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**Chemical analysis of refractory products by XRF -
fused cast bead method**

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(ISO 12677: 2003, MOD)

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Foreword

This Standard modifies and adopts ISO IM77:2003 *Chemical Analysis of Refractory Products by XRF - Fused Cast Bead Method* (English version). The relevant technical differences between this Standard and ISO 12677:2003 are marked with single vertical line at the page margin of the involved clause. The main revised contents are as follows:

- a) Change the quoted standard to Chinese standards that are equivalent to ISO standards;
- b) Replace "Massive sampling does not belong to the scope of this method." in the first paragraph of Chapter 5 to be "The laboratory sample shall be collected in accordance with GB/T 10325 and GB/T 17617".
- c) Add "high purity reagents ammonium dihydrogen phosphate and potassium dihydrogen phosphate" to 10.2.1;
- d) Add "Note: other calibration equation can be also used" to 10.4.2.2;
- e) Add part of solvent and dilution ratio contents to Annex C;
- f) In Annex C, for ease of understanding, add "Note: the number behind the material is the sequence number of the listed material type in Chapter 3, for example, 1 is high aluminum $\text{Al}_2\text{O}_3 > 45\%$, 2 is alumina-silica Al_2O_3 7%~45%,, 17 is magnesium silicate" corresponding to the contents of Chapter 3.
- g) In Annex D, add the contents of standard samples for the domestic refractory products;
- h) In Annex E, add the contents of series standard samples for the domestic refractory products;
- i) In Annex F, add "the matrix correction coefficient a can be calculated according to the software provided by the instrument supplier";
- j) Appropriately modify the permissible error of ferric oxide in Annex G according to the joint test results;
- k) In Annex H, add "Note: the correction method provided by the manufacturer can be used";
- l) In Annex I, add the application of fusion representation results for the domestic series standard samples;
- m) Change the notes under the titles in 12. 9 and Annex A into the paragraphs according to our expression habit;
- n) Delete the references.

In addition, editorially modify the places that need to be corrected in ISO 12677:2003; and add the footnotes at the corresponding places.

Annexes A, B, D, E, F, G and H of this Standard are normative; Annexes C and I are

Chemical analysis of refractory products by XRF – fused cast bead method

1 Scope

This Standard specifies a method for chemical analysis of refractory products and materials, and technical ceramics composed of oxides, including the determination of oxide at levels between 0.01% and 99% by means of the XRF fused cast bead method.

NOTE: Constituents at concentrations greater than 99% (on a dried basis) should be reported on by difference, provided that all likely minor constituents and any loss on ignition have been determined. These figures should also be checked by direct determination.

2 Normative references

The articles contained in the following documents have become part of this Standard when they are quoted herein. For the dated documents so quoted, all the modifications (excluding corrections) or revisions made thereafter shall not be applicable to this Standard. For the undated documents so quoted, the latest editions shall be applicable to this Standard.

GB/T 3286 Methods for chemical analysis of limestone and dolomite

GB/T 6005 Test sieves - Metal wire cloth perforated metal plate and electroformed sheet - Nominal sizes of openings (GB/T 6005-1997, eqv ISO 565: 1990)

GB/T 6900 Chemical analysis of alumina-silica refractories

GB/T 8170 Rules of rounding off for numerical values & expression and judgement of limiting values

GB/T 10325 Shaped refractory products - Rule of acceptance, sampling and inspection

GB/T 15000.7-2001 Directives for the work of reference materials(7) - General requirements for the competence of reference material producers (ISO Guide 34:2000, IDT)

GB/T 17617 Refractory products - Sampling of raw materials and unshaped products

ISO/IEC Directives (1992) - Part 2: Methodology for the development of International Standards - Annex B Mention of reference materials

3 Types of materials

- 1) High alumina (Al_2O_3) $\geq 45\%$;
- 2) Alumino-silicate (Al_2O_3) 7% to 45%;
- 3) Silica (SiO_2) $\geq 93\%$;

- 4) Zircon;
- 5) Zirconia and zirconates;
- 6) Magnesite;
- 7) Magnesite/alumina spinel (~ 70/30);
- 8) Dolomite;
- 9) Limestone;
- 10) Magnesite/chromite oxide;
- 11) Chromite ore;
- 12) Chromite alumina;
- 13) Alumina/magnesite spinel (~ 70/30);
- 14) Zirconia-alumina-silica cast material (AZS);
- 15) Calcium silicates;
- 16) Calcium aluminates;
- 17) Magnesium silicates.

A list of elemental ranges and required detection limits are given in Annex A. Some of the above material types can be accommodated on to common calibrations (see 10.3.4).

4 Principle

The powdered sample is fused with a suitable flux to destroy its mineralogical and particulate composition. The resultant melt is casted into the shape of a glass bead which is then introduced into an XRF 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 and applying corrections for inter-element effects. The calibration equations and inter-element corrections are established from beads produced using pure reagents and/or series reference materials (SeRMs), prepared in the same way as the samples.

Because of the universality of the fused cast bead technique, various fluxes and modes of calibration are permitted, providing they have been demonstrated to be able to meet certain criteria of reproducibility, sensitivity and accuracy. Provided that a laboratory's own methods conform to all the various criteria set down, they will be accepted as conforming to this Standard.

5 Sample preparation

Bulk sampling a laboratory sample according to GB/T 10325 and GB/T 17617.

It is permissible to apply the sample grinding methods cited in conventional chemical methods for the classes of materials covered. In addition, the use of tungsten carbide is permitted and is the preferred method, provided that the appropriate corrections for tungsten carbide (and its binder if necessary) are applied to loss on ignition and analysis figures.

Corrections for tungsten carbide (and its binder) on loss on ignition and analysis are given in Annex B. The purpose of grinding is to obtain a sample sufficiently fine for it to be fused easily, but below a set limit of introduced contamination. In general, a maximum particle size of 100 μm is sufficiently fine, but for certain samples that are difficult to fuse (e.g. chrome ores) finer grinding to less than 60 μm may be necessary.

Two methods of obtaining the required particle size are permissible:

- a) For mechanical grinding devices, establish what grinding times are sufficient to grind the various samples analysed to the correct fineness and thereafter apply these minimum times for grinding. When grinding hard materials, such as chromite, sieving is used, but this may induce segregation.
- b) After hand grinding for 20 s, sieve the ground powder through a sieve of 100 μm aperture in accordance with GB/T 6005. Regrind any material remaining on the sieve for a further 20 s, sieve and repeat this procedure until the whole of the sample passes through the sieve. Transfer the sample to a suitable container and mix for 1 min, using a mechanical mixer such as a vertical linear mixer.

NOTE: As the object of the exercise is to obtain a sample suitable for fusion, and not to test the fineness of the sample itself, method a) is generally preferred.

6 Apparatus

6.1 Fusion vessels

A non-wetted platinum alloy (Pt/Au 95% / 5% is suitable). Lids, if used, shall be of a platinum alloy (not necessarily non-wetted).

6.2 Casting moulds

A non-wetted platinum alloy (Pt/Au 95% / 5% is suitable).

NOTE: Vessels that serve both as a fusion vessels and casting moulds may be used.

6.3 Heat reservoir for casting mould (optional)

Required in special circumstances 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 dimensions 10 mm x 50 mm x 50 mm.

6.4 Air jet (optional)

Required to cool the mould rapidly. This can be any device where on a narrow jet of air that can be directed to the centre of the base of the casting dish. A convenient way of doing this is to use the base of a bunsen burner without a barrel to serve as an air jet.

In most cases, it is very important to cool the melt rapidly. This is necessary to obtain a

8.1.5 At a reasonable counting time (200 s), the counts recorded for each element determined shall give the required standard of reproducibility for the determination of that element (see 12.2).

8.1.6 A heavy element absorber may be incorporated into the flux provided that:

- a) it does not reduce sensitivities so that conditions 8.1.4 and 8.1.5 are not met;
- b) the heavy element does not have a line overlap with any of the elements to be determined.

8.1.7 If volatile components are to be determined, then a flux of sufficiently low melting point, which permits a fusion temperature low enough to retain that element during fusion shall be used.

8.1.8 For the determination of elements that alloy with platinum (e.g. lead, zinc, cobalt), the melting point shall be such as to allow fusion below the temperature at which this reaction occurs (1 050°C).

8.1.9 The flux shall be pure with respect to the analytes determined. As the flux to sample ratio is greater than 1 (see Annex C), impurities to the flux can influence the measured result negatively. The greater the ratio of the flux to sample, the greater the influence, therefore, the permitted levels of impurity of analyte levels in the flux shall be no more than $3D/R^{(1)}$.

Where,

R is the ratio of flux to sample;

D is the detection limit claimed for the determination of the analyte element.

Most reagents sold by reputable manufacturers as 'flux' grade quality meet this requirement but an analysis shall be obtained for each batch of flux supplied. Recheck calibrations when batches of flux are changed.

8.2 Compensations for moisture in flux

The flux contains a certain amount of moisture, which shall be compensated for in one of two ways.

- a) Calcine the entire quantity of flux required overnight at 700°C immediately before it is used for analysis and afterwards store it in a desiccator.
- b) Carry out duplicate losses on ignition on 1 g portions of well-mixed flux for each kilogram of flux used. Carry out the calcining at the normal fusion temperature for 10 min, or the normal fusion time, whichever is the greater [see 9.2.2 f)]. Store the flux in a tightly sealed container 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 ($F \times \text{required mass of ignited flux} = \text{required mass of}$

¹⁾ There are editorial changes for ISO Standard.

of the melt is transferred to the mould as possible. Remove the mould from the furnace and place on a horizontal surface.

- c) Combined fusion mould: after 5 min at $(1\,200 \pm 50)^{\circ}\text{C}$ remove the fusion vessel from the furnace and by swirling, ensure the transfer of the whole of the melt into the mould.
- d) Mould heated over a burner: after preparation of the melt at the fusion temperature and time chosen for that type of material, pour the melt into the preheated mould and turn the burner off. Allow the melt to solidify and use an air jet (6.4) as described in 9.2.4.2., or a water-cooled metal plate to accelerate the cooling process.

NOTE 1: 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 rippled effect the melt should be poured into the mould at a point nearer to the edge of the mould than the centre. 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.

NOTE 2: Most refractory materials contain small or minor amounts of Cr_2O_3 , ZrO_2 , and $\alpha\text{-Al}_2\text{O}_3$ which, if the fusion is not completed at $1\,200^{\circ}\text{C}$ will cause the melt to de-vitrify. However, if experience shows that this de-vitrification is not a problem, samples can be cast in furnaces at as low as $1\,100^{\circ}\text{C}$, providing calibration standards are prepared the same way.

NOTE 3: Fusions at $1\,200^{\circ}\text{C}$ will volatilize sulfur even when an oxidising agent is used.

9.2.4.2 Cooling of beads

If no air jet is used, allow the mould to cool on a horizontal surface. If the air jet 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 1: It may be necessary to encourage the release of the beads at this stage by gently tapping the casting mould on a solid surface.

NOTE 2: Small amounts of lithium iodide or iodate, or ammonium iodate may be added to the melt to assist in preventing cracking of fused beads on cooling and to aid release from the mould. If small amounts of releasing agents are to be used, then all samples and any calibration standards prepared should include the same releasing agent added in the same quantity and at the same stage of bead preparation. Maintaining a good polish on the casting moulds should obviate the need of such agents, but there are problems with samples containing high levels of Cr_2O_3 . It is also possible to use NH_4Br or LiBr but it should be noted that there is a Br La line near the Al Ka line. High amounts of Br can cause problems when measuring low alumina concentrations. The amount of NH_4Br or LiBr added should not exceed 1 mg per gram of sample. If a chromium tube is used, the effect of bromine will be greater, therefore, the effect of bromine on aluminium should be checked before using a bromine based releasing agent.

9.3 Automatic bead preparation

Automatic bead equipment may be used as an alternative to 9.2.4, and shall be in accordance with 9.2.2 and 12.2.

9.4 Storage

Beads can deteriorate because of adverse temperature and humidity conditions. It is suggested that the bead be stored in a polythene self-seal bag. If the laboratory environment is suitably controlled (e.g. air conditioned) then the bag shall be stored in desiccators. Alternatively, if the environment is not controlled the bags shall be stored in temperature controlled ovens at 25°C to 30°C.

The bags themselves may cause surface contamination due to the use of 'anti-blocking agents' (the effect being more apparent for the lighter elements). Measuring surfaces of beads shall be thoroughly cleaned before use, or possibly polished after long term storage.

NOTE: Reported sources of contamination are as follows:

- 1) Sulfur from vacuum oil in the spectrometer or from the laboratory atmosphere.
- 2) Sodium and chlorine from the atmosphere if the laboratory is near the sea.
- 3) Potassium from cigarette smoke.

9.5 Special problems

There are special problems associated with fusing samples with a high zirconia or chromium oxide content. In addition to the circumstances given, it is necessary to carry out fusion trials for either zircon or zirconia whichever is the sample with the highest ZrO_2 content, fused using a particular flux composition/flux ratio. Similarly for chrome-bearing materials, magnesia chrome or chrome ore shall be used to relate to the highest Cr_2O_3 content used with a particular flux composition/flux ratio.

10 Calibration

10.1 Calibration standards

The calibration equations and inter-element corrections are established using beads produced with pure reagents or series reference materials (SeRMs). The SeRMs are different from certified reference materials (CRMs) which validate the calibrations using pure reagents. CRMs and SeRMs are shown in Annexes D and E, respectively. Series of CRMs meeting the requirements of 10.2.2 and 10.4.1 can be regarded as SeRMs.

10.2 Reagents and Series Reference Materials (SeRMs)

10.2.1 Purity and preparation of reagents

Whenever possible, reagents shall be pure oxides or carbonates, except for the calibration of such elements as sulfur or phosphorus which do not form stable oxides or carbonates, where some guarantee of stoichiometry is required.

It is essential that the reagents be free of (or corrected for) the presence of water (and in the case of oxides, carbon dioxide) when weighed out for fusion. Also the reagents shall be in a known oxidation state.

The procedures listed ensure that the correct oxidation state is obtained. It is essential that reagents used for calibration be of high purity and that when fresh batches of reagents are purchased they be compared with previous batches. Therefore, a fresh bead shall be made at the highest level of content calibrated, and measured against a similar bead prepared from

- c) three or more major constituents (e.g. chrome ores).

In the first case the matrix can be taken as 100% of the major oxide and corrections made back to this. This allows the calibration ranges to be easily extended with a minimum of effort. The calibration of all minor constituents is made using binary mixtures of the major oxide and the minor oxide giving a total of 100%.

In the other two cases one constituent is chosen as the main one and binary standards are made with it as in 10.3.2.4. This oxide is usually chosen as the predominant one (e.g. in the case of aluminosilicates it would be SiO_2). The only difference from the first case is that 100% of the second major oxide is taken as the zero point for the main major oxide and that calibration of both these major oxides is made from binary mixtures of the two. When applying line overlaps, corrections are made back to 100% of the major oxide (or in the case of the major oxide itself to 100% of the second major oxide). Mass absorption coefficients are designed normally (see 10.3.2.9, 10.3.2.10 and 10.3.2.11) to correct back to a binary mixture of the minor constituent and the major oxide.

10.3.2.3 Drift correction

There are two methods of compensating for drift of the spectrometer.

- a) Monitor standards (compensation using count rate).

When using this method, the off-peak background for each element shall be measured.

Monitor standards are stable beads which contain all elements of the calibration in a concentration that leads directly to a count rate with a statistical uncertainty less than or equal to the statistical uncertainty of the calibration. Before starting the calibration, monitor standards shall be measured and be used every time for the first measurement of samples to be analysed.

The count rates of the first measurement (i.e., when the calibration is initially set up) and the last measurement are stored and give the correction factor for the drift of the spectrometer.

A recalibration [second method, see b)] is necessary for the case when the drift factor is greater than 1.3 and less than 0.7 (maximal drift $\pm 30\%$).

- b) Drift correction standards (recalibration standards).

In order to compensate for drifts in background or sensitivity a set of drift correction standards is required. A zero plus a high range concentration for each element calibrated shall be contained within the set of standards. The high range concentration shall be greater than 0.6 x the maximum concentration of the oxide calibrated. An additional 100% major oxide standard serves as the zero for all other constituents (where applicable 100% of the second major constituent serves as zero for the major constituent). In some cases alternatives shall be sought if line overlaps exist (e.g. 100% SiO_2 cannot serve as zero for SrLa or 100% TiO_2 for BaLa). Similarly it is wrong to combine two line overlap interfering elements in the same drift correction standard.

The drift correction standards shall be taken out of the set of standards used for calibration.

These standards shall be used each time samples are analysed. Software supplied with most instruments automatically applies two-point recalibration to the results. If the instrument is not supplied with such software, suitable algorithms are given in 11.3, which can be written into the user's own software.

10.3.2.4 Calibration standards

These are binary mixtures of the major oxide and the oxide calibrated. The following number of standards shall be made up in addition to the zero point:

- $\leq 2\%$, at least two approximately evenly-spaced concentrations.
- $\leq 10\%$, at least three approximately evenly-spaced concentrations.
- $\leq 20\%$, at least four approximately evenly-spaced concentrations.
- $> 20\%$, at least a 5% standard plus 10%, 20%, 30%..., etc. up to the next whole multiple of 10% above the calibration range, to a maximum of 100%.

NOTE: Multi-oxide synthetic standards or SeRMs may also be used.

10.3.2.5 Calculation of calibration coefficients

The relationship of intensity (or its ratio to a drift correction standard) is plotted against concentration. If any points are out of line, rerun that standard bead. If the standard still misplots, prepare a fresh bead. Most calibrations will appear as straight lines and therefore linear equations may be used to express the relationship and subsequently calculate unknown concentrations. Other calibrations may be smooth curves, which may be expressed in one of three ways:

- a) a quadratic equation;
- b) a linear equation applying a mass absorption correction of the analyte oxide on itself (this approximates to a quadratic equation and for some manufacturer's software is the only way of expressing quadratic relationship);
- c) a linear equation applying a mass absorption correction of the major oxide of the analyte.

NOTE: These equations are not recommended for less than 10 standards.

For very slight curves (e.g. alumina in alumino-silicates) any of the three methods above can be applied. For pronounced curves method c) shall be applied, and if the relationship is still not linear either alternative a) or b) shall be combined into the model.

10.3.2.6 Line overlap correction standards

In all cases the standards given in 10.3.2.3 are used. In the case of a single major element matrix these standards are sufficient. Where two major oxides are present, an additional set of standards is required to correct for the line overlap of minor constituents on the second major oxide. These standards consist of binary mixtures of the minor constituent and the second major oxide giving a total of 100%. The amount of the minor oxide added to these mixtures shall be equal to or greater than the maximum amount of this minor oxide calibrated.

10.3.2.7 Line overlap corrections

Having first established the calibration coefficients, these are calculated by measuring on the spectrometer the set of binary standards (see 10.3.2.3) as unknowns. The apparent percentages that the binary mixtures of one element has on another are recorded and used to calculate line overlap corrections. As there are a series of such standards it is possible to identify erroneous results by comparison. When calculating average line overlap coefficients greater weighting shall be given to standards containing the larger amounts of interfering element. For these calibration ranges, it is likely that line interferences can always be expressed because 1% of interfering oxide gives an interference equivalent to x% of the analyte oxide, where x is the line overlap coefficient.

These corrections are to be iterated during analysis together with the mass absorption corrections.

The same approach can be applied to background effects, although in the case of the effects of ZrO_2 on NaKa and MgKa second order relationship may be necessary if the range of ZrO_2 content exceeds 20%.

In some cases where there are large first order line overlaps, and the interfering line is actually measured on the same crystal/detector combination, a non-iterative intensity correction may be preferable. This is up to the discretion of the individual laboratory, but such a correction and the reason for its choice shall be reported.

10.3.2.8 Mass absorption correction standards

The calibrations standards and method given in 10.3.2.4 are used to calculate the mass absorption correction coefficients of minor constituents on major constituents and, where applicable, those under 10.3.2.5 are used to calculate the mass absorption correction coefficients of minor constituents on the second major constituents and vice versa. The mass absorption correction coefficients of major constituents on each other or on minor constituents (where applicable) are often determined as part of the regressions carried out using instrumental software.

Standards to determine the mass absorption correction coefficients of minor constituents on each other require ternary mixtures of the two minor constituents at their maximum content with the major constituent oxide making the balance up to 100%. If no other data are available these standards are required in duplicate in order to check for weighing errors. To make up a set of standards for even eight minor elements in duplicate, is a time-consuming task, so an alternative approach is permissible if previously calculated empirical mass absorption correction coefficients are available for the same matrix and the same X-ray tube or if theoretical mass absorption corrections are calculated. The latter can be supplied by the instrument manufacturer or can be calculated using other commercially available software or suitable in-house software. The model used to calculate theoretical mass absorption correction coefficients is given in Annex F, values previously established on another instrument using an X-ray tube with the same anode, the same material type (Clause 3) and the same flux-to-sample ratio can also be applied. These theoretical and empirical mass absorption correction coefficients can be used instead of those derived from specially made standards providing the following conditions are met:

$$a) \quad \alpha_j \times C_j \leq 0.025 \quad \dots\dots\dots (2)$$

Where:

In order to avoid the need to produce large numbers of standards to calculate empirical mass absorption corrections, acceptable theoretical mass absorption corrections can be calculated using in-house, commercially available or spectrometer manufacturer's software. The software as used shall meet the following criteria:

- a) the model used includes not only mass absorption effects on the fluorescent radiation, but also the exciting radiation(s); the latter can be treated as a single wavelength;
- b) the model used includes terms to allow for the incident angle to the sample of exciting radiation and the take off angle from the sample of the fluorescent radiation;
- c) the ratio of flux to sample is treated as a constant;
- d) the matrix used in calculating theoretical coefficients corresponds to the matrix used in calibration (see 10.3.2.2).

In 10.3.2.5 various ways to generate the calibration coefficients are given.

If no mass absorption correction coefficients are required of the main matrix oxide on the oxide determined when producing the calibration, the matrix can be regarded as a binary mixture of the analyte oxide and the main matrix oxide and the effect of adding the interfering oxide is to replace the main matrix oxide. The matrix can usually be regarded as a mixture of the maximum amount of the determined oxide calibrated with the main matrix oxide making up the balance to 100%.

If, on the other hand, a correction is applied for the effect of the main matrix oxide on the oxide determined, the matrix is 100% of the oxide determined and the effect of adding the interfering oxide is to replace the oxide determined.

10.3.3 Multi-element calibration

In the procedures described in 10.3.1 and 10.3.2.1, calibrations are produced with a minimal effect from other elements, and inter-element interferences (mass absorption corrections) are evaluated using binary and ternary beads. Thus the effect of one element on another is determined in the absence of any other interfering elements. An alternative to this is the multi-element calibration method in which calibrations are produced and the effects of many elements on a particular element are evaluated at the same time.

A series of synthetic calibration beads or Series Reference Materials (see 10.2.2) prepared from high purity reagents (see 9.2) containing different mixtures of the elements determined is produced. The concentrations of the elements determined are varied from bead to bead so as to cover the analytical range for each element and also to allow line overlap and inter-element effects to be evaluated.

The complexity of the mathematics involved in working out the various correction factors is such that a computer program, such as M.V.R. (multi-variable regression) is an essential requirement.

The number of calibration beads required will obviously depend on the size of the analytical program. An approximate estimate of the number, N , can be obtained from the formula:

$$N = n^2 + 1$$

Where n is the total number of factors to be determined by the regression calculation, including calibration curve, line and background corrections and mass absorption corrections.

In order to make the system work, an in-depth knowledge of expected interferences is needed and also careful planning of the composition of the beads. As the size of the analytical programme and hence the number of beads increases, the chance of errors will increase, e.g. weighing or bead preparation errors. These errors may be difficult to identify and will be used to produce interference factors which are erroneous. A way of identifying errors is to make each calibration bead in duplicate so that a comparison of intensities for each set of duplicates can be made. This will obviously double the amount of work required to produce the calibration. Also, if the analytical programme is very large, the M.V.R. programme shall be investigated to ensure that it is capable of performing the task required of it.

10.3.4 Calibration ranges

Although this method is not restrictive, typical ranges are tabulated for the most important oxides in the materials covered and given in Annex A.

The material types in Clause 3 are classified according to type. However, this classification need not be applied for purposes of calibration; e.g. magnesia-chromite, chrome magnesia and chrome ore could all be part of a continuous series included in one calibration. Another example of this is magnesium silicate which could share all the same calibrations and inter-element correction as aluminosilicate refractories, except for a magnesia calibration which is simply extended. Other possible combinations are given below but the list is not exhaustive.

Silica, and high alumina could be regarded as part of the aluminosilicate range, provided short range alumina and silica calibration ranges respectively are used.

Zircon, AZS and alumina magnesia spinel could be an extension of the aluminosilicate range.

Zircon could be a part of the zirconia range.

Dolomite and limestones could be combined into a series.

Magnesia alumina spinel could be an extension of magnesia.

10.4 Calibration using SeRMs

10.4.1 Calibration standards

Calibration beads shall mainly be prepared using the SeRMs shown in Annex E. It is desirable to prepare the calibration standards to cover the content range of samples for analysis. If the content ranges of the samples to be analysed are not covered by those of the standards, a mixture of SeRMs or addition of pure reagents may be permitted. When SeRMs are used to establish a calibration, the calibration shall be checked using a synthetic standard (see Annex G).

NOTE: When the SeRMs are used to establish calibrations, the difference between the theoretical value for a synthetic standard (calculated from the weight of reagents added and expressed as a percentage in a sample) and the results obtained from the calibration, should be to the same tolerance as certified reference materials (CRMs). See Annex G.

N is the number of beads used for the calibration curve;

ϕ is the number of coefficients obtained (linear equation = 2, quadratic equation = 3).

In many cases, this value can be obtained together with the calculation of the calibration curves by the computer attached to the X-ray fluorescence spectrometer. In cases where the accuracy is significantly improved, and even if the accuracy is less than the analysis tolerance, it is still desirable to use the calibration equation with coexisting correction coefficients.

NOTE: Overlapping correction in calibration using SeRMs is the same as that in calibration using reagents (see 10.3.2.6 and 10.3.2.7).

11 Corrections

11.1 Line overlap correction

The corrections are best devised from binary standards. Corrections may be percent oxide determined per percent interferant, or in some cases be intensity corrections.

NOTE: There is an interference of Zr on HfLa therefore HfL β or HfMa with a fine collimator should be used. Interferences of Zr on NaKa, Ca on MgKa and Cr on MnKa should also be noted.

11.2 Background correction

These effects are generally applied in the same manner as given in 11.1, especially in the case of simultaneous spectrometers. An alternative is the use of one or two off peak background measurements, if a sequential spectrometer is used. The use of off-peak background is recommended as necessary in the measurement of Na or Mg using a Cr target tube, or when constituents with less than 0.05% oxide content are determined.

An alternative approach is to use a number of short range calibrations designed so that change in background within the ranges is insignificant.

The complete analysis of the continuous background and its accurate measurement render the measurements independent both from physical differences due to the preparation of samples and from variations in the primary excitation.

In X-ray fluorescence spectrometry, the background has three essential sources.

a) The radiation diffused by the tube:

- 1) with the same energy: it cannot be eliminated because it corresponds to photons with the same energy as those of the peak studied.

NOTE: Unless a primary beam filter is used it is not advisable to use analytical lines adjacent to the primary tube lines (e.g. MnKa if a Cr target tube is used).

- 2) its harmonics: they correspond to photons with energy two x, three x or four x higher than that of the photons measured. (At 50 kV, the higher orders are not excited.)

b) The radiation fluoresced by the sample:

- c) Mass absorption corrections.
- d) Line overlap corrections.
- e) Correction for loss on ignition for tungsten carbide (Annex B).

Software shall allow drift correction (see 11.3) which shall be applied at two points. If off-peak backgrounds are measured, then drift correction is only required at the top end of the calibration because the off-peak background serves as the bottom point. The correction may be applied as a ratio or by correcting back to those counts obtained from the drift standards when the element in question was calibrated.

11.5 Software requirements

11.5.1 The software shall be capable of producing a regression from the calibration data, containing the following features:

- a) the possibility of mathematically weighting the zero point;
- b) the possibility of deleting calibration standards (for other elements) from the regression.

11.5.2 For at least a normal analytical programme (approximately 10 oxides), it shall be possible to store all line overlaps and coefficients, up to approximately 20 corrections per element for the ten-element program. Similarly, greater correction matrices would be necessary if the intended program were to be larger.

It shall be possible to enter coefficients, line overlaps, calibration coefficients and recalibration (ratio) data manually, as well as being able to edit them. This will enable any theoretical mass absorption correction coefficients or other coefficients calculated off-line to be entered. As corrections are improved, using sets of standards rather than a single figure, it is essential to be able to insert this new data. These methods of calibration cannot be carried out if the only entry facility is via data from a regression.

11.5.3 Non-XRF acquired data is often needed to permit the computation of an analysis. Thus, the entries itemized below shall be possible whether the spectrometer is used in either the manual or the sample-changer mode.

- a) Lithium oxide content.
- b) Boric oxide content.
- c) Fluorine content.
- d) Loss on ignition, even if negative (a gain in mass on ignition).
- e) Other elements or oxides found in less common materials.

11.5.4 Mass absorption correction coefficients and background effects of lithium oxide, boric oxide and fluorine, together with any other elements or oxides not determined by XRF found in less common materials shall be included in the iterative loops together with concentration data derived from the spectrometer.

A 100% pure silica standard shall be run ten times in each of the sample holders that will be used for future analysis. Each set of results obtained for all elements of interest shall fall within the limits set in Annex G⁴⁾. If any results fall outside these limits, that particular holder shall not be used until corrective action is taken.

NOTE 1: If the reference surface on which the sample rests is part of the instrument and independent of the sample holder, this test is not necessary.

NOTE 2: This procedure should be carried out after installation of the spectrometer or prior to using this method only.

12.4 Sample measuring positions

A 100% pure silica bead shall be run 10 times in each possible measuring position for each element of interest.

The results obtained from each position shall fall within the limits of:

- SiO_2 : $\pm 0.2\%$ of the mean;
- minors: $\pm$ detection limits from the mean.

If any results fall outside these limits, corrective action shall be taken.

NOTE: This procedure should be carried out only if there is more than one measuring position available on the spectrometer and after installation or repair to this part of the spectrometer.

12.5 Instrument repeatability

For sample batches taking greater than one hour to run, in order to monitor any medium term drift of the spectrometer, for overnight running or other long periods, the appropriate CRMs shall be measured in one of the following ways.

- a) The bead produced from the CRM shall be measured at hourly intervals. The difference in these analytical results and those achieved when measured at the start of the run shall meet the tolerances given in Annex G. If all samples measured after the CRM do not meet the criteria in Table G.1 they shall be re-measured.
- b) Establish within the previous six months, or after the last repair or service of the instrument (whichever is the shorter period), that a bead produced from the CRM measured every hour as in a) above meets the criteria given in Annex G. This is achieved by measuring the CRM every hour for the total time period of the maximum sample batch that is intended to be run. This total time period shall not exceed 24 h. Thereafter it is sufficient to measure the CRM bead only at the start and end of the analytical run. The difference in these analytical results and those achieved when it was measured at the start of the run shall also meet the tolerances given in Table G.1, otherwise all samples measured after an hour from the start of that batch shall be re-measured.

NOTE: A monitor bead measured at the start and end of the run represents an alternative to show whether there has been drift on the spectrometer.

⁴⁾ There are editorial changes for ISO Standard.

12.6 Sequential systems

The 2 θ position for elements to be determined via the goniometer shall be checked against the positions given in standard 2 θ tables, after goniometer calibrations have been carried out using suitable interference free standards as supplied and/or recommended by the manufacturer.

This procedure usually requires a minimum of two such standards for each crystal/detector combination (including multilayer crystals).

NOTE: This test should be carried out after installation, prior to using this method and after any annual service or repair to the goniometer system. For systems that do not have a mechanical linkage between θ and 2 θ of Moire fringe principle it is also recommended that the goniometer system be zeroed daily or prior to use (if used less frequently).

12.7 Dead time

Dead time is the time when the counter is unable to respond because it is already occupied in counting a previous pulse.

One of the following methods shall be used to overcome dead time:

- a) the detector shall be used within its linear response region;

NOTE: For most minor constituents the response will effectively be 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.

12.8 Other tests

Unless found to be in error, the supplier's instructions shall be followed.

12.9 Flow gas

This flow gas is used in gas flow proportional counters of the XRF spectrometer.

The temperature of the flow gas cylinder and connecting pipework is critical in order to prevent drift in sensitivity of the flow, proportional counters. Pipework shall be as short as practical and run, whenever possible, within the temperature controlled room housing the spectrometer. Where fire and safety regulation allow, the cylinder shall also be kept in the same room as the spectrometer. Where this is not possible, the cylinder shall be kept in a temperature-controlled cabinet ($\pm 2^\circ\text{C}$) or otherwise maintained at constant room temperature. For the same reason, new cylinders shall be allowed to equilibrate for about 2 h to room temperature before use.

Because of changes in composition of the gas as the cylinder becomes exhausted, cylinders shall not be used at less than 10% of their capacity.

13 Accuracy as measured using certified reference

materials

13.1 Validation of synthetic calibrations

A bead prepared from a CRM shall be presented to the spectrometer with each batch of samples. The results achieved shall be in accordance with Annex G. Suitable CRMs are also listed in Annex G. (See 10.4.1 and Annex G.)

If the results obtained for a CRM are outside the presented limits, it shall be rerun. If the results are still unacceptable, a fresh bead of the CRM shall be prepared and run. If the results from the fresh bead are out of limits, the necessary remedial action shall be taken and re-calibration made.

13.2 Validation of SeRM calibrations

A standard bead prepared synthetically shall be presented to the spectrometer with each batch of samples. The results achieved shall be in accordance with Annex G.

13.3 Fresh beads of the CRMs or synthetic standards

These shall be prepared:

- a) when the batch of flux is changed;
- b) when the methods of preparation are changed;
- c) at intervals of six months, unless it can be demonstrated that the beads produced from the CRM and synthetic standard are stable, and free of contamination for a longer period.

14 Definitions of limits of detection

The detection limit D , expressed as a percentage, is given by:

$$D = \frac{3}{S} \sqrt{2R_b} \quad \dots\dots\dots (10)$$

Where:

S is the sensitivity of the oxide, expressed as net collected counts per percentage.

R_b is the number of counts obtained for that oxide from a standard that consists of 100% of the matrix oxide for the particular class of material being analysed.

Counts for S and R_b shall be collected over the same time limit.

NOTE: For aluminosilicates, 100% SiO_2 is taken as the zero matrix for all oxides except SiO_2 itself. For SiO_2 , 100% Al_2O_3 should be used as the zero. For single major oxides, e.g. magnesia or zirconia, the detection limit of that major oxide is not required.

The definition allows a square root of two factor over and above the third term to allow for errors in drift correction.

RM 203A magnesium silicates (talc).

G. 2.4 Silica

BCS 313/1 high purity silica, for pure silicas (see Table 1.10 for reproducibility); or BCS 314 silica brick, for silica bricks.

G.2.5 Zircon/AZS

BCS 388 (see Table I.5 for reproducibility) a mixture of BCS 388 (33.3%) and BCS 394 (66.7%).

G.2.6 Zirconia

BCS 358.

G.2.7 Magnesite

BCS 389 high purity magnesite (see Table I.3 for reproducibility).

G.2.8 Spinel

A mixture of BCS 389 (30%) and BCS 394 (70%) (see Table I.9 for reproducibility) or BCS 394 (30%) and BCS 389 (70%).

G.2.9 Dolomite

ECRM 782-1 (see Table I.6 for reproducibility of previous CRM BCS 368).

G.2.10 Limestone

BCS 393 (see Table I.7 for reproducibility).

G.2.11 Chrome bearing

BCS 369 magnesite chrome (see Table I.4 for reproducibility).

BCS 308 grecian chrome ore (see Table I.8 for reproducibility).

G.2.12 Calcium aluminate

A mixture of BCS 394 (33.3%), and of BCS 372/1 (66.7%).

G.2.13 Others

CRMs not included above may also be used.

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