

**Methods of testing**

# **Refractory materials —**

**Part 9: Chemical analysis by  
instrumental methods —**

**Section 9.2 Analysis of silica  
refractories by X-ray fluorescence**

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- British Ceramic Research Ltd.
- British Steel Industry
- Electricity Supply Industry in England and Wales
- Engineering Equipment and Materials Users' Association
- Refractories Association of Great Britain
- Refractory Contractors' Association
- Society of Glass Technology

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## Foreword

This Section of BS 1902-9 has been prepared under the direction of the Refractory Products Standards Committee. It is one of a series of Sections covering chemical analysis by instrumental methods, and describes the X-ray fluorescence (XRF) technique.

The method is based on the fused, cast bead technique which is the current accurate industrial method for the preparation of oxide materials for XRF in the United Kingdom and much of Europe. The flux used is of low melting point, which greatly assists mixing and dissolution of the samples. The flux has successfully been applied to the analysis of silica/alumina materials from sand through clays, feldspars, etc. to pure alumina materials, and is also suitable for a whole range of other materials including zircon, steatite, glazes, frits, fluxes, glasses, fluorspar and gypsum.

The standard was amended in 1991 to include an appendix covering the analysis of silica sands used in glass manufacturing.

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### Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 12, 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 Section of BS 1902-9 describes a method for analysing silica refractories using X-ray fluorescence.

The method is intended for materials containing more than 92 % of silica ( $\text{SiO}_2$ ) on the ignited basis. The ranges of content of constituents are given in Table 1 except for those used in glass manufacture which are given in Appendix C.

Appendix C gives modifications to this method which are required where it is to be used for the analysis of silica sands used in glass manufacture.

**Table 1 — Ranges of content**

| Oxide                                                                                                                                                                              | Range       |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
|                                                                                                                                                                                    | %           |
| Silica ( $\text{SiO}_2$ )                                                                                                                                                          | 92 to 100   |
| Titanium oxide ( $\text{TiO}_2$ )                                                                                                                                                  | 0.01 to 0.5 |
| Alumina ( $\text{Al}_2\text{O}_3$ )                                                                                                                                                | 0.01 to 2.0 |
| Iron (III) oxide ( $\text{Fe}_2\text{O}_3$ )                                                                                                                                       | 0.01 to 2.0 |
| Calcium oxide ( $\text{CaO}$ )                                                                                                                                                     | 0.01 to 3.0 |
| Magnesium oxide ( $\text{MgO}$ )                                                                                                                                                   | 0.03 to 0.5 |
| Sodium oxide ( $\text{Na}_2\text{O}$ )                                                                                                                                             | 0.05 to 0.5 |
| Potassium oxide ( $\text{K}_2\text{O}$ )                                                                                                                                           | 0.01 to 2.0 |
| Tungsten oxide ( $\text{WO}_3$ )                                                                                                                                                   | 0.02 to 1.0 |
| Cobalt oxide <sup>a</sup> ( $\text{Co}_3\text{O}_4$ )                                                                                                                              | 0.01 to 1.0 |
| Nickel oxide <sup>a</sup> ( $\text{NiO}$ )                                                                                                                                         | 0.01 to 1.0 |
| NOTE Other elements may be added as necessary.                                                                                                                                     |             |
| <sup>a</sup> These ranges are for the analysis of the binder in the tungsten carbide mortar, which may be either cobalt or nickel. The appropriate analysis should be carried out. |             |

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

## 2 Principle

The powdered sample 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 analysed by reference to previously determined calibration graphs or equations.

## 3 Preparation of the analysis sample

The sample shall be finely ground (the bulk to be finer than 125  $\mu\text{m}$  equivalent spherical diameter), either by using a suitable mechanical device and appropriate grinding times, or by hand. The grinding media shall be agate, boron carbide or tungsten carbide. If the latter is used, the contamination shall be monitored and the appropriate corrections applied to the analysis and loss on ignition figure (see clause 11).

## 4 Reagents

**4.1 Flux<sup>1)</sup>** 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 ( $\text{LiBO}_2$ ), the ratio being of the dry fluxes. It shall be of an analytical quality.

In practice the flux will contain a certain amount of moisture. This shall be corrected for in one of two ways.

- Ignite the entire quantity of flux required overnight at 700 °C immediately before it is used for analysis and then store in a desiccator.
- Carry out duplicate losses on ignition on 1 g portions of the well mixed contents of each kilogram of flux used. The ignition is either at 700 °C for 1 h or at 1 200 °C for 10 min. Keep the flux tightly sealed except when in use. The loss on ignition, expressed as a percentage  $L$ , is then used to calculate a factor  $f$  (see equation 1) which is in turn used to calculate the mass of the unignited flux needed to produce the required mass of flux on the ignited basis ( $f \times$  required mass of ignited flux = required mass of unignited flux). Carry out this loss on ignition weekly, or for each kilogram of flux used, whichever is the more frequent.

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

where

$L$  is the loss on ignition (in %).

Re-check calibrations when batches of flux are changed.

**4.2 Oxides or carbonates for glass beads.** The reagents used to prepare the standard beads for cations shall be pure oxides or carbonates of at least 99.95 % purity (excluding moisture or  $\text{CO}_2$ ) for minor constituents and of at least 99.99 % purity for silica.

<sup>1)</sup> 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.

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

a) *Silica, alumina and magnesium oxide.*

Determine the loss on ignition as follows. Ignite the material at 1 200 °C and keep it at this temperature for 30 min before use. Cool in a desiccator to room temperature. After allowing for this loss weigh the appropriate amount of the unignited material to prepare the standard bead.

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

c) *Iron (III) oxide.* Ignite the material at 700 °C and keep it at this temperature for 30 min before use. Cool in a desiccator to room temperature.

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

NOTE 1 A 2 h treatment is usually sufficient for drying.

NOTE 2 Tungsten carbide (WC) will be introduced as a contaminant if this media is used for grinding. Laboratories using tungsten carbide for sample grinding should calibrate for WO<sub>3</sub> in order to monitor its presence in samples, and hence correct the analysis and the loss on ignition for WC contamination (see clause 11). Unlike the chemical analysis procedure, X-ray fluorescence determinations are not subject to any significant interference due to tungsten and furthermore the contaminant tungsten can be easily monitored.

## 5 Apparatus

**5.1 Vessels** used for the fusion of samples with flux, with the exception of the lids (5.5) shall be constructed from a platinum alloy that is not wetted by the melt.

The casting moulds shall be made from any suitable material not wetted by the melts, which does not contaminate the sample or cause reduction.

NOTE A mould consisting of 95 % platinum and 5 % gold is suitable.

**5.2 Fusion dishes** of sufficient capacity to hold the quantity of unfused flux and sample required by the size of the casting mould.

NOTE 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.

**5.3 Casting moulds**<sup>2)</sup> 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 1 Calibration and analysis are carried out using the same pattern and size of casting mould throughout.

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

### 5.4 Fusion moulds<sup>2)</sup>

NOTE 1 As an alternative method to fusion in a dish followed by casting into a mould, it is permissible to use a combined vessel which functions both as a fusion dish and a casting mould (see Figure 1).

The volume of the dish shall be sufficient to hold the 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 addition, if it is intended that the top surface of the bead produced by the vessel is to be used for presentation to the X-ray fluorescence spectrometer, a horizontal rim shall be interposed between the top of the mould and the sides of the dish.

NOTE 2 If the rim is not present concave top surfaces will be produced on the beads, which are not conducive to accurate analysis.

NOTE 3 Once a size and type of mould has been selected it should be used throughout; if it is changed, re-calibration is required.

**5.5 Lids for dishes and fusion moulds** large enough to completely cover the dishes; they are not required to be of a non-wetted alloy of platinum.

NOTE Platinum itself is suitable.

### 5.6 Heat reservoir for casting mould (optional)

NOTE 1 A heat reservoir is usually required when using moulds of small sizes, so that the mould does not cool too rapidly when removed from the furnace.

NOTE 2 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.

### 5.7 Air jet (optional)

NOTE 1 An air jet is usually required to free the melt from the dish and to 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.

NOTE 2 A convenient way of doing this is to use the base of a bunsen burner without the barrel.

<sup>2)</sup> 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.