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Chemical analysis of refractory products by X-ray fluorescence (XRF) — Fused cast-bead method (ISO 12677:2011)

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National foreword

This British Standard is the UK implementation of EN ISO 12677:2011. BS 1902-9.1:1987 was superseded by BS EN ISO 12677:2003 which is superseded by BS EN ISO 12677:2011.

The UK participation in its preparation was entrusted to Technical Committee RPI/1, Refractory products and materials.

A list of organizations represented on this committee can be obtained on request to its secretary.

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English Version

Chemical analysis of refractory products by X-ray fluorescence (XRF) - Fused cast-bead method (ISO 12677:2011)

Analyse chimique des matériaux réfractaires par fluorescence de rayons X - Méthode de la perle fondue (ISO 12677:2011)

Chemische Analyse von feuerfesten Erzeugnissen durch Röntgenfluoreszenz-Analyse (RFA) - Schmelzaufschluss-Verfahren (ISO 12677:2011)

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Foreword

This document (EN ISO 12677:2011) has been prepared by Technical Committee ISO/TC 33 "Refractories" in collaboration with Technical Committee CEN/TC 187 “Refractory products and materials” the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2012, and conflicting national standards shall be withdrawn at the latest by April 2012.

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The text of ISO 12677:2011 has been approved by CEN as a EN ISO 12677:2011 without any modification.

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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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.

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

This second edition cancels and replaces the first edition (ISO 12677:2003), which has been technically revised. Although the method in this International Standard has been considerably modified editorially and in layout, the technical changes are limited. Some minor corrections have been made to certain equations. The only significant changes are a reference to a further International Standard method (being prepared) for the preparation of reduced materials for analysis by this standard, and instructions on how to add other constituents to calibrations at the end of 10.2.1, *Purity and preparation of reagents*.

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INTERNATIONAL STANDARD ISO 12677:2011(E)

Chemical analysis of refractory products by X-ray fluorescence (XRF) — Fused cast-bead method

1 Scope

This International Standard specifies a method for the chemical analysis of refractory and technical ceramic raw materials, intermediates and products, by means of the X-ray fluorescence (XRF) fused cast-bead method. Typical materials that can be analysed by this standard are given in Clause 3. This International Standard is not applicable to non-oxide materials, such as silicon carbides or nitrides, etc. The method is applicable to a wide range of materials containing a wide range of elements.

NOTE 1 The presence of significant amounts of certain elements, such as tin, copper, zinc and chromium, can present difficulties in the fusion process. In this case, the Bibliography can be referred to.

NOTE 2 Constituents at concentrations greater than 99 % (on a dried basis) are reported by difference, provided that all likely minor constituents and any loss on ignition have been determined. These figures can 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 35:2006, *Reference materials — General and statistical principles for certification*

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

ISO 26845, *Chemical analysis of refractories — General requirements for wet chemical analysis, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) methods*

3 Types of material

Listed below are various types of ceramic material that have been successfully analysed by this method and for which statistical data is available (see Annex I). The list is not exhaustive but serves as a guide to those using this International Standard for the first time.

a) High alumina > 45 % Al_2O_3

b) Alumino-silicate 7 % to 45 % Al_2O_3

c) Silica > 93 % SiO_2

d) Zircon

e) Zirconia and zirconates

f) Magnesia

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g) Magnesia/alumina spinel (~70/30)

h) Dolomite

i) Limestone

j) Magnesia/chromic oxide

k) Chrome ore

l) Chrome-alumina

m) Alumina/magnesia spinel (~70/30)

n) Zirconia-alumina-silica cast material (AZS)

o) Calcium silicates

p) Calcium aluminates

q) Magnesium silicates

A list of elemental ranges and required detection limits are given in Annex A.

NOTE 1 Some of the above material types can be accommodated for common calibrations (see 10.3.4).

NOTE 2 Reduced materials, such as silicon carbide, cannot be determined directly by this International Standard and so are not listed above. Such materials require special methods both for loss on ignition and fusion into a bead prior to XRF analysis. Suitable procedures are described in ISO 21068-1, ISO 21068-2 and ISO 21068-3 and further methods are under development by the refractory standards system. Once reduced materials are suitably ignited and subsequently prepared as fused beads, this standard can be applied to the rest of the procedure.

WARNING — Failure to pretreat reduced materials, such as silicon carbide, properly not only leads to erroneous results but will also cause damage to valuable platinum alloy crucibles and dishes.

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) may be used providing they meet all the requirements of 10.2.2 and 10.4.1.

Because of the universality of the fused cast-bead technique, various fluxes and modes of calibration are permitted, providing they have been demonstrated as being able to meet certain criteria of repeatability, 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 Apparatus

5.1 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).

NOTE A useful guide to the care of platinum is given in Reference [5] of the Bibliography.

5.2 Casting moulds, of a non-wetted platinum alloy (Pt/Au 95 %/5 % is suitable).

NOTE Vessels that serve both as fusion vessels and casting moulds can be used.

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5.3 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.

5.4 Air jet (optional), required to cool the mould rapidly. This may 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.

NOTE 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.

A water-cooled metal plate may also be used.

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

5.6 Automatic fusion apparatus, for use in automatic bead preparation (see 9.2) where required.

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

5.8 Mechanical mixer, that moves in a linear or rotary way.

NOTE Vibratory mixers cannot be used as they induce segregation.

6 Sample grinding

This International Standard shall start with a laboratory sample.

NOTE 1 Bulk sampling is not within the scope of this method but can be found in ISO 26845.

The sample shall be ground using tungsten carbide. The appropriate corrections for tungsten carbide (and its binder if necessary) shall be applied to loss on ignition and analysis figures in accordance with Annex B.

NOTE 2 It is permissible to apply the sample grinding methods cited in conventional chemical methods for the classes of materials covered. However, the tungsten carbide method is the preferred method.

The maximum particle size shall be 100 µm.

NOTE 3 The purpose of grinding is to obtain a sample sufficiently fine to be fused easily but below a set limit of introduced contamination. But for certain samples that are difficult to fuse (e.g. chrome ores), finer grinding to less than 60 µm might be necessary.

One of the following two methods shall be used to obtain the required particle size.

a) For mechanical grinding devices, establish what grinding times are sufficient to grind the various samples to be analysed to the correct fineness and thereafter apply these minimum times for grinding. In order to establish grinding times, use the mechanical grinder to prepare typical materials analysed for progressively increasing lengths of time of ~2 min. Sieve each ground sample through a 100 µm sieve until a grinding time is reached where the entire sample passes through the sieve. Then use this time for that material or the longest time of any material analysed, if applied to all materials. When grinding hard materials, such as chromite, sieving shall be used, but this might induce segregation. Therefore, after sieving, the sample shall be mixed thoroughly by stirring or tumbling prior to transferring to a sample tube. Because heavier minerals can segregate on standing, it is advisable to stir the sample once more, prior to weighing out.

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.

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NOTE 4 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.

7 Loss on ignition (and/or drying)

Loss on ignition shall be carried out in accordance with ISO 26845.

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. Prefused 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 (≤200 s), the required detection limits shall be achieved for the elements determined. Detection limits are defined as in Clause 14 and listed in 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 repeatability for the determination of that element (as measured according to 12.1 and defined as in G.1).

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:

$$D/(3R)$$

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 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 9.1.2 f)]. Store the flux in a tightly sealed container except when in use. The loss on ignition, expressed as a percentage by mass, w_L, is then used to calculate a flux 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 the 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.

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

NOTE The compensation might be unnecessary if the loss on ignition is 0,50 % or lower (prefused fluxes).

9 Fusion casting procedures

9.1 Fusion of samples and casting of beads

9.1.1 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.

9.1.2 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) The variations of any loss of flux shall be minimized by using consistent times and temperature during fusion in the preparation of both calibration standards and samples.

g) The sample shall not be contaminated in any way by the sample preparation by any constituent being measured on that sub-sample. This can either be established by knowing the composition of the grinding media or by measuring the amount of contamination added in grinding pure materials or materials of known composition.

h) The 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.

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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 for 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.

9.1.3 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

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

where w_{L} is the percentage by mass of sample lost during ignition at (1 025 ± 25) °C.

As in item 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 9.4.

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 can be specified according to material type.

9.1.4 Manual casting of beads

9.1.4.1 General

The final part of the fusion process consists of heating the fusion vessel, the mould and the heat reservoir (if used) in a muffle furnace (1 200 ± 50) °C for 5 min. Then cast the beads using one of the following methods.

a) **Outside the furnace**: after 5 min at (1 200 ± 50) °C, remove the heat reservoir (5.3) from the furnace (5.5) and place it on a horizontal surface. Immediately place the mould onto the heat reservoir. Then remove the lid from the fusion vessel and immediately pour the melt into the casting mould (5.2).

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b) **In the furnace**: after 5 min at (1 200 ± 50) °C, remove the lid from the fusion vessel (5.1) and pour the melt into the mould (5.2) inside the furnace (5.5), ensuring that as much of the melt is transferred to the mould as possible. Remove the mould from the furnace and place it on a horizontal surface.

c) **Combined fusion mould**: after 5 min at (1 200 ± 50) °C, remove the fusion vessel from the furnace. If a releasing agent is not used, the melt can rise up the sides of the vessel. Therefore, careful manipulation of the vessel is required to work the melt into the mould part of the vessel. Then put the fusion vessel on a graphite brick to cool.

d) **Mould heated over a burner**: after preparation of the melt at the fusion temperature and the 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 (5.4), as described in 9.1.4.2., or a water-cooled metal plate to accelerate the cooling process.

When the top surface of the bead is used [not c)] 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 Most refractory materials contain small amounts (as low as 0,1 %) of Cr_2O_3, ZrO_2, and α-Al_2O_3 which, if the fusion is not completed at (1 200 ± 50) °C, will cause the melt to devitrify. However, if experience shows that de-vetrification is not a problem, samples can be cast in furnaces at as low as (1 050 ± 25) °C, providing calibration standards are prepared the same way.

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. Iodine does have a small line overlap with Ti$K\alpha$, so if low levels of TiO_2 are to be determined, corrections may be needed. 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 for such agents, but there are further 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 $L\alpha$ line near the Al $K\alpha$ line. High amounts of Br may cause serious line-overlap problems when measuring low alumina concentrations and corrections may need to be applied. For low levels of Al_2O_3, iodide or iodate is recommended. 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.

9.1.4.2 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 onto the centre of the base of the mould. When the bead has solidified and released itself, turn off the air jet.

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

9.2 Automatic bead preparation

Automatic bead equipment may be used as an alternative to 9.1.4, and shall be in accordance with 9.1.2 and 12.1.

9.3 Storage

Beads can deteriorate because of adverse temperature and humidity conditions. Therefore they should be stored in such a manner as to avoid hydration and contamination.

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The 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:

a) sulfur from vacuum oil in the spectrometer or from the laboratory atmosphere;

b) sodium and chlorine from the atmosphere if the laboratory is near the sea;

c) potassium from cigarette smoke;

d) contamination from the surface of plastic bags that may be used for storing the beads.

9.4 Special problems

Samples with high chromium oxide or zirconia content can create problems during fusion. Chromium oxide is difficult to dissolve in the molten flux and zirconia also suffers from this problem to a lesser degree but can also cause devitrification on cooling, even after complete dissolution. Before establishing methods of fusion for these materials, fusion trials are required to establish a method for preparing the samples of the highest content of these oxides, likely to be encountered by the laboratory. In these trials, optimum flux, sample/flux ratio, temperatures and fusion times need to be established. Normally, different procedures will be required for chrome-bearing material, zircon and zirconia.

NOTE Even if the storage conditions in 9.3 are observed, beads containing high levels of ZrO_2 tend to absorb moisture onto the surface more than other beads. This causes increased backgrounds on light elements. The problem can be cured by drying the bead overnight at 220 °C.

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. The series of CRMs meeting the requirements of 10.2.2 and 10.4.1 may be regarded as SeRMs.

10.2 Reagents and series reference materials (SeRMs)

10.2.1 Purity and preparation of reagents

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. For the calibration of elements such as sulfur or phosphorus which do not form stable oxides or carbonates, 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. The reagents used for calibration shall be of high purity and, when fresh batches of reagents are purchased, they shall 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.

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 5 g of the material, as received, at (1 200 ± 50) °C and keep them at this temperature for a minimum of 30 min. Cool in a

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desiccator to room temperature and reweigh. After allowing for this loss, weigh the appropriate amount of the uncalcined material to prepare the standard bead.

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 5 g of the material at (1 000 ± 25) °C and keep them 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 5 g of the material at (700 ± 25) °C and keep them 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 sulfate. Dry the material at (230 ± 20) °C before use. Cool in a desiccator to room temperature before use.

Other oxides may be added to calibrations, as long as the oxides or their compounds used for the calibration are of a sufficient purity and of guaranteed stoichiometry by heat treatment, etc. In addition, problems regarding volatility of that element/oxide in fusion are taken into account, as well as any tendency for the element to alloy with the fusion vessel during the fusion process. A list of useful references to deal with these points is given in References [5] to [9]. This list is not exhaustive and other references may also be of use. In addition, the calibrations should meet the other requirements of this International Standard.

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

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 Annex B). 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 may 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 may be used for calibration instead of synthetic standards. The SeRMs shall cover the following points.

a) SeRMs shall satisfy the requirements of ISO Guide 35:2006.

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.

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

e) The SeRMs shall be homogeneous.

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

g) The chemical analyses shall be checked by a second technique [e.g. inductively coupled plasma (ICP)].

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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 can be used, provided they meet all other criteria, serious difficulties might 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 the calibration range or to add additional elements without having to redefine or remeasure 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:

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

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

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

In the first case, the matrix may 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.

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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 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 ±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 measured during the entire calibration process, which may take place over a number of days.

NOTE Normally, drift correction standards would not be used as calibration standards.

These standards shall be used each time the 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 may 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:

— <2 %, at least two approximately evenly-spaced concentrations;

— <10 %, at least three approximately evenly-spaced concentrations;

— <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 can 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

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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 a 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 may 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 10.3.2.4 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.

NOTE The set of binary standards can also be used for the determination of mass-absorption correction coefficients in 10.3.2.8.

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 10.3.2.4) as unknowns. The apparent percentages that the binary mixtures produce 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. If the software fails to apply drift correction to line overlap, corrections shall always be of concentration on concentration. In this case, the intensity approach may lead to errors as sensitivity of crystals and detectors change over time. For concentration on concentration corrections, it is likely that line interferences would be expressed normally as 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 may be applied to background effects, although in the case of the effects of ZrO_2 on NaKα and MgKα, 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 at 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 calibration 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 10.3.2.6 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.

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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, even for 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 may be supplied by the instrument manufacturer or may 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 type of material (Clause 3) and the same flux-to-sample ratio may also be applied. These theoretical and empirical mass-absorption correction coefficients may be used instead of those derived from specially made standards, providing the following conditions are met:

a) That $\alpha_{ij} \times C_j < 0{,}025$ (2)

where

α_{ij} is the mass-absorption coefficient of an interfering oxide on the analyte oxide;

C_j is the maximum concentration, expressed as a percentage, of the interfering oxide.

NOTE The above expression will limit the error in determination of an analyte to 5 parts in 1 000 if the mass-absorption coefficient used is 20 % in error.

b) The mass-absorption coefficient is not due to an absorbance of an analyte line near to an absorption edge of the interfering element.

If either condition a) or b) given above is not met, then synthetic standards shall be made to establish empirical mass-absorption correction coefficients.

NOTE There might be variations in the take-off angle and exciting kV. In this case, it is advisable to measure such corrections.

10.3.2.9 Model for mass-absorption correction coefficients

$$nV_C = V_u(1 + \Sigma\alpha_{ij} \times C_j) \quad (3)$$

where

α_{ij} is the mass-absorption correction coefficient of interfering oxide j on analyte oxide i;

C_j is the concentration of interfering oxide j;

V_u is the apparent intensity, ratio or concentration of the analyte oxide (after correction for line overlap or background effects) as given by the spectrometer for the standard (value before correction);

V_C is the true intensity or ratio read from the calibration graph that corresponds to the actual concentration of the analyte oxide in the standard or, if concentrations are used, the actual concentration (value after correction).

More complex terms are not normally required for fused bead calibrations.

10.3.2.10 Calculation of mass-absorption correction coefficients

The standards used for determination of mass-absorption correction coefficients are designed to determine one correction at a time; therefore the single interference case of Equation (3) may be rewritten as follows:

$$\alpha_{ij} = (V_C - V_u)/(V_u \times C_j) \quad (4)$$

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The same values, i.e. intensity, ratio or concentration, should be used throughout for values of V.

The difference between duplicate determinations $\Delta\alpha_{ij}$ of empirical mass-absorption correction coefficients shall be such that $\Delta\alpha_{ij} \times C_j < 0{,}005$ [see Equation (2)]. In the case of single determinations, $\Delta\alpha_{ij} \times C_j < 0{,}005$ [see Equation (2)] where $\Delta\alpha_{ij}$ is calculated using the empirical and theoretical alpha correction. If these conditions are not met, the relevant bead(s) shall be rerun, and if this fails to produce agreement, further beads shall be prepared to redetermine this coefficient.

10.3.2.11 Criteria for determination of theoretical mass-absorption correction coefficients

In order to avoid the need to produce large numbers of standards to calculate empirical mass-absorption corrections, acceptable theoretical mass-absorption corrections may 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 may 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.

In the case of many modern instruments, it may not be possible to establish if the above requirements are met. If this is the case, the coefficients shall always be checked, as described at the end of 10.3.2.1.

If the software does not generate alpha corrections but applies fundamental parameters, the accuracy of the calibrations shall be checked with a range of Certified Reference Materials. If CRMs are not available then “in-house” or synthetic standards of known concentration shall be employed.

If no mass-absorption correction coefficients of the main matrix oxide on the oxide determined when producing the calibration are required, the matrix shall 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 may usually be regarded as a mixture of the maximum amount of the determined oxide complemented 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

10.3.3.1 In the procedures described in 10.3.1 and 10.3.2.1, calibrations are carried out with a minimal effect from other elements, and inter-element effect (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.

10.3.3.2 A series of synthetic calibration beads or Series Reference Materials (see 10.2.2) prepared from high-purity reagents (see 10.2.1) 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.

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The number of calibration beads required will obviously depend on the number of analytical components, n, of the analytical program. An approximate estimate of the number, N, may 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.

10.3.3.3 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 number of analytical components, n, 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 may 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 materials listed in Clause 3 are classified according to type. However, this classification need not be applied for purposes of calibration; for example 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 alumino-silicate refractories, except for a magnesia calibration which is simply extended. Other possible combinations are given below but the list is not exhaustive.

If mass-absorption corrections for SiO_2 on Al_2O_3 are applied, and vice versa, and the zero point is over-weighted, then a single calibration for these two oxides from 0 % to 100 % shall be set up, which is accurate at both the top and bottom ends. Despite applying these mass absorbtion corrections, the calibration may still not be linear. In this case, it is permitted to express the calibration as a quadratic equation but never of higher terms. Both ends of the extended calibration shall always be checked with suitable synthetic standards.

Zircon, AZS and alumina magnesia spinel could be an extension of the alumino-silicate 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 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).

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

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10.4.2 Calibration curve and equation

10.4.2.1 Preparation of calibration curve

Measure the X-ray intensities of the standard beads to obtain a calibration curve. Obtain a relation of the contents of the components and the X-ray intensities of the beads used for the calibration curve with the quadratic regression equation or the linear regression equation in accordance with the least-squares method.

$$C_i = aI_i^2 + bI_i + c \tag{5}$$

where

C_i is the content of component i;

I_i is the X-ray intensity of component i;

a, b, c are coefficients (in the case of the linear function equation, $a = 0$).

10.4.2.2 Preparation of calibration equation

In the case where adequate accuracy in the calibration curve in 10.4.2.1 has not been obtained, the following calibration equation shall be obtained by the method defined in Annex H.

$$C_i = (aI_i^2 + bI_i + c)(1 + \sum a_j C_j) + l_j C_j \tag{6}$$

where

C_i is the concentration of the analyte;

α_j is the matrix correction coefficient of coexisting component j;

C_j is the content of coexisting element j;

l_j is the line-overlap correction coefficient of coexisting component j.

Verify the accuracy of the calibration curve with the following equation. If the value exceeds the required analysis uncertainty, it is necessary to use the calibration equation with the correction coefficients of coexisting components.

$$s_i = \sqrt{\frac{\sum (C_i - C_i')^2}{N - \phi}} \tag{7}$$

where

s_i is the standard error of estimate of component i;

C_i' is the content of component i from the calibration curve, as a percentage;

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 may be obtained together with the calculation of the calibration curves by the computer attached to the X-ray fluorescence spectrometer. In cases where the standard error of estimate is significantly improved, and even if the standard error of estimate is less than the required analysis uncertainty, it is still desirable to use the calibration equation with coexisting correction coefficients.

NOTE The line-overlap correction in calibration using SeRMs is the same as that in calibration using reagents (see 10.3.2.6 and 10.3.2.7).

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11 Corrections

11.1 Line-overlap correction

The corrections are best devised from binary standards. Corrections shall normally be expressed as the percentage of oxide determined per percentage of interferant (see 10.3.2.7). In exceptional cases it is possible to use intensity on intensity corrections.

There is an interference of Zr on HfLα, therefore HfLβ or HfMα with a fine collimator should be used. Interferences of Zr on NaKα, Ca on MgKα and Cr on MnKα 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 an 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 a change in background within the ranges is insignificant.

The background subtraction renders 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) Scattered tube radiation:

   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. MnKα if a Cr target tube is used).

   2) its higher-order reflections: they correspond to photons with energy two $\times$, three $\times$ or four $\times$ higher than that of the photons measured in wavelength-dispersive X-ray spectrometry. (At 50 kV, the higher orders are not excited.)

b) Radiation fluoresced by the sample:

   1) spectral lines of the 2nd, 3rd or 4th order of a different element present in the sample;

   2) radiation of the same energy emitted by another element and corresponding to a peak of a different type than that measured. (This is a case of insoluble interference which requires the choice of another spectral line.)

c) Radiation due to fluorescence from the analysing crystal. This depends on the type of sample and analysing crystal.

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11.3 Drift correction

Both top and bottom ends of each calibration shall be monitored at calibration and with each batch of samples. A set of ratio (or recalibration) standards shall be made to correct for drift (see 10.3.2.3). Intensities are calculated as follows:

$$R = N_b + \frac{(N'_s - N'_b) \times (N_t - N_b)}{N'_t - N'_b} \tag{8}$$

where

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

N'_s is the count obtained for the sample or standard bead for the relevant element;

N'_b is the current count obtained for the bottom ratio-standard bead for the same element;

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

N'_t is the current count obtained for the top ratio-standard bead for the same element.

If we let $N_b = 0$ and $N_t = 1$, then Equation (8) reduces to the ratio:

$$R = \frac{N'_s - N'_b}{N'_t - N'_b} \tag{9}$$

NOTE As long as drift correction is applied on background as well as sensitivity, it will be suitable.

11.4 Calculation of results

Normally stages b) to d) below require iteration. Mass-absorption corrections shall normally be applied to drift-corrected intensities (or ratios); subsequently, concentrations are calculated and then concentration line overlap is applied. However, if calibrations approximate to straight lines, mass-absorption corrections may be applied to concentrations and only stages c) and d) require iteration. Line-overlap corrections may be applied as intensity on intensity or concentration on concentration. The former approach shall not be used when the line of the interfering element measured differs considerably in energy from the one causing the interference.

a) Drift correction.

b) Conversion of ratios or counts to concentrations.

c) Mass-absorption corrections.

d) Line-overlap corrections.

e) Correction for loss on ignition for tungsten carbide in accordance with Annex B.

Software shall allow drift correction (see 11.3) with a top and a bottom drift-correction sample. 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.

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