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Chemical analysis of refractory products by XRF — Fused cast bead method

Analyse chimique des matériaux réfractaires par fluorescence de rayons X — Méthode de la perle fondue

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 12677 was prepared by Technical Committee ISO/TC 33, *Refractories*.

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INTERNATIONAL STANDARD **ISO 12677:2003(E)**

Chemical analysis of refractory products by XRF — Fused cast bead method

1 Scope

This International 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 following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO Guide 34:2000, *General requirements for the competence of reference material producers*

ISO 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

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ISO 10058, *Magnesites and dolomites — Chemical analysis*

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

EN 955-2, *Chemical analysis of refractory products — Part 2: Products containing silica and/or alumina (wet method)*

3 Types of material

High alumina $\geqslant$ 45 % Al_2O_3

Alumino-silicate 7 % to 45 % Al_2O_3

Silica $\geqslant$ 93 % SiO_2

Zircon

Zirconia and zirconates

Magnesia

Magnesia/alumina spinel (~ 70/30)

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Dolomite

Limestone

Magnesia/chromic oxide

Chrome ore

Chrome alumina

Alumina/magnesia spinel (~ 70/30)

Zirconia-alumina-silica cast material (AZS)

Calcium silicates

Calcium aluminates

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 cast 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. Certified Reference Materials (CRMs) can be used providing they meet all the requirements of 10.2.2 and 10.4.1.

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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 International Standard.

5 Sample grinding

Bulk sampling is not within the scope of this method, which should start with a laboratory sample.

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 ISO 565. 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, of 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, of 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 × 50 mm × 50 mm.

6.4 Air jet, (optional) required to cool the mould rapidly. This can be any device whereon a narrow jet of air 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.

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In most cases it is very important to cool the melt rapidly. This is necessary to obtain a homogeneous bead and to free the melt from the dish.

NOTE A water-cooled metal plate may also be used.

6.5 Fusion apparatus, electric resistance furnaces or high frequency induction furnaces that can be heated up to a fixed temperature of between 1 050 °C and 1 250 °C may be used.

6.6 Automatic fusion apparatus, for use in automatic bead preparation (see 9.3) where required.

6.7 Balance, capable of weighing to ± 0,1 mg.

7 Loss on ignition (and/or drying)

Carry out the loss on ignition test in accordance with the method for chemical analysis of magnesites and dolomites (see ISO 10058) or the method for wet analysis of products containing alumina and/or silica (see EN 955-2).

Corrections shall be applied for tungsten carbide grinding if used (see Annex B).

NOTE “Carbosorb" and calcium chloride are recommended as desiccants for carbonates. For all other materials “silica gel" is a suitable general purpose desiccant.

For materials not listed above, dry at (110 ± 10) °C and ignite at (1 025 ± 25) °C, in both cases to constant mass.

When vacuum desiccators are used the appropriate desiccator inlet trap must be used when any vacuum is released. Phosphorus pentoxide shall be avoided where surface active materials are being stored, as P_2O_5 is absorbed by the sample, particularly under vacuum conditions.

8 Flux

8.1 Choice of flux and ratio of flux to sample

8.1.1 One of the advantages of the XRF fused cast bead method is that a wide variety of fluxes may be chosen. For a given calibration the same flux shall be used throughout. The conditions given in 8.1.2 to 8.1.9 shall be met for any flux and flux/sample ratio used.

NOTE Fluxes used with success in the analysis of refractory materials are given in Annex C. Pre-fused fluxes have the advantage of lower moisture contents.

8.1.2 Under the conditions of preparation used, the sample shall be totally dissolved by the flux and shall not come out of solution during the casting procedure.

8.1.3 The resulting bead shall be transparent and show no signs of devitrification.

8.1.4 At a reasonably high counting time the required detection limits shall be achieved for the elements determined. See Clause 14 and Annex 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).

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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;

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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 $3RD$,

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.

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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 required mass of ignited flux = required mass of unignited flux). Carry out this loss on ignition, at weekly intervals or for each kilogram of flux used, whichever is the more frequent.

$$F = \frac{100}{100 - L} \tag{1}$$

NOTE The compensation may be unnecessary if the loss on ignition is 0,50 % or lower (pre-fused fluxes).

9 Fusion casting procedures

9.1 General

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The laboratory shall demonstrate that it can achieve the required reproducibilities (see 12.1).

9.2 Fusion of samples and casting of beads

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9.2.1 Choice of procedure

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

9.2.2 Requirements

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

a) Duplicate or single beads may be prepared; the number used shall be stated in the test report.

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, R, by mass of the flux to that of the sample shall be the same for the material type analysed.

d) The melts produced shall be visually homogeneous.

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

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

g) The sample shall not be contaminated in any way by the sample preparation.

h) Beads produced shall be free from blemishes on the chosen measuring 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 glass beads of known composition shall be prepared in the same way as sample beads.

k) If moulds become distorted in use, they shall be reshaped by pressing in a suitable former. If the bottom (flat) surface of the bead is used for analysis, the top surface of the mould shall also be kept flat and free from blemishes.

l) Beads shall be infinitely thick to the X-ray wavelengths measured. For line parameters used in refractory analysis, infinite thickness is normally achieved.

NOTE 1 Duplicate beads are preferable to single beads. However, if all the oxides given in Annex A are determined for the relevant class of material, an analytical total will be achieved, which acts as a check on the result of analysis.

NOTE 2 Fusions at 1 200 °C will volatilize certain elements, e.g. sulfur, even when an oxidizing agent is used.

9.2.3 Conversion of the sample to bead form

The sample to be analysed may be converted into bead form in a number of ways.

a) Calcine the sample to constant mass at (1 025 ± 25) °C, desiccate and allow to cool to room temperature. Weigh it in the fusion dish and record the mass, m, to the nearest 0,000 1 g. Weigh the flux samples as described in 8.2.

b) Take a sample of uncalcined flux of mass $R \cdot m \cdot F$ and mix thoroughly with the sample, where F is the flux factor determined in 8.2 b). Dry the sample to constant mass at (110 ± 10) °C. Weigh in the fusion dish and record, to the nearest 0,000 1 g, the sample mass

$$m\left(1+\frac{L}{100}\,\%\right),$$

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where L, is the percentage by weight of sample lost during ignition at (1 025 ± 25) °C.

As in 9.2.3 a) the sample may be mixed with either calcined or uncalcined flux.

NOTE 1 For problems affecting the fusion of materials containing chromium oxide or zirconia, see 9.5.

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

During the initial part of the fusion process, fuse carbonate samples slowly to avoid ‘spurting' (ejection of sample or flux).

NOTE 2 In the case of limestone, dolomite and magnesium carbonate it is preferable to weigh out an amount of the dried sample, corrected for loss on ignition, for fusion.

NOTE 3 The fusion temperature may be specified according to material type.

9.2.4 Casting of beads

9.2.4.1 General. Cast the beads using one of the following methods.

a) Outside the furnace: after 5 min at (1 200 ± 50) °C remove the fusion vessel (6.1) and the heat reservoir (6.3) from the furnace (6.5) and place on a horizontal surface. Remove the lid from the fusion vessel, remove the vessel from the furnace and immediately pour the melt into the casting mould (6.2).

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.

b) In the furnace: after 5 min at (1 200 ± 50) °C remove the lid from the fusion vessel (6.1) and pour the melt into the mould (6.2) inside the furnace (6.5), 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.

NOTE 2 Most refractory materials contain small or minor amounts of Cr_2O_3, ZrO_2, and α-Al_2O_3 which, if the fusion is not completed at 1 200 °C will cause the melt to de-vitrify. However, if experience shows that this de-vetrification is not a problem, samples can be cast in furnaces at as low as 1 100 °C, providing calibration standards are prepared the same way.

NOTE 3 Fusions at 1 200 °C will volatize sulfur even when an oxidising agent is used.

Proceed in accordance with 9.2.4.2.

c) Combined fusion mould: after 5 min at (1 200 ± 50) °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.

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.

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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 Lα line near the Al Kα 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.

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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 the previous batch of the same reagent. The intensities achieved for elements other than those in the reagent shall not differ by more than the detection limit for that element.

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 CO_2) for minor constituents and of at least 99,99 % purity for silica and alumina.

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

a) Silica, alumina and magnesia: determine the loss on ignition as follows. Calcine $\leqslant$ 5 g of the material, as-received, at 1 200 ± 50 °C and keep it at this temperature for a minimum of 30 min. Cool in a desiccator to room temperature and reweigh. After allowing for this loss, weigh the appropriate amount of the uncalcined material to prepare the standard bead.

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b) Manganese oxide (Mn_3O_4), titanium(IV) oxide and nickel(II) oxide, chromium(III) oxide, zirconia, hafnia, ceria, yttria, lanthia and other rare earths. Calcine $\leqslant$ 5 g of the material at 1 000 ± 25 °C and keep it at this temperature for a minimum of 30 min. Cool in a desiccator to room temperature before use.

NOTE 1 Rare earths absorb water and carbon dioxide from the atmosphere.

c) Iron(III) oxide, tin(IV) oxide, cobalt oxide (Co_3O_4) and lithium orthophosphate. Calcine $\leqslant$ 5g of the material at 700 ± 25 °C and keep it at this temperature for a minimum of 30 min. Cool in a desiccator to room temperature before use.

d) Calcium carbonate, barium and strontium carbonates, potassium and sodium carbonates, tungstic oxide, gallium oxide, lithium sulphate. Dry the material at (230 ± 20) °C before use. Cool in a desiccator to room temperature before use.

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

NOTE 3 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_3 in order to monitor its presence in samples, and hence correct the analysis and the loss on ignition for WC contamination (see Clause 5). Unlike the wet chemical analysis procedure, X-ray fluorescence determinations are not subject to any significant cross interference due to tungsten and furthermore the contaminating tungsten can be easily monitored. If tungsten contamination exceeds 0,5 %, corrections shall be applied. See Annex B.

10.2.2 Preparation of Series Reference Materials (SeRMs)

SeRMs can be used for calibration instead of synthetic standards. The SeRMs shall cover the following points:

a) SeRMs shall satisfy the conditions in Annex B of the ISO/IEC Directives (1992) — Part 2 and in Annex A of ISO Guide 34:2000.

b) SeRMs shall be formulated to provide regular intervals of concentration.

c) The variation in concentrations of the oxides of the SeRMs shall be independent of each other.

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d) There shall be a minimum of ten SeRMs in a series.

e) The SeRMs shall be checked for homogeneity.

f) Full statistics shall be provided of between and within laboratory variation in their certification.

g) The chemical analyses shall be checked by a second technique (e.g. ICP).

10.3 Calibration using reagents

10.3.1 Calibration standards

The binary calibration standard is recommended for its simplicity.

Calibrations so produced are unambiguous and mistakes in weighing are easily spotted and rectified.

NOTE Whilst multi-linear regressions from multi-oxide synthetic standards may be used, provided they meet all other criteria, serious difficulties may be encountered by inexperienced users. These include weighing errors and a possible inability to isolate line overlap effects.

10.3.2 Method of calibration using binary and ternary standards

10.3.2.1 General

The principle of this approach to calibration is to create calibration standard beads, in the same way as sample beads are prepared but from simple mixtures of pure oxides or carbonates. The composition of these standards is designed to determine specifically and independently each of the three parts that make up the calibration:

a) the coefficients to describe the shape of the calibration curve;

b) the line overlap corrections;

c) the mass absorption corrections (e.g. alpha coefficients).

This approach has the advantage that each parameter is clearly separated from any other and that errors in weighing standards are easily identified. Although initially it may require more standards than a multi-element calibration, the standards used only involve the additions of one, two or at most three constituents and calibrations once set up are easily extended to increase calibration range or to add additional elements without having to redefine or re-measure already established calibration coefficients, line overlap corrections or mass absorption corrections.

10.3.2.2 Definition of matrix

The materials listed in Clause 3 may be split into three types of matrix:

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a) one single major constituent (e.g. zirconias);

b) two major constituents (e.g. alumino-silicates);

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

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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 alumino-silicates 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.

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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 ± 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 × 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 SrLα or 100 % TiO_2 for BaLα). 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:

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— $\leqslant$ 2 %, at least two approximately evenly-spaced concentrations.

— $\leqslant$ 10 %, at least three approximately evenly-spaced concentrations.

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— $\leqslant$ 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.