimized, so that any corrections applied shall be small and not contribute a significant proportion of the measured intensity for that element.

NOTE Typical lines used are given in column 1 of Table 7 in Appendix C.

d) The reproducibility due to the combined effects of instrumental variability and drift shall be:

1) ± 0.5 % relative (e.g. ± 0.25 % at 50 %) for major oxides greater than 10 %;

2) ± 0.1 % actual for minor oxides between 1 % and 10 %;

3) ± 0.03 % actual for minor oxides less than 1 %.

NOTE If the requirements cannot be achieved, a diagnosis should be made and remedial action should be taken. If the requirements are not met for any element for the particular X-ray spectrometer used, then results should not be reported for the element by the XRF method.

A bead prepared using a certified reference material[4)] shall be presented to the spectrometer with each batch of samples and the results achieved shall satisfy these requirements.

8.2 Dead time

One of the following methods shall be used to overcome dead time, i.e. the time when the counter is unable to respond because it is already occupied in counting a previous pulse.

a) The detector shall be used within its linear response region.

NOTE For most constituents, the response will effectively be linear, but for iron it is likely to be non-linear.

b) An electronic dead-time corrector shall be used to produce linear response.

c) Dead times shall be calculated for each detector and a mathematical correction applied to their counts.

[4)] For information on the availability of suitable certified reference materials, apply to the Enquiry Section, BSI, Linford Wood, Milton Keynes MK14 6LE.

8.3 Detection limits

The maximum allowable detection limits shall be as given in Table 2.

Table 2 — Maximum allowable detection limits

Oxide	Detection limit[a]
	(%)
SiO_2	0.05
TiO_2	0.05
Al_2O_3	0.05
Fe_2O_3	0.05
CaO	0.05
MgO	0.05
P_2O_5	0.05
Ga_2O_3	0.005
WO_3	0.02

[a] The percentage detection limit = $\frac{3\sqrt{2N}}{M}$

where

N is the number of counts (count rate × integration time) obtained for the oxide from the 100 % Al_2O_3 standard or the 100 % SiO_2 standard in the case of Al_2O_3;

M is the sensitivity of the oxide expressed as number of counts per percentage.

NOTE If these requirements are not met for any element, the determination should be carried out by the appropriate wet chemical method given in BS 6870-2.

9 Ratio standard beads

9.1 General

In order to monitor and compensate for drift, which as in any instrumental technique can be a problem on a long-term basis (greater than 1 day), both sensitivity and background shall be monitored with a series of ratio standard beads.

The sensitivity shall be measured in accordance with **9.2** and **9.3** or alternatively using the method described in note 1 to Appendix B.

The ratios shall be used for plotting the calibrations, for calculation of interelement corrections and for determinations in the course of analysis. In addition, the ratio standard beads shall also be used to monitor backgrounds and sensitivities for the various oxides measured. If the count ratios for check standard beads change significantly, then the fault causing this change shall be rectified.

The 100 % Al_2O_3 standard bead serves as the ratio standard bead for Al_2O_3 and the zero or background standard bead for SiO_2, TiO_2, Fe_2O_3, CaO, MgO, P_2O_5, Ga_2O_3, and WO_3. A 100 % SiO_2 standard bead serves as the zero or background standard bead for Al_2O_3.

The composition of these standard beads shall be as shown for ratio standards 1 and 2 in Table 3.

Table 3 — Composition of ratio standard beads[a]

Oxide	Ratio standard 1	Ratio standard 2	Ratio standard 3
	(%)	(%)	(%)
SiO_2	0	100	30
TiO_2	0	0	8
Al_2O_3	100	0	16.8
Fe_2O_3	0	0	35
CaO	0	0	2
MgO	0	0	2
P_2O_5	0	0	5
Ga_2O_3	0	0	0.2
WO_3	0	0	1

[a] These percentages are expressed on the basis of a sample fused into a bead in the manner described (see **6.2**) (not the bead itself).

A third standard bead is necessary to compensate for changes in sensitivity for minor constituents.

NOTE The concentration of the minor constituents in the standard bead chosen should be close to the highest content in each case. A recommendation for the composition of a single bead for minor constituents is given in ratio standard 3 in Table 3.

These three ratio standard beads shall be used every time calibration standard beads or a sample or series of samples for analysis are run. The counts produced for a standard bead or sample shall be converted to a ratio, R, in accordance with **9.2** and **9.3**.

9.2 For aluminium oxide

Determine the ratio for aluminium oxide, R_A, from the equation:

$$R_A = \frac{N_{A2} - N_A}{N_{AR} - N_A} \quad (2)$$

where

N_A is the count obtained for Al_2O_3 on the ratio standard 2 bead;

N_{AR} is the count obtained for Al_2O_3 on the ratio standard 1 bead;

N_{A2} is the count obtained for Al_2O_3 on the sample or calibration standard bead.

9.3 For minor constituents

Determine the ratio for minor constituents, R_M, from the equation:

$$R_M = \frac{N_{M2} - N_M}{N_{MR} - N_M} \quad (3)$$

where

N_{M2} is the count from the sample or standard bead for the relevant minor constituent;

N_M is the count from the ratio standard 1 bead for the relevant minor constituent;

N_{MR} is the count from ratio standard 3 bead (see Table 3) or other composition used, for the relevant minor constituent.

10 Calibration standard beads

The pure aluminium oxide standard bead acts as a zero standard bead for all oxides but aluminium oxide. The other calibration standard beads are binaries of the oxide in question and aluminium oxide which add up to the equivalent of 100 %.

For WO_3 and Ga_2O_3, there shall be at least two equally spaced standard beads plus the zero. For TiO_2, CaO, MgO and P_2O_5 (see note) there shall be at least three equally spaced standard beads plus the zero. For Fe_2O_3 there shall be five equally spaced standard beads plus the zero. The top standard in each case shall be at the top of the range (see Table 1).

NOTE P_2O_5 cannot be added as the oxide. Its addition in the form of lithium orthophosphate, Li_3PO_4, is therefore recommended. When preparing the standard beads, the oxides excluding Li_2O should add up to 100 %, i.e. the extra mass of Li_2O should be subtracted from the mass of flux used for the standard bead. (0.63 % Li_3O_4 is added for 1 % P_2O_5.)

Calibration standards for SiO_2 and Al_2O_3 are given in Table 4.

All the calibration standard beads shall be used to establish line interference effects and background effects of these oxides on the other oxides.

Table 4 — Silicon dioxide/aluminium oxide binaries

Standard bead no.	Composition
1	5 % SiO_2 + 95 % Al_2O_3
2	10 % SiO_2 + 90 % Al_2O_3
3	20 % SiO_2 + 80 % Al_2O_3
4	30 % SiO_2 + 70 % Al_2O_3
5	40 % SiO_2 + 60 % Al_2O_3
6	50 % SiO_2 + 50 % Al_2O_3
7	60 % SiO_2 + 40 % Al_2O_3
8	70 % SiO_2 + 30 % Al_2O_3
9	80 % SiO_2 + 20 % Al_2O_3
NOTE All nine standards are used to calibrate aluminium oxide and to derive the alpha effects of Al_2O_3 on SiO_2. Standards 1 to 4 are used in the ultimate calibration of silicon dioxide.	

11 Alpha correction standard beads

The standard beads described in Table 5 shall be used to establish the effects of SiO_2 and on SiO_2. Those described in Table 6 shall be used to establish the effects of Fe_2O_3 and the other minor constituents on each other. Each constituent of the standard bead shall be weighed to an accuracy of 0.0005 g.

NOTE Although corrections for the effects of each oxide on all other oxides are theoretically necessary, in practice they do not all need to be determined. For example, it does not add significantly to the accuracy to determine the effect of WO_3 or Ga_2O_3 on the other constituents, or (because it is serving only as a correction) the effects of the other oxides on WO_3.

12 Calibration

12.1 Oxides other than aluminium oxide, silicon dioxide and iron (III) oxide

NOTE For all oxides except SiO_2 and Fe_2O_3 and possibly Al_2O_3 the calibrations are straight lines; it is not necessary to correct for the alpha correction of Al_2O_3 on the oxide calibrated.

For each oxide, plot the ratio defined in clause **9** against the concentration, ensuring that all points on the calibration graph are within the limits of experimental error [see **8.1** d)]. Rerun any standard beads that are out of line, and if they still do not plot, remake them.

12.2 Aluminium oxide

Plot the ratio against the concentration in accordance with **12.1** for all the standards in Table 4 plus the 100 % SiO_2 (ratio standard 2) zero point.

NOTE 1 The alpha correction of SiO_2 on Al (Kα) is small ($\simeq 2 \times 10^{-4}$) and it is not therefore necessary to calculate the correction in accordance with **12.3**.

NOTE 2 The relationship between the ratio and concentration is normally a straight line, but it may be necessary to express it as a quadratic or even cubic equation (with low non-linear terms) in order to obtain the best fit. Cubic equations should be avoided wherever possible. However, if needed, a method of calculation is given in Appendix D.

12.3 Silicon dioxide and iron (III) oxide

Plot the ratio against the concentration in accordance with **12.1**. For Si (Kα) and Fe (Kα), the alpha correction is significant and a correction has to be applied. Calculate the alpha correction effect of the matrix oxide as follows.

Calculate the ratios for the non-zero standard beads. Calculate an E factor by dividing the ratio into the concentrations of the percentage oxide calibrated. Plot the E value on the y axis against the interfering oxide (Al_2O_3) concentration expressed as a percentage. In the case of silicon dioxide, include the ratio standard 2 bead and all the standards from Table 4 in this plot. The intercept of the y axis will give E_o (which is the calibration slope if no aluminium oxide were present). Calculate the slope of the graph K (increasing left to right being positive); the alpha correction is given by K/E_o.

NOTE The graph should be a straight line and the slope factor should be positive for SiO_2 and negative for Fe_2O_3.

Table 5 — Minor constituents and silicon dioxide

Standard bead	Alpha corrections identified
8 % TiO_2 + 30 % SiO_2 + 62 % Al_2O_3	TiO_2 on SiO_2; SiO_2 on TiO_2
2 % CaO + 30 % SiO_2 + 68 % Al_2O_3	CaO on SiO_2; SiO_2 on CaO
2 % MgO + 30 % SiO_2 + 68 % Al_2O_3	MgO on SiO_2; SiO_2 on MgO
5 % P_2O_5 + 30 % SiO_2 + 65 % Al_2O_3	P_2O_5 on SiO_2; SiO_2 on P_2O_5

Table 6 — Iron (III) oxide and minor constituents

Standard bead	Alpha corrections identified
32 % Fe_2O_3 + 8 % TiO_2 + 60 % Al_2O_3	Fe_2O_3 on TiO_2; TiO_2 on Fe_2O_3
32 % Fe_2O_3 + 2 % CaO + 66 % Al_2O_3	Fe_2O_3 on CaO; CaO on Fe_3O_3
32 % Fe_2O_3 + 2 % MgO + 66 % Al_2O_3	Fe_2O_3 on MgO; MgO on Fe_2O_3
32 % Fe_2O_3 + 5 % P_2O_5 + 63 % Al_2O_3	Fe_2O_3 on P_2O_5; P_2O_5 on Fe_2O_3
32 % Fe_2O_3 + 0.2 % Ga_2O_3 + 67.8 % Al_2O_3	Fe_2O_3 on Ga_2O_3 only
8 % TiO_2 + 2 % CaO + 90 % Al_2O_3	TiO_2 on CaO; CaO on TiO_2
8 % TiO_2 + 5 % P_2O_5 + 87 % Al_2O_3	TiO_2 on P_2O_5; P_2O_5 on TiO_2
8 % TiO_2 + 0.2 % Ga_2O_3 + 91.8 % Al_2O_3	TiO_2 on Ga_2O_3 only
2 % CaO + 2 % MgO + 96 % Al_2O_3	CaO on MgO; MgO on CaO
2 % CaO + 5 % P_2O_5 + 93 % Al_2O_3	CaO on P_2O_5; P_2O_5 on CaO
NOTE CaO will have an α-correction on Ga_2O_3, but for the small amounts of Ga_2O_3 and CaO present, the α-correction derived for TiO_2 on Ga_2O_3 will serve as the (α-correction for CaO on Ga_2O_3.	

In order to produce the corrected ratio, R_T, the ratios obtained from the standard beads are corrected using the equation:

$$R_T = R_A (1 + \alpha C) \quad (4)$$

where

R_A is the apparent ratio obtained directly from the standard bead;

α is the alpha correction as derived above;

C is the percentage concentration of aluminium oxide in the standard bead.

In the case of silicon dioxide, standards above 30 % SiO_2 are not necessary for the calibration itself.

The calibration is now the relationship of concentration of the oxide calibrated against these values of R_T and should be linear. These values of R_T are used in the calculation of alpha corrections of other oxides on Fe_2O_3 and SiO_2.

If the calibration point produced by any bead is noticeably further away from the calibration curve than any of the other points, it shall be rerun. If it still misplots, it shall be remade.

12.4 Replacement of flux

Whenever a new batch of flux is used, check the blank levels of all minor constituents and the sensitivities of all elements determined. If the calibrations are affected, either reject the flux and use a fresh batch or carry out a new calibration, for the elements affected, with the new flux.

13 Line interference and background effects

These effects shall be measured as the apparent percent of the oxide being interfered, which is produced by 1 % of the interfering oxide.

NOTE For example, if a 2 % CaO + 98 % Al_2O_3 standard gives an apparent figure of 0.01 % of MgO, the interference correction of CaO on MgO is 0.005.

14 Alpha corrections

The alpha corrections shall be measured using the alpha correction standard beads. The ratio obtained from the alpha correction standard bead shall first be corrected for any background or line interference effects, giving a value of the apparent ratio. The alpha correction, α, is then derived from the equation:

$$\alpha = \frac{R_T - R_A}{C_j \, R_A}. \quad (5)$$

where

R_T is the true ratio as derived from the established calibrations (see clause **12**);

R_A is the apparent ratio;

C_j is the concentration of the interfering oxide (in %).

NOTE 1 As an example in calculating the α-correction of CaO on TiO_2, a standard bead with 2 % CaO + 8 % TiO_2 gives a ratio of 0.9778 for TiO_2. Correcting for a 2 % CaO + 98 % Al_2O_3 standard bead giving a ratio of 0.0002, the ratio becomes 0.9776. The 8 % TiO_2 calibration has a ratio of 0.998.

Therefore

$$\alpha = \frac{0.998 - 0.9776}{0.9776 \times 2} = 0.01043$$

NOTE 2 As a guide, alpha corrections obtained for a rhodium end window X-ray tube are given in Appendix C.

15 Analysis

15.1 In most cases the X-ray spectrometer will have a computer attached, which can store the calibrations in terms of their coefficients and can rapidly go through the necessary correction loops in order to produce the final figures. Failing that, an off-line computer can be used for this purpose. If neither of these situations pertain, it is possible to compute the results by hand using the coefficients derived in accordance with Appendix D.

15.2 Run the samples and any check standard beads against the top and bottom ratio standard beads for each oxide being determined. From the raw intensities, calculate the ratios. From these and the calibration coefficients (see **15.1**), use a first estimate of percentages to apply alpha corrections to the true ratio, R_T, using the equation:

$$R_T = R_A \, (1 + \Sigma \, \alpha_{ij} \, C_j) \quad (6)$$

where

R_A is the apparent ratio, as defined in clause **14**;

C_j is the concentration of the interfering oxide (in %);

α_{ij} is the alpha correction of the interfering oxide on the oxide being determined.

Using the corrected true ratios, R_T, calculate the apparent concentrations C_A (in %) and then correct these for line interference to give the true concentrations C_T (in %), using the following equation for element j on element i:

$$C_T = C_A - \Sigma \, K_{ij} \, C_j \quad (7)$$

where

K_{ij} is the line interference correction.

This process will be iterative until a constant value is obtained for all the concentrations. Correct the results for loss on ignition and any possible WO_3 contamination (clause **16**).

Ensure that the results for duplicates for major oxides are within 0.3 % of each other. For minor constituents, ensure that the duplicates are within 0.1 % of each other where the constituent is present in quantities of 1 % or more. Where the constituent is present in quantities of less than 1 %, ensure that the duplicates are within 0.05 % of each other. If this is not the case, rerun the beads and if this still fails to give agreement prepare new fused beads.

Run a standard bead prepared from a suitable certified reference material [see **8.1** d)] with each batch and report its results with those of the samples.

16 Correction for tungsten carbide contamination and loss on ignition

The true loss on ignition at 1 025 °C, L_T, is given as a percentage by the equation:

$$L_T = 100\left(1 - \left[\frac{\left(\frac{1 - W}{100}\right)}{\left(\frac{1}{1 - \frac{L}{100}}\right) - \left(\frac{WB}{100}\right)}\right]\right) \quad (8)$$

where

L is the measured loss on ignition at 1 025 °C (in %);

W is the tungsten oxide measured by the XRF spectrometer on the cast bead (in %);

B is the $\frac{\text{relative molecular mass of tungsten carbide}}{\text{relative molecular mass of tungsten oxide}}$

$= 0.8847$.

The factor f to correct back the results both for the effects of dilution with tungsten carbide and the loss on ignition is given by the equation:

$$f = \frac{1}{\left(\frac{1}{1 - \frac{L}{100}}\right) - \left(\frac{WB}{100}\right)} \quad (9)$$

where

L, W and B are as defined in equation (8).

If tungsten carbide has not been used during the grinding of the sample then $W = 0$ and equation (9) reduces to:

$$f = \frac{100 - L_T}{100} \quad (10)$$

The percentage oxide concentration in the original sample C_o (oven dried at 110 °C) is given by the equation:

$$C_o = C_{om} \times f \quad (11)$$

where

C_{om} is the concentration of the oxide as measured (in %).

NOTE Equations 8 to 11 do not account for the cobalt or nickel binder usually used in tungsten carbide mortars. This will not cause any significant error. The full equation is given in Appendix A.

17 Reporting of results

Results shall be reported on a dry basis (dried to constant mass at 110 °C).

18 Test report

The test report shall contain the following information.

a) The name of the testing establishment.

b) The date of the test.

c) A reference to this British Standard, i.e. BS 6870-3:1989.

d) A description of the material tested.

e) Whether single or duplicate beads were used [see **6.2.1** a)].

f) The results (see clause **17**).

g) The results on the chosen certified reference material [see **8.1** d) and clause **15**].

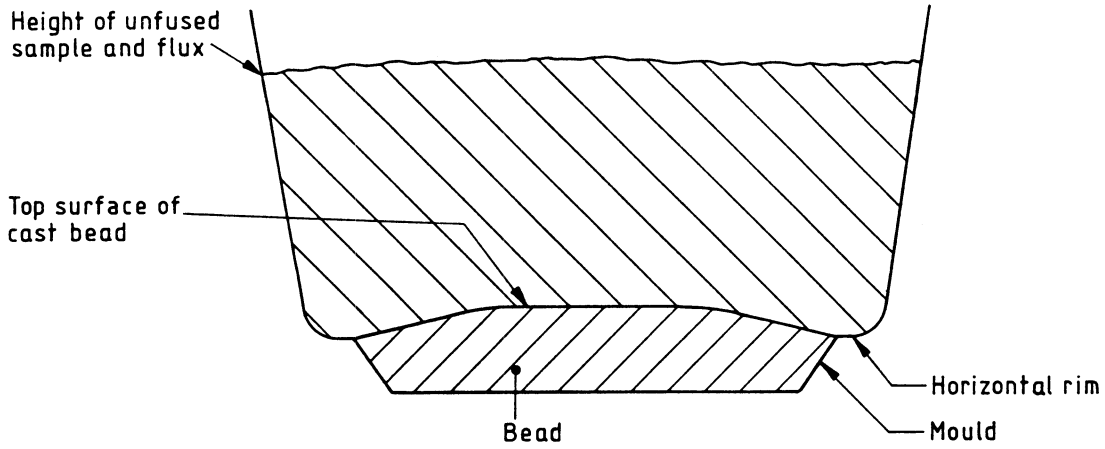

Figure 1 — Example of a fusion mould

Appendix A Tungsten carbide corrections with cobalt or nickel binder

The following additional corrections may be applied to account for the cobalt or nickel binder used in tungsten carbide mortars (see clause **16**):

$$L_T = \frac{100\left\{\left(\frac{L}{100-L}\right) - \left(\frac{W}{100}\right)(B + C\phi - 1 - \phi)\right\}}{\left(\frac{100}{100-L}\right) - \left(\frac{W}{100}\right)(B + C\phi)} \quad (12)$$

$$f = \frac{100 - L_T}{100\left\{\left(1 - \frac{W}{100}\right)(1 + \phi)\right\}} \quad (13)$$

where

f, L, L_T, B and W are as defined in clause **16**;

C is the $\dfrac{\text{relative atomic mass of Co}}{\text{relative molecular mass of } Co_3O_4}$

= 0.7342 or

$\dfrac{\text{relative atomic mass of Ni}}{\text{relative molecular mass of NiO}}$

= 0.7858;

ϕ is the $\dfrac{\text{concentration of binder metal in mortar}}{\text{concentration of tungsten in mortar}}$

$= \dfrac{Co_3O_4}{WO_3}$ or $\dfrac{NiO}{WO_3}$

NOTE The cobalt or nickel content should be determined only once and then used for all subsequent corrections.

Appendix B Monitoring of background and sensitivity

NOTE 1 The computer software supplied by some instrument manufacturers takes a slightly different approach to the problem of monitoring background and sensitivity changes. In this case the same standards are used but count rates are corrected back to the values obtained for the zero and high level count ratio standard beads, when they were first introduced prior to calibration or analysis. Providing the software corrects the zero counts back to a set level, corrects the top level ratio standard for this change and then corrects the so-corrected top level standard counts to its own set level, this approach is an acceptable alternative to the procedures outlined in **9.2** and **9.3**.

The general equation for this type of correction is:

$$R = N_b + \frac{(N_s - N_b')(N_t - N_b)}{(N_t' - N_b')} \quad (14)$$

where

R is the ratio, as defined in **9.2** or **9.3**;

N_s is the count obtained for the sample or standard bead for the relevant element;

N_b is the count obtained *originally* for the bottom ratio standard bead for the same element;

N_b' is the current count obtained for the bottom ratio standard bead for the same element;

N_t is the count obtained *originally* for the top ratio standard bead for the same element;

N_t' is the current count obtained for the top ratio standard bead for the same element.

NOTE 2 If it is assumed that $N_b = 0$ and $N_t = 1$, then the equation reduces to:

$$R = \frac{N_s - N_b'}{N_t' - N_b'}$$

which is the same form as used in **9.2** and **9.3**.

Appendix C Typical alpha corrections for rhodium end window X-ray tubes

Typical alpha corrections for rhodium end window tubes are given in Table 7.

Table 7 — Rhodium end window tube empirical alpha corrections ($\times 10^5$)

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	WO_3
Si (Kα)	0	72	290	245	54	259	8	336
Ti (Kα)	47	0	0	– 115	1 043	– 93	288	542
Al (Kα)	0	106	0	272	65	280	8	139
Fe (Kα)	– 213	847	– 270	0	883	– 287	– 98	567
Ca (Kα)	43	– 225	0	– 126	0	– 28	13	967
Mg (Kα)	11	202	0	309	64	0	11	209
P (Kα)	46	– 170	0	– 55	– 196	– 13	0	540
Ga (Kα)	64	1 052	0	(2 668)	1 221	(– 30)	(120)	(2 251)

NOTE Figures in brackets were derived by plotting known empirical alpha corrections against theoretically calculated ones for the line in question.

These corrections were determined using a Telsec TXRF X-ray spectrometer with a Machlette Rhodium tube at 50 KV and 50 mA. The incident angle was 90° and the take-off angles were 38.8° for Al and Si, 37.2° for Mg, 34.8° for Fe, 32.5° for Ti and 26.5° for Ca. The values for Ga were determined using an ARL 8480 spectrometer with a Machlette Rhodium tube.

Appendix D Computation of third order equations

The following equation and procedures shall be used where no computer facilities are available in association with the X-ray spectrometer for calculating the concentrations, P, and correcting for line interference.

$$P = 0.0 + aR + bR^2 + cR^3 \quad (15)$$

where

R is the ratio.

Method 1. Equispaced ratios. This method is carried out as follows.

a) Plot the calibration points (ratio against percentage) on a large piece of graph paper and draw the curve.

b) Read off the graph the percentages P_1, P_2 and P_3 corresponding in equispaced divisions of ratio R, $2R$, and $3R$. In practice R, $2R$ and $3R$ will normally be 0.3333, 0.6667 and 1.0000 if 100 % SiO_2 or 100 % Al_2O_3 is used as the ratio standard.

c) Using the values of R, P_1, P_2 and P_3 found in (b) the coefficients can be derived from the following three equations:

$$a = \frac{18P_1 - 9P_2 + 2P_3}{6R} \quad (16)$$

$$b = \frac{-5P_1 + 4P_2 - P_3}{2R^2} \quad (17)$$

$$c = \frac{3P_1 - 3P_2 + P_3}{6R^3} \quad (18)$$

where

P and R are as defined in equation (15).

Method 2. Least squares. This is the method best used when a computer is available.

The equations below are solved.

$$\Sigma R^2 a + \Sigma R^3 b + \Sigma R^4 c = \Sigma RP \quad (19)$$

$$\Sigma R^3 a + \Sigma R^4 b + \Sigma R^5 c = \Sigma R^2 P \quad (20)$$

$$\Sigma R^4 a + \Sigma R^5 b + \Sigma R^6 c = \Sigma R^3 P \quad (21)$$

where

P and R are as defined in equation (15);

giving

$$a = \frac{D_1}{D_0}$$

$$b = \frac{D_2}{D_0}$$

$$c = \frac{D_3}{D_0}$$

where

$$D_0 = \begin{bmatrix} \Sigma R^2 & \Sigma R^3 & \Sigma R^4 \\ \Sigma R^3 & \Sigma R^4 & \Sigma R^5 \\ \Sigma R^4 & \Sigma R^5 & \Sigma R^6 \end{bmatrix} \quad (22)$$

$$D_1 = \begin{bmatrix} \Sigma R^1 P & \Sigma R^3 & \Sigma R^4 \\ \Sigma R^2 P & \Sigma R^4 & \Sigma R^5 \\ \Sigma R^3 P & \Sigma R^5 & \Sigma R^6 \end{bmatrix} \quad (23)$$

$$D_2 = \begin{bmatrix} \Sigma R^2 & \Sigma R^1 P & \Sigma R^4 \\ \Sigma R^3 & \Sigma R^2 P & \Sigma R^5 \\ \Sigma R^4 & \Sigma R^3 P & \Sigma R^6 \end{bmatrix} \quad (24)$$

$$D_3 = \begin{bmatrix} \Sigma R^2 & \Sigma R^3 & \Sigma R^1 P \\ \Sigma R^3 & \Sigma R^4 & \Sigma R^2 P \\ \Sigma R^4 & \Sigma R^5 & \Sigma R^3 P \end{bmatrix} \quad (25)$$

and noting

$$\begin{bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{bmatrix} = aei + bfg + cdh - ceg - fha - ibd \quad (26)$$

NOTE This method does not require graph paper but would be rather time-consuming even with a pocket calculator that gives values of Σx^2 and Σx. In practice it would be preferable to use method (1) or, even better, programme a computer for method (2).

blank

Publications referred to

BS 1902, *Methods of testing refractory materials*[5)].
BS 1902-9.1, *Analysis of alumino-silicate refractories by X-ray fluorescence.*
BS 6870, *Analysis of aluminium ores.*
BS 6870-1, *Introduction.*
BS 6870-2, *Chemical methods.*

[5)] Referred to in the foreword only.

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