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

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

Reference number
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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*.

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*.

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

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.

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.

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.

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.

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).

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 TiKα, 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 Lα line near the Al Kα 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.

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 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)].

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.

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 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 Na$K\alpha$ and Mg$K\alpha$, 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.

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 $\alpha_{\mathrm{ij}} \times C_{\mathrm{j}} < 0{,}025$ (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

$$nV_{\mathrm{C}} = V_{\mathrm{u}}(1 + \Sigma\alpha_{\mathrm{ij}} \times C_{\mathrm{j}}) \quad (3)$$

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:

$$\alpha_{\mathrm{ij}} = (V_{\mathrm{C}} - V_{\mathrm{u}})/(V_{\mathrm{u}} \times C_{\mathrm{j}}) \quad (4)$$

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.

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.

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.

$$C_\mathrm{i} = aI_\mathrm{i}^2 + bI_\mathrm{i} + c \qquad (5)$$

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.

$$C_\mathrm{i} = (aI_\mathrm{i}^2 + bI_\mathrm{i} + c)(1 + \Sigma a_\mathrm{j} C_\mathrm{j}) + l_\mathrm{j} C_\mathrm{j} \qquad (6)$$

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.

$$s_\mathrm{i} = \sqrt{\frac{\sum (C_\mathrm{i} - C_\mathrm{i}')^2}{N - \phi}} \qquad (7)$$

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).

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 ×, three × or four × 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.

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:

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

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:

$$R = \frac{N'_s - N'_b}{N'_t - N'_b} \qquad (9)$$

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.

11.5 Software requirements

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

a) the possibility of mathematically over-weighting the zero point;

b) the possibility of deleting calibration standards (for other elements) from the regression.

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

It shall be possible to enter inter-elemental-effect coefficients, line overlaps, calibration curve coefficients and recalibration (ratio) data manually, as well as being able to edit them. This will enable any theoretical mass-absorption correction coefficients or other coefficients calculated off-line to be entered.

After the initial calibration is set up, new demands may necessitate the extension of calibrations. In this case, the software shall be capable of accepting modifications to calibration coefficients, manually or otherwise.

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

a) Lithium oxide content.

b) Boric oxide content.

c) Fluorine content.

d) Loss on ignition, even if negative (a gain in mass on ignition).

e) Other elements or oxides found in less common materials.

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

11.5.5 It shall be possible to correct tentative output concentration data for the loss on ignition and tungsten carbide contamination, and also to correct the loss on ignition for the latter.

11.5.6 Mass-absorption corrections shall be of concentration on intensity, unless the calibrations are roughly straight lines when they may be of concentration on concentration.

11.5.7 In general, line overlaps shall be of concentration on concentration, but the added alternative of intensity on intensity, and concentration on intensity, is of value.

11.5.8 Iterations of inter-element corrections shall permit either convergence to give constant values (within 0,001 % concentration), or the number of iterations shall be capable of being pre-set (5 loops are normally sufficient), or both.

12 Reproducibility and repeatability

12.1 Fusion tests

Fusion tests shall be carried out in the following circumstances:

a) initially to demonstrate that the fusion method meets the criteria;

b) when the sample preparation is changed, e.g. from manual to automatic and/or when the fusion method is modified;

c) when a new type of flux or a different flux-to-sample ratio is put into use.

Statistics on sample preparation shall be applied to every flux used by the laboratory at every flux-to-sample ratio used; for example, $Li_2B_4O_7$ used at 5:1 for dolomite and the same flux used at 10:1 for magnesites shall be tested separately for the statistical trials. Repeatability trials shall require a minimum of six beads to be prepared in the same manner from the relevant certified reference material (CRM), as shown in Annex I. The beads shall be measured together on the XRF spectrometer using counting times selected to reduce the errors caused by counting statistics to be insignificant compared with the fusion errors. Annex I gives a guide to what fusion errors and counting errors are likely to be (the latter is ~10 times less than the former). Standard deviations shall be calculated for each oxide to be determined. If the standard deviations exceed those given in Annex I for any oxide, then the method of fusion shall be modified; otherwise the determination of that oxide is not considered to be covered by this International Standard.

NOTE Iron, nickel and cobalt suffer from reduction problems and might alloy with the fusion vessel. In this case, the use of more oxidizing fusion conditions can bring their standard deviations down to an acceptable level. Lithium nitrate (anhydrous) is effective as an oxidizing agent.

12.2 Frequency of instrument tests

Carry out the tests given in 12.3 to 12.7 on the instrument:

a) when the instrument/calibration method or sample preparation method is first set up;

b) after major instrumental changes, e.g. change of X-ray tube or counter window;

c) at a regular interval of one year.

12.3 Maximum allowance differences of sample holders

This procedure shall be performed after installation of the spectrometer, prior to using this method, or if the deterioration of at least one of the sample holders is suspected.

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

A 100 % pure silica standard shall be run ten times in each of the sample holders that will be used for future analysis, by removing and replacing the bead between each measurement. The mean result for silica intensity/concentration shall be calculated for each holder. This process is repeated for all the sample holders and then the overall mean is calculated for all the holders, except any holders that give obviously suspect results.

If the result of any sample holder differs from the overall mean result by more than the limit specified in Annex G, then the holder shall not be used until corrective action is taken.

12.4 Sample measuring positions

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

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

- SiO_2: ±0,2 % of the mean;
- minor elements: ± detection limits from the mean.

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

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

12.5 Instrument repeatability

For sample batches taking over 1 h to run, in order to monitor any medium-term drift of the spectrometer, for overnight running or other long periods, the appropriate CRMs shall be measured in one of the following ways.

a) The bead produced from the CRM shall be measured at hourly intervals. The difference in these analytical results and those achieved when measured at the start of the run shall meet the tolerances given in Annex G. If a measurement of the CRM does not fulfil the requirements of G.1 c), all samples measured afterwards have to be measured again.

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

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

12.6 Sequential systems

In the case of sequential spectrometers or simultaneous spectrometers with a goniometer, there is the additional requirement to ensure that analytical lines are correctly set up on their peaks. This is normally carried out using the manufacturer's software and special standards supplied by the manufacturer for that purpose. If this is not the case, then the operative will have to set up the θ and 2θ angles of the crystal and detector, respectively, themselves. This requires standards free of interfering elements for those lines used in setting up the goniometer.

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

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

12.7 Dead time

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

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

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

NOTE For most minor constituents, the response will effectively be linear.

b) an electronic dead-time corrector shall be used to produce linear response;

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

12.8 Other tests

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

12.9 Flow gas

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

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

13 Accuracy determined by certified reference materials

13.1 Validation of synthetic calibrations

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

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

13.2 Validation of SeRM calibrations

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

13.3 Fresh beads of the CRMs or synthetic standards used to check SeRM calibrations

These (see Annex D) shall be prepared and compared with certified values (see Annex G):

a) when the batch of flux is changed;

b) when the methods of preparation are changed;

c) at intervals of six months, unless it can be demonstrated that the beads produced from the CRM and synthetic standard are stable and free of contamination for a longer period.

14 Definitions of limits of detection

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

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

where

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

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

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

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

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

15 Test report

The test report certificate shall contain the following information:

a) a reference to this International Standard, i.e. ISO 12677:2011;

b) name and address of the laboratory;

c) name and address of the client;

d) unique identifier of certificate or report (such as a serial number);

e) on each sheet of the certificate or report, a unique form of sheet identifier (such as serial number of certificate or report, with unique page number in the form “page -- of -- pages”);

f) date of receipt of the test item and date(s) of the test, as appropriate;

g) date of issue of certificate or report;

h) results and basis on which they are reported; it shall be clear that concentrations are in percentage by mass;

i) signature and legible name of approved signatory or signatories taking responsibility for content of certificate or report, or equivalent form of technical authorization;

j) unambiguous identification of item(s) tested [including name given by the client of item(s), any grade or type designation, any relevant batch or serial numbers, as appropriate];

k) any abnormalities or departures from this International Standard;

l) details of any sampling, or item preparation, when relevant to the validity of test results;

m) estimated uncertainty of the calibration of the test result (this information need only appear in test reports and test certificates where it is relevant to the validity or application of the test result, where a client's instructions so require, or where uncertainty affects compliance with a specification or limit);

n) any other available information requested by a client, such as may be relevant to the validity or applicability of the test result.

Annex A
(normative)

Calibration range and required detection limits

Tables A.1 to A.8 give calibraton ranges and required detection limits for the most important oxides in the relevant class of material.

NOTE The bottom point is the detection limit, unless otherwise stated.

Table A.1 — High alumina, alumino-silicates, and other silicates

Oxide	Range %
Alumina (Al_2O_3)	1 to 99[a]
Silica (SiO_2)	0,05 to 99[a]
Titania (TiO_2)	0,01 to 5
Iron(III) oxide (Fe_2O_3)	0,01 to 20
Calcium oxide (CaO)	0,01 to 5
Calcium oxide (CaO)[b]	0,01 to 70
Magnesia (MgO)	0,03 to 5
Magnesia (MgO)[b]	0,03 to 50
Sodium oxide (Na_2O)	0,05 to 10
Potassium oxide (K_2O)	0,01 to 5
Tungsten oxide (WO_3)[c]	0,02 to 2
Cobalt oxide (Co_3O_4)[c]	0,01 to 1
Nickel oxide (NiO)[c]	0,01 to 1
Sulfur trioxide (SO_3)[d]	0,01 to 10

NOTE Other elements can be added as necessary.

[a] Detection limit 0,05 %.

[b] For calcium and magnesium silicates and aluminates.

[c] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

[d] Sulfur trioxide can be lost on fusion.

Table A.2 — Silica

Oxide	Range %
Silica (SiO_2)	93 to 100
Titania (TiO_2)	0,01 to 0,5
Alumina (Al_2O_3)	0,01 to 2,0
Iron(III) oxide (Fe_2O_3)	0,01 to 2,0
Calcium oxide (CaO)	0,01 to 3,0
Magnesia (MgO)	0,03 to 0,5
Sodium oxide (Na_2O)	0,05 to 0,5
Potassium oxide (K_2O)	0,01 to 2,0
Tungsten oxide (WO_3)[a]	0,02 to 1,0
Cobalt oxide (Co_3O_4)[a]	0,01 to 1,0
Nickel oxide (NiO)[a]	0,01 to 1,0

[a] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

Table A.3 — Zircon and AZS

Oxide	Range %
Silica (SiO_2)	10[a] to 90
Titania (TiO_2)	0,001 to 1
Alumina (Al_2O_3)	0,01 to 70
Iron(III) oxide (Fe_2O_3)	0,01 to 2
Calcium oxide (CaO)	0,01 to 2
Magnesia (MgO)	0,01 to 10
Sodium oxide (Na_2O)	0,1 to 2
Potassium oxide (K_2O)	0,01 to 2
Tungsten oxide (WO_3)[b]	0,01 to 2
Zirconia (ZrO_2)	10[a] to 70
Hafnia (HfO_2)	0,01 to 2
Phosphorus pentoxide (P_2O_5)	0,01 to 2
Tin oxide (SnO_2)	0,01 to 0,1
Cobalt oxide (Co_3O_4)[b]	0,01 to 1,0
Nickel oxide (NiO)[b]	0,01 to 1,0

[a] Not a detection limit.

[b] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

Table A.4 — Zirconia

Oxide	Range %
Silica (SiO_2)	0,01 to 30
Titania (TiO_2)	0,01 to 1
Alumina (Al_2O_3)	0,01 to 10
Iron(III) oxide (Fe_2O_3)	0,01 to 2
Calcium oxide (CaO)	0,01 to 6
Magnesia (MgO)	0,01 to 6
Sodium oxide (Na_2O)	0,2 to 2
Potassium oxide (K_2O)	0,01 to 2
Tungsten oxide (WO_3)[a]	0,01 to 2
Zirconia (ZrO_2)	70 to 100
Hafnia (HfO_2)	0,01 to 2
Phosphorus pentoxide (P_2O_5)	0,01 to 5
Yttria (Y_2O_3)	0,01 to 6
Ceria (CeO_2)	0,01 to 6
Lanthanium oxide (La_2O_3)	0,01 to 6
Cobalt oxide (Co_3O_4)[a]	0,01 to 1,0
Nickel oxide (NiO)[a]	0,01 to 1,0

[a] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

Table A.5 — Magnesia and magnesia/alumina spinel

Oxide	Range %
Silica (SiO_2)	0,01 to 15
Titania (TiO_2)	0,01 to 1
Alumina (Al_2O_3)	0,01 to 35
Iron(III) oxide (Fe_2O_3)	0,01 to 10
Calcium oxide (CaO)	0,01 to 5
Magnesia (MgO)	65 to 100
Sodium oxide (Na_2O)	0,05 to 10
Potassium oxide (K_2O)	0,05 to 1
Phosphorus pentoxide (P_2O_5)	0,02 to 5
Chromium(III) oxide (Cr_2O_3)	0,01 to 10
Manganese(II) oxide (MnO)	0,01 to 1
Zirconia (ZrO_2)	0,02 to 10
Hafnia (HfO_2)	0,01 to 1
Barium oxide (BaO)	0,01 to 1
Tungsten oxide (WO_3)[a]	0,01 to 1
Cobalt oxide (Co_3O_4)[a]	0,01 to 1,0
Nickel oxide (NiO)[a]	0,01 to 1,0

[a] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

Table A.6 — Dolomite

Oxide	Range %
Silica (SiO_2)	0,01 to 20
Titania (TiO_2)	0,01 to 1
Alumina (Al_2O_3)	0,01 to 5
Iron(III) oxide (Fe_2O_3)	0,01 to 2
Calcium oxide (CaO)	50 to 65
Magnesia (MgO)	30 to 45
Sodium oxide (Na_2O)	0,05 to 2
Potassium oxide (K_2O)	0,01 to 1
Chromium oxide (Cr_2O_3)	0,01 to 1
Manganese oxide (Mn_3O_4)	0,01 to 1
Phosphorus pentoxide (P_2O_5)	0,01 to 2
Strontium oxide (SrO)	0,01 to 1
Barium oxide (BaO)	0,01 to 1
Sulfur trioxide (SO_3)[a]	0,01 to 2
Zirconia (ZrO_2)	0,01 to 3
Tungsten oxide (WO_3)[b]	0,02 to 1,0
Cobalt oxide (Co_3O_4)[b]	0,01 to 1,0
Nickel oxide (NiO)[b]	0,01 to 1,0

[a] Sulfur trioxide can be lost on fusion.

[b] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

Table A.7 — Limestone

Oxide	Range %
Silica (SiO_2)	0,01 to 20
Titania (TiO_2)	0,01 to 1
Alumina (Al_2O_3)	0,01 to 5
Iron(III) oxide (Fe_2O_3)	0,01 to 2
Calcium oxide (CaO)	65 to 100
Magnesia (MgO)	0,03 to 30
Sodium oxide (Na_2O)	0,05 to 2
Potassium oxide (K_2O)	0,01 to 1
Chromium oxide (Cr_2O_3)	0,01 to 1
Manganese oxide (Mn_3O_4)	0,01 to 1
Phosphorus pentoxide (P_2O_5)	0,01 to 2
Strontium oxide (SrO)	0,01 to 1
Barium oxide (BaO)	0,01 to 1
Sulfur trioxide (SO_3)[a]	0,01 to 2
Tungsten oxide (WO_3)[b]	0,02 to 1,0
Cobalt oxide (Co_3O_4)[b]	0,01 to 1,0
Nickel oxide (NiO)[b]	0,01 to 1,0

[a] Sulfur trioxide can be lost on fusion.

[b] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

Table A.8 — Magnesia chrome, chrome ore and chrome alumina

Oxide	Range %
Silica (SiO_2)	0,01 to 10
Titania (TiO_2)	0,01 to 2
Alumina (Al_2O_3)	0,01 to 40
Iron(III) oxide (Fe_2O_3)	0,01 to 30
Calcium oxide (CaO)	0,01 to 10
Magnesia (MgO)	5 to 100
Sodium oxide (Na_2O)	0,1 to 5
Potassium oxide (K_2O)	0,01 to 5
Chromium oxide (Cr_2O_3)[a]	0,01 to 40
Manganese oxide (Mn_3O_4)	0,01 to 2
Phosphorus pentoxide (P_2O_5)	0,01 to 5
Sulfur trioxide (SO_3)[b]	0,01 to 5
Zirconia (ZrO_2)	0,01 to 1
Tungsten oxide (WO_3)[c]	0,02 to 1,0
Cobalt oxide (Co_3O_4)[c]	0,01 to 1,0
Nickel oxide (NiO)[c]	0,01 to 1,0

[a] Above 40 %, a dilution is often needed, or by using flux j) in Annex C, up to 50 % Cr_2O_3 may be accommodated.

[b] Sulfur trioxide can be lost on fusion.

[c] These ranges are for the analysis of abrasion from a tungsten carbide mortar, which may be either cobalt- or nickel-bonded.

Annex B
(normative)

Corrections for tungsten carbide grinding media

B.1 Corrections for pure tungsten carbide grinding media

This correction cannot be applied if the sample contains tungsten prior to grinding. In fact, if the presence of tungsten is suspected in the sample, it shall not be ground in tungsten carbide. The corrected loss on ignition is given by the Equation (B.1):

$$L_\mathrm{t} = \frac{100\left[\dfrac{L_\mathrm{m}}{100 - L_\mathrm{m}} - \dfrac{C\left(m_\mathrm{rW} - 1\right)}{100}\right]}{\dfrac{100}{100 - L_\mathrm{m}} - \dfrac{C m_\mathrm{rW}}{100}} \tag{B.1}$$

where

L_m is the measured percentage loss on ignition; see Equation (2);

L_t is the corrected percentage loss on ignition. This is the change in mass (as if the tungsten carbide contamination were not present) on igniting a dried sample divided by the original dried mass (see Clause 7). It is the mass of the volatile components in the sample divided by the mass of the whole sample;

C is the percentage of tungstic oxide (WO_3) measured by the XRF spectrometer on the cast bead;

m_rW is the $\dfrac{\text{molecular weight of tungsten carbide (WC)}}{\text{molecular weight of tungsten oxide (WO}_3\text{)}} = 0{,}844\,8$

The factor f to correct back the results, both for the effects of dilution with tungsten carbide and for loss of ignition, is given by the Equation (B.2):

$$f = \frac{100 - L_\mathrm{t}}{100\left[1 - \dfrac{C}{100}\right]} \tag{B.2}$$

B.2 Corrections for cobalt- or nickel-bonded tungsten carbide grinding media

The following additional corrections shall be applied to account for the cobalt or nickel binder used in tungsten carbide mortars.

$$L_\mathrm{t} = 100\frac{\left(\dfrac{L_\mathrm{m}}{100 - L_\mathrm{m}} - \dfrac{C(m_\mathrm{rW} + m_\mathrm{rC}\phi - 1 - \phi)}{100}\right)}{\dfrac{100}{100 - L_\mathrm{m}} - \dfrac{C}{100}(m_\mathrm{rW} + m_\mathrm{rC}\phi)} \tag{B.3}$$

$$f=\frac{100-L_t}{100\left[1-\frac{C}{100}(1+\phi)\right]} \tag{B.4}$$

where

m_{rC} is either the

$$\frac{\text{relative molecular mass of Co}}{\text{relative molecular mass of Co}_3\text{O}_4}=0{,}734\,2$$

$$\frac{\text{relative molecular mass of Ni}}{\text{relative molecular mass of NiO}}=0{,}785\,8$$

depending on which binding element is present

ϕ is the $\dfrac{\text{concentration of binder metal in mortar, expressed as an oxide}}{\text{concentration tungsten in mortar, expressed as an oxide}}$

In the case of W, the oxide is WO_3, cobalt: Co_3O_4 and nickel: NiO:

$$\frac{Co_3O_4}{WO_3} \text{ or } \frac{NiO}{WO_3}$$

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

Annex C
(informative)

Examples of fluxes/flux ratios

The fluxes tested are listed below, together with the classes of material listed in Clause 3 with which they may be used.

a) Lithium tetraborate (melting point 917 °C), 5:1 to sample.

Materials: a, b, c, d, g, h, m, o and p.

b) Lithium tetraborate, 9:1 to sample.

Materials: a, b, c, f, g, h and i.

c) Lithium tetraborate, 10:1 to sample.

Materials: a, b, c, d, e, f, g, h, j, m, n, o and p.

d) 20 % lithium tetraborate to 80 % lithium metaborate (melting point 840 °C), 5:1 to sample.

Materials: a, b, c, d, m, o, p and q.

e) 85 % lithium tetraborate, 15 % lanthanum oxide (melting point 900 °C), 9:1 to sample.

Materials: a, b and c.

f) 77 % lithium tetraborate, 13 % lithium carbonate, 10 % lanthanum oxide, 10:1 to sample.

Materials: a, b, c, d, e, f, g, h, m, n, o and p.

g) 75,6 % lithium tetraborate, 20,9 % lanthanum oxide, 3,5 % boric oxide, 16,67 to sample.

Materials: all.

h) Lithium tetraborate, 8,33:1 to sample.

Materials: e.

i) 55,6 % lithium tetraborate, 44,4 % lithium metaborate (melting point ≈ 860 °C), 22,5:1 sample.

Materials: j and k.

j) 66,7 % lithium tetraborate: 33,3 % lithium nitrate, 30:1 to sample.

Materials: j, k and l.

This should be mixed immediately before fusion.

k) 35,3 % lithium teraborate, 64,7 % lithium metaborate (Type 12-22) (melting point ≈ 825 °C), 10:1 sample.

Materials: a, b, c, d, m, n, o, p and q.

l) 50,0 % lithium teraborate, 50,0 % lithium metaborate, 10:1 sample.

Materials: a, b, c, d, m, n, o, p and q.

m) 66,0 % lithium teraborate, 34,0 % lithium metaborate, 10:1 sample.

Materials: a, b, c, d, m, n, o, p and q.

n) 57 % lithium tetraborate, 43 % lithium metaborate (Type 57:43) (melting point ≈ 880 °C), 10:1 sample.

Materials: e, f, g, h, i, j, o, p and q.

NOTE The fluxes d, k and l fuse extremely well at 1 050 °C and are therefore best for materials containing volatile components such as sulfur.

Annex D
(normative)

Examples of CRM to be used to check synthetic calibrations

D.1 High alumina

(1) CRMs of BCS (unit: %)

BCS No.	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**Li_2O**	**P_2O_5**	**Cr_2O_3**	**ZrO_2**	**Loss on ignition**
309 (sillimanite)	34,1	61,1	1,51	1,92	0,22	0,17	0,34	0,46	—	—	—	—	(0,10)
394 (calcined bauxite)	4,98	88,8	1,90	3,11	0,08	0,12	0,02	0,02	<0,01	0,22	(0,08)	(0,15)	(0,40)
395 (bauxite)	1,24	52,4	16,3	1,93	0,05	0,02	(0,02)	(0,02)	(0,01)	(0,14)	(0,07)	—	27,8

(2) CRMs of NIST (unit: %)

NIST No.	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**P_2O_5**	**Cr_2O_3**	**Loss on ignition**
77a (burnt refractory)	35,0	60,2	1,00	2,66	0,05	0,38	0,037	0,090	0,092	0,09	(0,22)
78a (burnt refractory)	19,4	71,7	1,2	3,22	0,11	0,70	0,078	1,22	1,3	0,25	(0,42)

(3) CRMs of the Ceramic Society of Japan (CerSJ) (unit: %)

JCRM No.	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**P_2O_5**	**ZrO_2**	**Loss on ignition**
R301 (calcined bauxite)	7,24	87,5	1,40	2,90	0,03	0,02	0,03	0,04	0,07	0,13	0,35
R302 (calcined bauxite)	3,45	90,6	1,76	3,17	0,02	0,03	0,02	0,02	0,05	0,30	0,22
R651 (alumina shale)	21,74	71,7	1,48	3,15	0,19	0,10	0,03	0,65	0,19	0,13	0,58

D.2 Fireclay

(1) CRMs of BCS and ECRM (unit: %)

BCS No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5
BCS 375/1 (soda feldspar)	69,26	17,89	0,291	0,313	0,78	0,180	8,89	1,47	0,226
BCS 376/1 (potash feldspar)	65,77	18,63	0,085	(0,008)	0,421	(0,03)	3,00	11,59	(0,02)
ECRM 776-1 (firebrick)	62,76	29,28	1,43	1,62	0,310	0,476	0,488	2,92	0,062
BCS 348 (ball clay)	51,1	31,6	1,04	1,08	0,17	0,30	0,34	2,23	0,071

BCS No.	ZrO_2	BaO	Cr_2O_3	Li_2O	PbO	Loss on ignition
BCS 375/1 (soda feldspar)	(0,010 7)	(0,010 6)	(0,001 8)	—	(0,000 4)	0,72
BCS 376/1 (potash feldspar)	(<0,01)	0,021 0	(0,001)	—	0,009 0	0,203
ECRM 776-1 (firebrick)	(0,04)	0,122	0,022	0,019	—	(0,3)
BCS 348 (ball clay)	(0,03)	(0,04)	0,016	—	—	11,8

(2) CRMs of NIST (unit: %)

NIST No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	Cr_2O_3	MnO
70a (feldspar potash)	67,12	17,9	0,075	0,01	0,11	—	2,55	11,8	—	—	—
99a (clay plastic)	65,2	20,5	0,065	0,007	2,14	0,02	6,2	5,2	0,02	—	—
98a (clay plastic)	48,94	33,19	1,34	1,61	0,31	0,42	0,082	1,04	0,11	0,03	—
76a (burnt refractory)	54,9	38,7	1,60	2,03	0,22	0,52	0,07	1,33	0,120	—	—
97b (flint clay)	42,38	39,22	1,188	2,48	0,034 8	0,187	0,066 3	0,618	(0,05)	0,033 2	0,006 1
98b (plastic clay)	57,01	27,02	1,69	1,35	0,106 2	0,594	0,201 6	3,38	(0,07)	0,017 4	0,015 0
679 (brick clay)	52,07	20,80	12,94	0,96	0,227 8	1,252	0,175 8	2,931	(0,172)	0,016 0	0,223 4

NIST No.	ZrO_2	BaO	Rb_2O	SrO	Loss on ignition
70a (feldspar potash)	—	0,02	0,06	—	0,40
99a (feldspar soda)	—	0,26	—	—	0,26
98a (clay plastic)	0,042	0,03	—	0,039	12,44
76a (burnt refractory)	—	—	—	0,037	(0,34)
97b (flint clay)	(0,07)	(0,020)	—	0,009 9	(13,3)
98b (plastic clay)	(0,030)	(0,08)	—	0,022 4	(0,75)
679 (brick clay)	—	(0,048 2)	—	0,008 7	—

(3) CRMs of the CerSJ (unit: %)

JCRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	Loss on ignition
R602 (refractory clay)	45,9	37,1	0,58	0,12	1,42	0,37	0,58	0,58	—	12,7
R701 (feldspar)	68,0	17,31	0,092	0,009	—	—	3,35	10,4	—	0,49
R802 (Roseki)	60,7	32,3	0,23	0,19	0,04	<0,01	0,09	0,07	0,05	6,0

D.3 Silica

(1) CRMs of BCS (unit: %)

BCS No.	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**MnO**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**Cr_2O_3**	**Loss on ignition**
313/1 (high-purity silica)	99,78	0,036	0,012	0,017	0,000 13	0,006	0,001 3	0,003	0,005	(<0,000 2)	(0,1)
516 (standard glass sand)	98,73	0,513	0,059 6	0,172	—	0,024 3	0,038 7	0,019 5	0,127	0,008 1	0,24

BCS No.	**Mn_3O_4**	**PbO**	**BaO**
516 (standard glass sand)	0,001 2	0,012 7	0,004 0

(2) CRMs of NIST (unit: %)

NIST No.	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**MnO**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**P_2O_5**	**Cr_2O_3**
198 (silica brick)	—	0,16	0,66	0,02	0,008	2,71	0,07	0,012	0,017	0,022	—
199 (silica brick)	—	0,48	0,74	0,06	0,007	2,41	0,13	0,015	0,094	0,015	—
81a (glass sand)	—	0,66	0,082	0,12	—	—	—	—	—	—	0,004 6
165 (glass sand, low iron)	—	0,059	—	0,12	—	—	—	—	—	—	(0,000 1)
1413 (glass sand, high alumina)	82,77	9,90	0,24	0,11	—	0,74	0,06	1,75	3,94	—	—

NIST No.	**ZrO_2**	**BaO**	**Loss on ignition**
198 (silica brick)	—	—	0,21
199 (silica brick)	—	—	0,17
81 (glass sand)	0,034	—	—
165a (glass sand, low iron)	0,034	—	—
1413 (glass sand, high alumina)	0,006	0,12	—

(3) CRMs of the CerSJ (unit: %)

JCRM No.	**SiO_2**	**Al_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**Loss on ignition**
R404 (quartz powder)	> 99,99	11[a]	6[a]	0,2[a]	<0,1[a]	1[a]	0,4[a]	0,00
R405 (silica)	97,76	1,07	0,022	0,029	0,023	0,060	0,71	0,13
R406 (silica)	96,71	1,31	0,564	0,016	0,005	0,030	0,13	0,97

[a] µg/g

D.4 Zircon and zirconia

(1) CRMs of BCS (unit: %)

BCS No	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	ZrO_2	Loss on ignition
388 (zircon)	32,7	0,291	0,049	0,232	(0,04)	(<0,05)	(<0,02)	(<0,03)	0,12	64,9	(0,20)
358 (zirconia)	0,20	0,08	0,064	0,20	1,50	3,42	(<0,01)	(<0,01)	—	92,70	0,08

BCS No	BaO	HfO_2	SrO	ThO_3	U_3O_8	Y_2O_3
388 (zircon)	—	1,30	—	0,018	0,034	0,136
358 (zirconia)	0,10	1,63	0,07	(0,000 7)	(0,08)	—

(2) CRMs of The CerSJ (unit: %)

JCRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	$ZrO_2(HfO_2)$	Loss on ignition
R501 (zircon sand)	32,6	0,39	0,06	0,16	66,5	0,11
R502 (zircon sand)	32,8	5,87	0,10	0,24	60,3	0,26

D.5 Magnesia, dolomite and limestone

(1) CRMs of BCS (unit: %)

BCS No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO
319/1 (magnesia)	1,093	0,109	0,291	0,007 0	0,108	3,00	95,38
389/1 (high-purity magnesia)	0,274	0,104	0,607	0,005 1	0,100	0,880	97,89
ECRM 782-1 (dolomite)	0,266	0,104	0,450	0,004 2	0,081	30,34	21,29
393 (limestone)	0,70	0,12	0,045	0,009	0,010	55,4	0,15
512 (dolomite)	0,379	0,055	0,030	0,002 0	0,003 6	30,61	21,59
513 (limestone)	0,228	0,108	0,027 5	(0,004)	0,009 5	55,59	0,182
362 (mine-tailings sample)	9,03	0,667	0,483	0,047	—	44,21	0,068

BCS No.	Na_2O	K_2O	P_2O_5	BaO	Cr_2O_3	SrO	Loss on ignition
319/1 (magnesia)	—	—	(0,007)	(0,003 8)	0,003 5	(0,006 0)	—
389/1 (high-purity magnesia)	—	—	0,029 5	(0,001 5)	(0,004)	(0,000 7)	—
ECRM 782-1 (dolomite)	—	0,026 0	0,012 8	(0,000 8)	0,000 9	—	47,25
393 (limestone)	(<0,03)	0,02	(0,01)	0,006	—	0,019	43,4
512 (dolomite)	(0,1)	(<0,02)	(<0,02)	(<0,02)	(<0,001)	0,024	46,80
513 (limestone)	(<0,3)	0,015 0	(0,005)	(0,01)	0,001 2	0,017 6	43,61
362 (mine-tailings sample)	0,084	0,14	(0,014)	(2,02)	(0,003)	0,034	32,81

BCS No.	Mn_3O_4	PbO	ZnO	S	Cd
ECRM 782-1 (dolomite)	—	0,002 9	0,008 2	(0,016)	—
362 (mine-tailings sample)	0,829	2,63	2,59	1,48	0,020

(2) CRM of NIST (unit: %)

NIST No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	SrO	Loss on ignition
1C (limestone argillaceous)	6,84	1,30	0,55	0,07	0,025	50,3	0,42	0,02	0,28	0,04	0,030	39,9
88b (limestone dolomite)	1,13	0,336	0,277	(0,016)	0,016 0	29,95	21,03	0,029 0	0,103 0	0,004 4	0,007 6	(46,98)

D.6 Chrome-magnesia

(1) CRMs of BCS (unit: %)

BCS No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
369 (magnesite-chrome)	2,59	14,7	10,3	0,14	0,11	1,17	53,5	—	—
370 (magnesite-chrome)	3,01	12,3	7,23	0,13	0,11	1,54	61,8	—	—
396 (low-silica magnesite-chrome)	1,37	5,73	10,9	0,26	0,17	1,12	64,6	(0,06)	(0,03)

BCS No.	Cr_2O_3	BaO	SrO	Loss on ignition
369 (magnesite-chrome)	17,2	(<0,01)	(<0,01)	—
370 (magnesite-chrome)	13,4	(<0,01)	(<0,01)	—
396 (low-silica magnesite-chrome)	15,6	—	—	(0,04)

(2) CRM of NIST (unit: %)

NIST No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	P_2O_5	Cr_2O_3	Loss on ignition
103a (chrome refractory)	4,63	29,96	12,43	0,01	0,11	0,69	18,54	0,01	32,06	—

Annex E
(normative)

Examples of SeRM

NOTE These values are LOI (loss on ignition) component-free values.

E.1 High alumina

(1) SeRM series of the Technical Association of Refractories, Japan (TARJ) (unit: %)

JRRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	B_2O_3[a]
301	43,97	46,86	3,534	1,032	0,018	0,798	0,691	0,170	2,010	(0,87)
302	37,71	53,95	4,492	0,597	0,200	0,871	0,697	0,565	0,667	—
303	36,19	59,29	1,477	0,164	0,008	1,040	0,856	0,700	0,207	—
304	27,53	63,02	3,467	4,337	0,059	0,183	0,376	0,276	0,388	—
305	20,06	68,78	2,820	3,304	0,010	0,656	0,304	0,809	3,120	—
306	17,38	74,30	1,959	2,689	0,019	0,627	0,100	0,996	1,761	—
307	10,92	80,53	2,987	1,235	0,016	0,153	0,615	1,089	2,372	—
308	10,24	86,51	0,412	1,794	0,112	0,099	0,053	0,263	0,108	—
309	2,127	89,97	1,279	3,862	0,003	1,025	0,289	0,423	0,923	—
310	0,413	94,93	0,024	2,069	0,045	0,038	0,981	0,081	1,329	—

[a] B_2O_3 value is uncertified.

E.2 Fireclay

(1) SeRM series No. 1 of TARJ (unit: %)

JRRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
101	88,67	8,11	0,314	0,302	0,115	1,062	0,217	1,014	0,165
102	80,55	13,81	3,982	0,454	0,015	0,049	0,673	0,304	0,145
103	80,42	18,09	0,407	0,370	0,005	0,072	0,015	0,124	0,350
104	67,35	22,52	3,245	2,944	0,017	0,258	0,070	0,300	3,049
105	69,33	25,41	0,768	2,254	0,119	0,408	0,223	0,653	0,819
106	63,72	29,95	1,925	0,680	0,024	0,145	0,982	0,600	1,819
107	55,41	37,14	2,205	1,155	0,019	0,711	0,493	0,218	2,577
108	55,38	40,14	1,549	1,055	0,020	0,277	0,270	0,207	0,810
109	54,30	41,30	0,893	1,964	0,011	0,145	0,125	0,307	0,794
110	49,59	46,73	0,849	1,668	0,014	0,107	0,165	0,085	0,342

(2) SeRM series No. 2 of TARJ (unit: %)

JRRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	Cr_2O_3	ZrO_2
121	86,35	6,077	0,407	0,056	0,023	1,968	0,126	3,208	0,234	0,324	0,018	1,119
122	78,34	10,27	0,248	1,039	0,204	0,435	0,658	1,042	2,059	4,905	0,819	0,203
123	79,20	13,32	4,136	0,459	0,012	0,135	1,329	0,296	0,109	0,807	0,014	0,008
124	73,99	16,58	2,605	2,748	0,246	1,101	0,109	0,313	1,793	0,191	0,117	0,112
125	79,33	18,72	0,504	0,309	0,008	0,130	0,084	0,072	0,691	0,046	0,010	0,023
126	67,07	21,42	3,355	2,853	0,038	0,457	0,127	0,285	3,140	0,498	0,651	0,049
127	68,64	23,10	0,926	2,196	0,174	0,182	0,153	1,757	0,542	1,786	0,273	0,046
128	54,39	26,06	4,459	1,379	0,244	2,804	3,107	0,374	1,849	3,363	0,854	1,014
129	62,33	30,14	1,462	0,967	0,018	0,157	2,234	0,234	1,930	0,201	0,107	0,112
130	53,53	32,78	0,531	3,362	0,370	1,957	0,619	2,323	1,422	0,920	1,056	0,836
131	52,80	36,69	2,212	1,165	0,032	0,786	1,025	0,769	2,624	1,614	0,070	0,265
132	50,69	39,18	1,647	0,298	0,119	1,300	0,349	2,165	0,799	2,390	0,116	0,753
133	50,15	39,05	3,697	1,934	0,017	0,109	2,035	0,335	0,915	0,344	1,278	0,574
134	47,35	44,43	1,080	1,742	0,245	0,200	0,205	0,132	0,376	3,840	0,244	0,359
135	37,33	49,01	3,063	0,076	0,049	2,364	1,248	2,884	2,781	0,488	0,428	0,203

E.3 Silica

(1) SeRM series of TARJ (unit: %)

JRRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
201	84,43	9,723	1,466	0,032	0,147	2,781	0,733	0,316	0,147
202	85,80	7,602	3,975	0,567	0,004	0,817	0,020	1,015	0,024
203	87,44	5,100	1,788	0,182	0,112	3,981	0,472	0,616	0,245
204	89,76	4,503	2,084	0,150	0,107	1,794	0,313	0,316	0,948
205	90,50	3,093	1,249	0,325	0,064	3,113	0,092	0,933	0,517
206	92,94	1,773	3,208	0,018	0,018	1,205	0,072	0,180	0,533
207	94,13	1,704	0,965	0,079	0,042	2,520	0,160	0,047	0,227
208	94,51	0,463	0,064	0,005	0,001	4,200	0,056	0,635	0,017
209	96,31	0,877	0,373	0,050	0,068	1,894	0,106	0,033	0,181
210	97,80	0,163	0,834	0,005	0,002	0,301	0,789	0,021	0,006

E.4 Zircon and zirconia

(1) SeRM series of TARJ (unit: %)

JRRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	Cr_2O_3	ZrO_2	HfO_2
601	0,263	0,119	0,101	0,168	5,586	0,064	0,004	0,002	0,007	0,003	92,08	1,592
602	0,335	0,078	1,622	0,164	0,221	5,304	0,768	0,004	1,342	0,015	88,48	1,526
603	0,967	5,299	2,861	0,934	0,954	0,968	0,187	0,653	0,838	0,029	84,80	1,454
604	3,052	6,933	0,430	0,134	0,094	0,017	1,090	1,942	1,997	3,069	79,45	1,359
605	10,82	4,847	0,177	0,127	1,945	1,999	0,458	0,543	0,354	1,553	75,59	1,318
606	22,10	0,534	0,936	0,117	0,021	0,321	2,034	0,014	0,019	0,008	72,59	1,269
607	32,94	3,539	0,121	0,137	0,048	0,031	0,026	0,043	0,086	0,002	61,66	1,218
608	34,65	0,707	0,092	0,102	0,521	3,127	0,031	0,019	0,117	0,497	58,88	1,217
609	40,55	0,887	0,150	0,153	0,300	0,150	0,943	0,028	0,081	0,012	55,62	1,124
610	45,70	0,451	0,308	0,099	3,078	0,548	0,043	0,010	0,113	0,009	48,74	0,987

E.5 Alumina-zirconia-silica

(1) SeRM Series of TARJ (unit: %)

JRRM No.											Uncertified values	
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Cr_2O_3	ZrO_2	HfO_2	MnO	P_2O_5
701	28,47	10,10	2,010	4,965	2,075	0,477	1,847	0,024	1,011	48,11	0,850	0,007	0,027
702	10,01	38,21	0,374	0,211	1,555	1,982	2,027	0,580	0,111	42,62	2,090	0,004	0,028
703	14,66	46,39	0,059	0,072	0,037	0,011	0,535	0,002	0,006	37,39	0,728	0,000	0,035
704	42,64	19,59	0,554	1,026	0,155	0,515	0,228	0,402	0,518	33,48	0,685	0,089	0,130
705	2,002	64,24	0,141	2,024	0,191	0,461	0,301	0,018	2,022	28,01	0,485	0,004	0,017
706	39,62	26,14	0,131	3,806	1,599	0,159	3,521	0,959	0,010	22,89	1,199	0,004	0,016
707	21,17	55,78	1,815	0,289	1,086	0,844	0,199	0,155	0,180	18,16	0,367	0,003	0,055
708	0,547	79,63	0,801	1,021	1,174	1,649	0,089	0,746	0,298	12,86	1,034	0,001	0,002
709	34,45	50,45	0,477	0,091	0,525	1,210	1,040	0,216	2,922	8,340	0,184	0,002	0,009
710	5,629	82,36	1,151	3,005	0,225	0,049	1,421	0,637	1,028	2,967	1,512	0,002	0,042

E.6 Magnesia

(1) SeRM series of TARJ (unit: %)

JRRM No.						Uncertified values						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	Na_2O	K_2O	Cr_2O_3	P_2O_5	B_2O_3
401	6,424	8,106	3,890	0,208	81,24	0,017	0,011	0,006	0,003	0,004	0,035	0,016
402	5,462	1,999	5,050	3,570	83,77	0,026	0,011	0,010	0,001	0,006	0,077	0,127
403	8,144	4,060	1,553	0,615	85,48	0,003	0,014	0,004	0,001	0,010	0,044	0,031
404	1,223	6,014	2,908	1,786	88,02	0,007	0,030	0,009	0,001	0,006	0,053	0,011
405	3,479	1,372	1,346	1,690	91,95	0,054	0,074	0,009	0,015	0,014	0,120	0,011
406	1,196	1,139	0,874	4,805	91,85	0,004	0,011	0,002	0,000	0,006	0,041	0,013
407	2,432	0,100	2,145	0,675	94,55	0,003	0,014	0,004	0,001	0,080	0,044	0,023
408	0,460	2,554	0,134	0,672	96,19	0,004	0,010	0,001	0,000	0,009	0,015	0,099
409	0,534	0,202	0,490	0,744	98,03	0,003	0,015	0,002	0,001	0,019	0,023	0,038
410	0,188	0,058	0,050	0,595	99,08	0,003	0,010	0,001	0,000	0,003	0,045	0,026

E.7 Chrome-magnesia

(1) SeRM series of TARJ (unit: %)

JRRM No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Cr_2O_3	Uncertified values			
									P_2O_5	V_2O_5	NiO	ZnO
501	0,928	2,926	4,813	0,006	0,020	0,924	87,72	2,832	0,036	0,019	0,018	0,006
502	3,120	11,99	1,022	0,013	0,018	0,201	76,33	7,503	0,026	0,024	0,026	0,004
503	9,106	7,155	3,009	0,047	0,038	3,819	63,19	13,61	0,032	0,037	0,036	0,013
504	2,192	17,58	4,117	0,014	0,011	2,611	54,88	18,37	0,034	0,016	0,015	0,011
505	1,824	7,775	17,77	0,118	0,109	0,493	50,18	21,75	0,023	0,075	0,078	0,021
506	2,167	14,70	7,495	0,134	0,072	0,460	46,69	28,21	0,018	0,086	0,094	0,010
507	5,692	24,99	12,96	0,166	0,115	1,613	22,34	31,99	0,010	0,130	0,204	0,037
508	3,082	3,983	22,71	0,014	0,006	1,031	30,88	38,20	0,016	0,008	0,010	0,005
509	1,967	20,31	10,16	1,205	0,082	2,871	20,47	42,63	0,013	0,118	0,044	0,037
510	4,902	12,18	14,95	0,133	0,176	0,290	16,82	50,25	0,016	0,111	0,193	0,041
511	2,895	6,652	27,09	0,105	0,126	0,071	10,57	52,26	0,004	0,054	0,108	0,052
512	10,57	29,26	26,02	0,047	0,025	4,063	24,82	4,990	0,019	0,012	0,018	0,013

E.8 Alumina-magnesia

(1) SeRM Series of TARJ (unit: %)

JRRM No.	SiO_2	Al_2O	Fe_2O	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	Uncertified values		
										MnO	Cr_2O_3	ZrO_2
801	0,355	93,49	2,009	0,217	0,141	3,261	0,199	0,014	0,002	0,002	0,003	0,008
802	3,329	84,25	1,035	1,484	2,003	6,132	0,159	0,462	0,957	0,003	0,002	0,002
803	0,583	74,23	4,904	2,516	0,576	16,20	0,869	0,007	0,017	0,005	0,002	0,004
804	5,178	64,66	4,020	0,132	4,767	20,84	0,089	0,044	0,111	0,020	0,010	0,002
805	2,498	58,03	0,732	1,059	0,282	36,04	0,540	0,015	0,682	0,006	0,001	0,000
806	0,514	48,85	0,165	0,004	0,979	49,41	0,049	0,001	0,048	0,026	0,006	0,001
807	0,586	39,96	0,323	0,198	2,759	55,07	0,329	0,153	0,530	0,005	0,002	0,001
808	0,799	28,68	0,565	0,714	0,994	67,01	0,409	0,692	0,229	0,017	0,001	0,001
809	0,363	19,86	0,115	2,888	4,479	70,11	0,049	0,989	1,068	0,006	0,001	0,001
810	4,211	10,08	3,118	1,916	0,180	78,96	0,759	0,167	0,513	0,016	0,004	0,004

Annex F
(normative)

Equation for theoretical calculations

$$\alpha_{\mathrm{Y}}^{\mathrm{X}} = \frac{\mu_{\mathrm{Y}}^{\mathrm{T}} - \mu_{\mathrm{M}}^{\mathrm{T}} + A\left(\mu_{\mathrm{Y}}^{\mathrm{X}} - \mu_{\mathrm{M}}^{\mathrm{X}}\right)}{100N\mu_{\mathrm{F}}^{\mathrm{T}} + o\mu_{\mathrm{X}}^{\mathrm{T}} + (100 - o)\,\mu_{\mathrm{M}}^{\mathrm{T}} + A\left[100N\mu_{\mathrm{Flux}}^{\mathrm{X}} + o\mu_{\mathrm{X}}^{\mathrm{X}} + (100 - o)\,\mu_{\mathrm{M}}^{\mathrm{X}}\right]}$$

where

T	denotes tube radiation;
F	denotes flux;
X	denotes oxide being determined;
Y	denotes interfering oxide;
M	denotes matrix oxide (i.e. $\mathrm{SiO_2}$ for silica/alumina materials);
N	is the ratio by mass of flux to sample;
o	is the mass fraction, in percentage, of oxide X in the material in question;
α	is the mass-absorption correction of Y on X;
μ	is the linear absorption coefficient;

$$A = \frac{\text{sin(angle in)}}{\text{sin(angle out)}}.$$

Annex G
(normative)

Certified reference materials (CRMs)

G.1 Statistical tolerances with certified reference materials

Acceptable tolerances for the various statistical tests required in the main part of this International Standard shall be calculated from a tolerance factor, f_T, as follows.

a) The standard deviation for fusion precision of any oxide in any CRM used for the fusion precision test (see 9.1 and 12.1) shall be less than or equal to f_T and rounded up to the nearest 0,01 %.

b) When synthetic calibrations are used, the differences between the certified value for CRM and the achieved value for any oxide (see 13.1) shall be less than or equal to $2f_T$ and rounded up to the nearest 0,01 % above. Similarly, when SeRMs are used to establish calibrations, the differences between the theoretical value for a synthetic standard and the results obtained from the calibration shall be to the same uncertainty.

c) The differences between subsequent measurements of CRMs measured to estimate drift (see 12.5) shall be less than or equal to f_T at maximum and rounded up to the nearest 0,01 % above.

d) The differences between measurements of a 100 % pure silica standard measured in any given sample holder from the overall mean (see 12.3) shall be less than or equal to f_T and rounded up to the nearest 0,01 % above.

NOTE 1 f_T is equal to 0,3 % silica. See Tables G.1 and G.2.

The value f_T is calculated using Equation (G.1), feeding in the values of lower tolerance factor f_L, given in Table G.1.

$$f_T = f_L + 0{,}004\,867\,1C - 0{,}000\,020\,52C^2 \qquad \text{(G.1)}$$

NOTE 2 Equation (G.1) creates an envelope that included over 95 % of the standard deviations achieved by Working Group CEN/TC 187/WG 4 during the round-robin testing, irrespective of the oxide determined or the material analysed.

Table G.1 — Values for f_L near-zero concentration

Oxide	f_L
Na_2O	0,021
MgO	0,011
Al_2O_3	0,014
SiO_2	0,018
All others	0,004 7

NOTE Various values for Equation (G.1), when $f_L = 0$ are given for information in Table G.2.

Table G.2 — Values of $0{,}004\ 867\ 1C - 0{,}000\ 020\ 52C^2$

C %	Value
100	0,282
90	0,272
80	0,258
70	0,241
60	0,218
50	0,192
40	0,161
30	0,128
20	0,089
10	0,047
9	0,042
8	0,038
7	0,033
6	0,028
5	0,023
4	0,019
3	0,015
2	0,010
1	0,005
0,75	0,004
0,5	0,002
0,25	0,001
0	0

G.2 Examples of certified reference materials (CRMs)

G.2.1 General

Typical examples of CRMs are shown in G.2.2 to G.2.13. It is also permissible to use SeRMs (see Annex E).

G.2.2 Bauxite

BCS 394 bauxite (see Table I.2 for repeatability standard deviations).

G.2.3 Silicates

ECRM 776-1 firebrick (alumino-silicate) (see Tables I.1 and I.10 for repeatability standard deviations and Table I.11 for standard deviations).

For refractories in classes given by Tables I.2 and I.3, a CRM as close as possible to the materials being analysed is recommended.

BCS 372/2 calcium silicate (cement).

RM 203A magnesium silicates (talc).

NIST 76a burnt refractory (Al_2O_3: 40 %) (see Table I.13 for reproducibility).

G.2.4 Silica

BCS 313/1 high-purity silica, for pure silicas (see Table I.10 for reproducibility), or BCS 314 silica brick, for silica bricks.

G.2.5 Zircon/AZS

BCS 388 (see Table I.5 for repeatability standard deviations), a mixture of BCS 388 (33,3 %) and BCS 394 (66,7 %).

BCS 388 zircon (see Table I.14 for reproducibility).

G.2.6 Zirconia

BCS 358.

G.2.7 Magnesia

BCS 389 high-purity magnesite (see Table I.3 for repeatability standard deviations).

G.2.8 Spinels

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

G.2.9 Dolomite

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

G.2.10 Limestone

BCS 393 (see Table I.7 for repeatability standard deviations).

G.2.11 Chrome-bearing

BCS 369 magnesia chrome (see Table I.4 for repeatability standard deviations).

BCS 308 grecian chrome ore (see Table I.8 for repeatability standard deviations).

TARJ internal reference material CR1 chrome ore (see Tables I.15 for reproducibility and repeatability standard deviations).

G.2.12 Calcium aluminate

A mixture of BCS 394 (33,3 %) and BCS 372/1 (66,7 %).

G.2.13 Others

CRMs not included above may also be used.

Annex H
(normative)

Method of inter-element correction used to compensate for the effects of co-existing components when using SeRM for calibration

H.1 General

This annex defines the principle and method for co-existing component correction for X-ray fluorescence spectrometric analysis of refractory bricks and mortars.

H.2 Kinds of correction

Two kinds of co-existing component effects are corrected:

- line-overlap correction;
- mass-absorption correction.

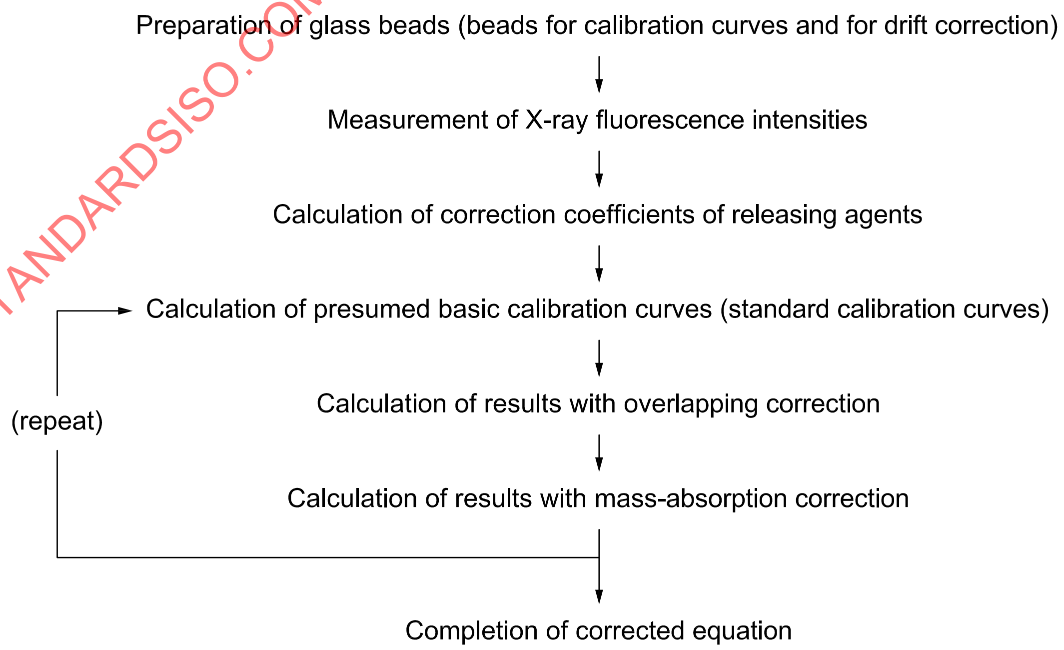
H.3 Outline of correction

H.3.1 General

X-ray fluorescence spectrometric analysis with co-existing component corrections is as described in H.3.2 and H.3.3.

H.3.2 Calculation of calibration curves and corrected equations

The procedure is shown in Figure H.1. Beads for calibration curves and for drift correction are measured.



NOTE If spectral interference from the remnants of releasing agents occurs, the overlap effect is also to be corrected.

Figure H.1 — Procedure chart for calculation of corrected equation

H.3.3 Analysis of unknown sample

The corrected equations obtained from H.3.2 are used in routine analysis. The procedure is shown in Figure H.2.

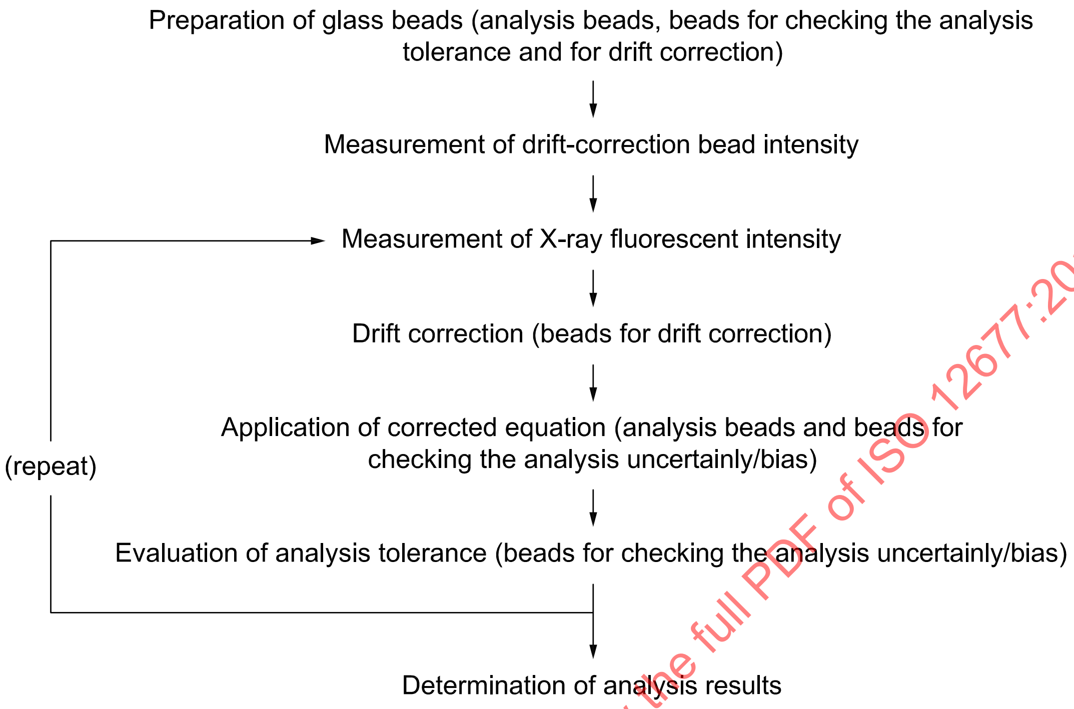


Figure H.2 — Procedure chart for routine analysis

H.4 Principle, method and procedure

H.4.1 Line-overlap correction

H.4.1.1 General

If the spectrum of a co-existing component overlaps that of the one which is to be analysed, the effect may be corrected using Equation (H.1).

$$C_i = (aI_i^2 + bI_i + c) + \Sigma l_{ij} C_j \tag{H.1}$$

where

C_i is the content of analysis component i;

I_i is the X-ray intensity of analysis component i;

l_{ij} is the line-overlap correction coefficient of interfering component j on analysis component i;

C_j is the content of co-existing component j;

a, b and c are the calibration curve coefficients.

H.4.1.2 Calculation procedure for line-overlap correction coefficients

The line-overlap correction coefficients, which vary with different X-ray spectrometric systems, are to be calculated individually as follows.

a) Calculation method using a presumed basic calibration curve

Equation (H.2) of the presumed basic calibration curve is derived using bead samples which do not contain an overlap component. The contents and measured X-ray fluorescence intensities of the bead samples which contain an overlap component are plotted on the presumed basic calibration curve. The deviations between the chemical contents and X-ray results obtained using a curve determine the line-overlap correction coefficient [Equation (H.3)].

$$\hat{X}_{\mathrm{i}} = aI_{\mathrm{i}} + b \tag{H.2}$$

$$\Delta C_{\mathrm{i}} = l_{\mathrm{ij}} \ W_{\mathrm{j}} \ + e \tag{H.3}$$

where

$\hat{X}_{\mathrm{i}}$ is the presumed basic value of analysis component i, as a percentage;

ΔC_{i} is the percentage deviation between the chemical content and the X-ray results of analysis component i from the presumed basic calibration curve;

e is the error.

Example 1: The calibration procedure for obtaining the line-overlap correction coefficient of CrKβ on MnKα using the SeRM series for chrome-magnesia bricks and mortars.

Step 1-1: The MnKα intensities from JRRM 501 to 512, JRRM 401, 404 and 405 are measured.

Step 1-2: The measured intensities from JRRM 401, 404 and 405 are arranged in Table H.1.

Table H.1 — Values for the calculation of the presumed basic calibration curve

	C_{MnO} (MnO %)	I_{MnO} X-ray intensity (kc/s[a]) of MnO	y	x	x^2	xy
JRRM 401	0,011	2,681 8	−0,027	−0,464 5	0,215 76	0,012 54
JRRM 404	0,030	2,997 2	−0,008	−0,149 1	0,022 23	0,001 19
JRRM 405	0,074	3,759 9	0,036	0,613 6	0,376 50	0,022 09
Average	$\bar{C}_{\mathrm{MnO}} = 0{,}038$	$\bar{I}_{\mathrm{MnO}} = 3{,}146\ 3$	—	—	—	—

[a] kc/s = kilocounts per second.

y stands for $C_{\mathrm{MnO}} - \bar{C}_{\mathrm{MnO}}$ and x stands for $I_{\mathrm{MnO}} - \bar{I}_{\mathrm{MnO}}$.

a and b are calculated by the least-squares method as follows:

$$a = \frac{\sum\left(I_{\mathrm{MnO}} - \bar{I}_{\mathrm{MnO}}\right)\left(C_{\mathrm{MnO}} - \bar{C}_{\mathrm{MnO}}\right)}{\sum\left(I_{\mathrm{MnO}} - \bar{I}_{\mathrm{MnO}}\right)^2} = \frac{\sum xy}{\sum x^2} \tag{H.4}$$

$$b = \bar{C}_{\mathrm{MnO}} - a\bar{I}_{\mathrm{MnO}} \tag{H.5}$$

The values from Table H.1 are calculated using Equations (H.4) and (H.5) (Example 1).

$$a:\ \frac{0{,}035\,82}{0{,}614\,49} \approx 0{,}058\,3$$

$$b:\ 0{,}038 - 0{,}058\,3 \times 3{,}146\,3 \approx -0{,}145$$

Equation (H.6) of the presumed basic calibration curve is

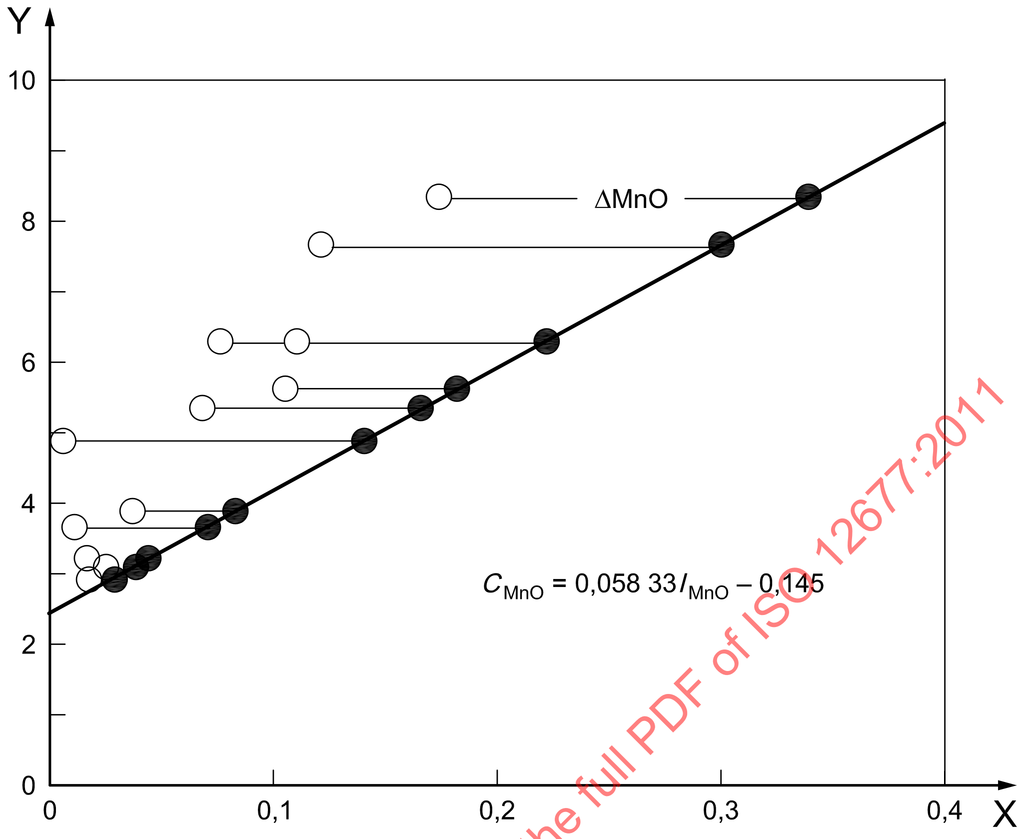
$$\hat{X}_{\mathrm{MnO}} = 0{,}058\,3\, I_{\mathrm{MnO}} - 0{,}145 \tag{H.6}$$

Step 1-3: The measured values from JRRM 501 to 512 are arranged in Table H.2.

Table H.2 — Values for the calculation of the line-overlap correction coefficient

JRRM No.	C_{MnO}	I_{MnO}	$\hat{X}_{\mathrm{MnO}}$	ΔC_{MnO}	$C_{\mathrm{Cr_2O_3}}$				
	MnO certified value %	MnKα X-ray intensity kc/s	**Calculation value using Example 3** %	$(W_{\mathrm{MnO}} - \hat{X}_{\mathrm{MnO}})$ %	**Co-existing component j certified value average** %	x[a]	x^2	y[a]	xy
501	0,020	2,987 7	0,029	–0,009	2,832	–23,219	539,122	0,077	–1,788
502	0,018	3,249 5	0,044	–0,026	7,503	–18,548	344,028	0,060	–1,133
503	0,038	3,916 7	0,083	–0,045	13,62	–12,431	154,530	0,041	–0,510
504	0,011	3,710 1	0,071	–0,060	18,37	–7,681	58,998	0,026	–0,200
505	0,109	5,589 6	0,181	–0,072	21,76	–4,291	18,413	0,014	–0,060
506	0,072	5,359 9	0,167	–0,095	28,21	2,159	4,661	– 0,009	–0,019
507	0,115	6,269 1	0,220	–0,105	31,99	5,939	35,272	– 0,019	–0,113
508	0,006	4,893 8	0,140	–0,134	38,20	12,149	147,598	– 0,048	–0,583
509	0,082	6,292 7	0,222	–0,140	42,63	16,579	274,863	– 0,054	–0,895
510	0,176	8,304 4	0,339	–0,163	50,25	24,199	585,592	– 0,077	–1,863
511	0,126	7,640 6	0,300	–0,174	52,26	26,209	686,912	– 0,088	–2,306
512	0,025	3,166 0	0,040	–0,015	4,990	–21,061	443,566	0,071	–1,495
Average	0,066	5,115 0	0,153	$\Delta\bar{C}_{\mathrm{MnO}} =$ $-0{,}086$	$\bar{C}_{\mathrm{Cr_2O_3}} =$ 26,051	—	—	—	—
Sum	0,798	61,380 1	1,836	–1,038	312,615	—	3 293,555	—	–10,945

[a] $y = \Delta C_{\mathrm{MnO}} - \Delta\bar{C}_{\mathrm{MnO}}$; $x = C_{\mathrm{Cr_2O_3}} - \bar{C}_{\mathrm{Cr_2O_3}}$.



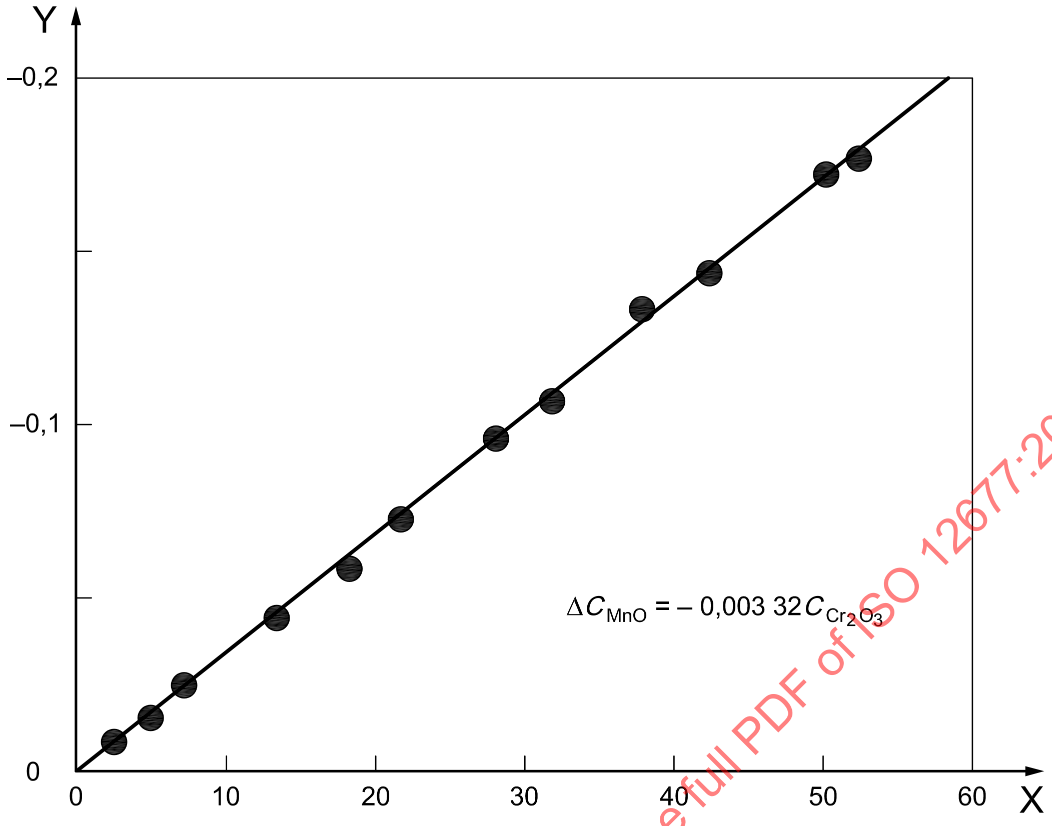
Key

X = C_{MnO}, %

Y = X-ray intensity (I) of MnKα

Figure H.3 — Estimation of MnO

The ΔMnO percentage by mass of ΔMnO is shown by the difference between measured value (open circles) and calculated value (solid circles) on the presumed basic calibration curve for Cr_2O_3-free MnO.



Key

X = $C_{Cr_2O_3}$

Y = ΔC_{MnO}, %

Figure H.4 — Calculation of line-overlap correction coefficients ΔC_{MnO} and Cr_2O_3 contents

The relationship between ΔC_{MnO} and $\Delta C_{Cr_2O_3}$ in Table H.2 is shown in Figure H.4.

The line-overlap correction coefficient, l_{ij}, is calculated using the least-squares method.

$$l_{ij} = \frac{\sum\left(C_{Cr_2O_3} - \bar{C}_{Cr_2O_3}\right)\left(\Delta C_{MnO} - \Delta\bar{C}_{MnO}\right)}{\sum\left(C_{Cr_2O_3} - \bar{C}_{Cr_2O_3}\right)^2} = \frac{\sum xy}{\sum x^2}$$

$$= \frac{-10{,}945}{3\ 293{,}555} = -0{,}003\ 32 \qquad \text{(H.7)}$$

The derived line-overlap correction coefficient, $l_{MnO,\ Cr_2O_3}$, CrKβ on MnKα, of chrome-magnesia bricks and mortars is 0,003 32. This coefficient depends on the equipment.

b) Multiple regression method

Coefficients a, b and c and the line-overlap correction coefficient, l_{ij}, of which the deviations are minimized, shall be simultaneously calculated by the least-squares method.

c) Standard addition method

The line-overlap correction coefficients are calculated by obtaining the difference in X-ray intensities from the glass beads without an overlap component and glass beads which contained fixed amounts of an overlap component.

H.4.2 Matrix correction

H.4.2.1 General

The X-ray intensity may be roughly explained by Equation (H.8).

$$I_{\mathrm{i}} = \frac{kC_{\mathrm{i}}}{\sum(\mu/\rho)_{\mathrm{ij}} C_{\mathrm{j}}} \tag{H.8}$$

where

I_{i} is the X-ray intensity of component i;

k is a constant;

C_{i} is the content of analysis component i;

μ is the linear absorption coefficient;

ρ is the density;

$(\mu/\rho)_{\mathrm{ij}}$ is the mass-absorption coefficient of co-existing component j for the analytical line of component i;

C_{j} is the content of co-existing component j.

Equation (H.8) shows that the intensities from samples which contain the same content of analysis component and variable contents of the co-existing component are different. This is called the matrix effect. Therefore, all spectra measured are influenced by co-existing components. The influence is usually negligible. The influence of major components and heavy components (CaO and heavier) on results is, however, sometimes significant. The correction of co-existing components is derived using Equation (H.9).

$$C_{\mathrm{i}} = (aI_{\mathrm{i}}^2 + bI_{\mathrm{i}} + c)(1 + \sum \alpha_{\mathrm{ij}} C_{\mathrm{j}}) \tag{H.9}$$

where

a, b, c are the calibration curve coefficients;

α_{ij} is the mass-absorption correction coefficient of component j on component i.

H.4.2.2 Calculation of mass-absorption correction coefficients using the multiple regression method

Non-corrected results, $\hat{X}_{\mathrm{i}}$, are calculated with as many calibration curve beads as possible. The mass-absorption correction coefficients, α_{ij}, are calculated by the multiple regression method using Equation (H.5). The presumed basic calibration curves and the line-overlap coefficients are also calculated simultaneously.

H.4.2.3 Theoretical mass-absorption correction coefficients

The coefficient is theoretically calculated using a personal computer on the basis of the mass-absorption coefficients. Tables H.5 to H.12 are examples of the theoretical mass-correction coefficients for several types of refractories.

H.4.2.4 Correction procedure using the theoretical mass-absorption correction coefficients

The calibration curve is obtained using Equation (H.9) and the theoretical mass-correction coefficients. Common mass-absorption correction coefficients can be used in any chemical laboratory. These coefficients are usable only when the following correction-coefficient calculating conditions coincide with the calibration-curve bead-measuring conditions in the laboratory:

1) type of X-ray tube;

2) kind of the target material of X-ray tube;

3) incident and take-off angles;

4) exciting voltage;

5) dilution ratio of sample and flux, including the oxidizing agent.

Using the theoretical mass-absorption correction coefficient in Tables H.5 to H.12, both methods, one using and one not using the presumed basic calibration curves, are possible.

a) Method using the presumed basic calibration curves

Equation (H.9) leads to Equation (H.10).

$$\frac{C_\text{i}}{1 + \sum \alpha_\text{ij} C_\text{j}} = aI_\text{i}^{\ 2} + bI + c \qquad \text{(H.10)}$$

If the theoretical mass-absorption correction coefficients are used as α_ij, the presumed basic value $(\hat{X}_\text{i})$ can be easily calculated.

$$\hat{X}_\text{i} = \frac{C_\text{i}}{1 + \sum \alpha_\text{ij} C_\text{j}} \qquad \text{(H.11)}$$

$$\hat{X}_\text{i} = aI_\text{i}^{\ 2} + bI_\text{i} + c \qquad \text{(H.12)}$$

The calibration curve coefficients a, b and c are calculated using Equation (H.12), which is defined as the presumed basic calibration curve. The calculation procedure for analysis results, C_i, consists of entering the intensities, alpha coefficients and tentative concentrations of the co-existing components into Equation (H.9). This is an iterative procedure. This calculation procedure can usually be derived by the personal computer attached to the equipment.

Example 2: Calculation of the presumed basic Fe_2O_3 value of JRRM 501

$$\begin{aligned}\hat{X}_{\text{Fe}_2\text{O}_3} = 4{,}813/(1 &+ \underbrace{\overset{\substack{\text{A value from Table H.9}\\ \downarrow}}{0{,}000\,34} \times 0{,}927}_{\text{SiO}_2} + \underbrace{\overset{\substack{\text{A value from Table H.7}\\ \downarrow}}{0{,}000\,12} \times 2{,}926}_{\text{Al}_2\text{O}_3} + \underbrace{0{,}004\,43 \times 0{,}006}_{\text{TiO}_2} \\ &+ \underbrace{0{,}001\,22 \times 0{,}020}_{\text{MnO}} + \underbrace{0{,}004\,50 \times 0{,}924}_{\text{CaO}} + \underbrace{0{,}006\,77 \times 2{,}832}_{\text{Cr}_2\text{O}_3}) \\ = 4{,}670 &\end{aligned}$$

High values of $\alpha_{ij} \times C_j$ actually affect the analysis results. Components for which the values are low do not affect the results. If only element j were to have an effect, Equation (H.11) would be expressed as follows:

$$\hat{X}_i = \frac{C_i}{1+\alpha_{ij}C_j} \tag{H.13}$$

Example 3: An Fe_2O_3-corrected calibration curve with only a Cr_2O_3 component using the SeRM series for chrome-magnesia bricks and mortars is performed as follows.

Step 3-1: The measured intensities and contents of JRRM 501 to 512 calibration-curve beads are arranged in Table H.3, and the presumed basic values, $\hat{X}_{Fe_2O_3}$, are calculated.

Table H.3 — Practice 3: the presumed basic values of Fe_2O_3

JRRM No.	Fe_2O_3				
	$C_{Fe_2O_3}$ %	$I_{Fe_2O_3}$ kc/s	$\alpha_{Fe_2O_3,\,Cr_2O_3} \times C_{Cr_2O_3}$	$1 + \alpha_{Fe_2O_3,\,Cr_2O_3} \times C_{Cr_2O_3}$	$\hat{X}_{Fe_2O_3} = \frac{C_{Fe_2O_3}}{1+\alpha_{Fe_2O_3,\,Cr_2O_3} \times C_{Cr_2O_3}}$
501	4,813	21,534	0,019 2	1,019 1	4,722
502	1,022	5,218	0,050 8	1,050 8	0,973
503	3,009	12,724	0,092 2	1,092 2	2,755
504	4,117	16,574	0,124 4	1,124 4	3,662
505	17,78	66,829	0,147 3	1,147 3	15,497
506	7,495	27,881	0,191 0	1,191 0	6,293
507	12,97	45,983	0,216 6	1,216 6	10,661
508	22,71	76,147	0,258 6	1,258 6	18,044
509	10,16	34,109	0,288 6	1,288 6	7,885
510	14,95	47,983	0,340 2	1,340 2	11,155
511	27,09	83,774	0,353 8	1,353 8	20,010
512	26,02	103,590	0,033 8	1,033 8	25,169

$\alpha_{Fe_2O_3,\,Cr_2O_3} \times C_{Cr_2O_3}$ stands for the value of $\alpha_{Fe_2O_3,\,Cr_2O_3} \times 0{,}006\,77$ (Table H.9, Case 3) $\times\, C_{Cr_2O_3}$ (Table E.7).

Step 3-2: The presumed calibration curve (Example 4) is computed by the least-squares method using the X-ray intensities, $I_{Fe_2O_3}$, and the presumed basic values of Fe_2O_3.

$$\hat{X}_{Fe_2O_3} = 0{,}000\,17 I_{Fe_2O_3} - 0{,}156 \tag{Example 4}$$

Equation (H.9) may be expressed as follows:

$$C_{Fe_2O_3} = (0{,}000\,17 I_{Fe_2O_3} - 0{,}156)(1 + 0{,}006\,77 C_{Cr_2O_3}) \tag{Example 5}$$

In the case of unknown sample analyses, the results of component j, of which no mass-absorption correction factor is found, may be expressed as follows:

$$C_{\mathrm{j}} = a_{\mathrm{j}} I_{\mathrm{j}}^{2} + b_{\mathrm{j}} I_{\mathrm{j}} + c_{\mathrm{j}} \qquad \text{(H.14)}$$

The results of component i may be expressed as follows:

$$C_{\mathrm{i}} = \hat{X}_{\mathrm{i}} (1 + \sum \alpha_{\mathrm{ij}} C_{\mathrm{j}}) \qquad \text{(H.15)}$$

Example 4: The Fe_2O_3 content of an unknown sample is calculated using the Fe_2O_3 presumed basic calibration curve and mass-absorption correction coefficients.

Step 4-1: The measured values and calibration curves are arranged in Table H.4.

Table H.4 — Practice 4: calculation sequence

	Fe_2O_3	Cr_2O_3
X-ray intensities of an unknown sample	$I_{Fe_2O_3} = 58{,}853$ kc/s	$I_{Cr_2O_3} = 315{,}39$ kc/s
Presumed basic calibration curve	$\hat{X}_{Fe_2O_3} = 0{,}000\,171 (I_{Fe_2O_3})^2 + 0{,}226\,36 I_{Fe_2O_3} - 0{,}156$	
Corrected calibration curve	$C_{Fe_2O_3} = \hat{X}_{Fe_2O_3} (1 + 0{,}006\,77 C_{Cr_2O_3})$	$C_{Cr_2O_3} = 0{,}114\,87\ I_{Cr_2O_3} - 0{,}737$

Step 4-2: The Cr_2O_3 content is calculated by Equation (H.14) using the values of Table H.4.

$$C_{Cr_2O_3} = 0{,}114\,87 \times 315{,}39 - 0{,}737 = 35{,}492$$

Step 4-3: The Fe_2O_3 content is calculated by Equation (H.15) using the Cr_2O_3 content value and that obtained in Table H.4.

$$C_{Fe_2O_3} = [0{,}000\,171 \times (58{,}853)^2 + 0{,}226\,36 \times 58{,}853 - 0{,}156]\ (1 + 0{,}006\,77 \times 35{,}492) = 17{,}064$$

On the other hand, if component j is also affected by the other co-existing components, measured component i and corrected component j are calculated as follows.

$$C_{\mathrm{i}} = \hat{X}_{\mathrm{i}} (1 + \sum \alpha_{\mathrm{ij}} C_{\mathrm{j}}) \qquad \text{(H.16)}$$

$$C_{\mathrm{j}} = \hat{X} (1 + \sum \alpha_{\mathrm{jk}} C_{\mathrm{k}}) \qquad \text{(H.17)}$$

When component j is to be corrected by component i, which is represented as k, it is necessary to carry out iterated convergent calculations in order to obtain accurate results for both components i and j.

Example 5: The iteration values of Fe_2O_3 and Cr_2O_3 are calculated as follows.

The Cr_2O_3 presumed basic calibration curve is

$\hat{X}_{Cr_2O_3} = 0{,}116\,49 I_{Cr_2O_3} - 0{,}854\,18$ $\alpha_{Fe_2O_3} = -\,0{,}000\,65$ and intensities are given in Table H.4.

Step 5-1: The presumed basic values of Fe_2O_3 and Cr_2O_3 are calculated thus:

$$\hat{X}_{\mathrm{Fe_2O_3}} = 0{,}000\ 171 \times (58{,}853)^2 + 0{,}226\ 36 \times 58{,}853 - 0{,}156 = 13{,}758$$

$$\hat{X}_{\mathrm{Cr_2O_3}} = 0{,}116\ 49 \times 315{,}39 - 0{,}854\ 18 = 35{,}886$$

Step 5-2: The first iteration calculation

$$C_{\mathrm{Fe_2O_3}} = 13{,}758\ (1 + 0{,}006\ 77\ \hat{X}_{\mathrm{Cr_2O_3}}) = 13{,}758 \times (1 + 0{,}006\ 77 \times 35{,}886) = 17{,}100$$

$$C_{\mathrm{Cr_2O_3}} = 35{,}886\ (1 - 0{,}000\ 65\ \hat{X}_{\mathrm{Fe_2O_3}}) = 35{,}886\ (1 - 0{,}000\ 65 \times 13{,}758) = 35{,}565$$

Step 5-3: The second iteration calculation

$$C_{\mathrm{Fe_2O_3}} = 13{,}758\ (1 + 0{,}006\ 77\ W_{\mathrm{Cr_2O_3}}) = 13{,}758\ (1 + 0{,}006\ 77 \times 35{,}565) = 17{,}071$$

$$C_{\mathrm{Cr_2O_3}} = 35{,}886\ (1 - 0{,}000\ 65\ W_{\mathrm{Fe_2O_3}}) = 35{,}886\ (1 - 0{,}000\ 65 \times 17{,}100\ ) = 35{,}487$$

Step 5-4: The third iteration calculation

$$C_{\mathrm{Fe_2O_3}} = 13{,}758\ (1 + 0{,}006\ 77\ W_{\mathrm{Cr_2O_3}}) = 13{,}758\ (1 + 0{,}006\ 77 \times 35{,}487) = 17{,}063$$

$$C_{\mathrm{Cr_2O_3}} = 35{,}886\ (1 - 0{,}000\ 65\ W_{\mathrm{Fe_2O_3}}) = 35{,}886\ (1 - 0{,}000\ 65 \times 17{,}071) = 35{,}488$$

Step 5-5: The fourth iteration calculation

$$C_{\mathrm{Fe_2O_3}} = 13{,}758\ (1 + 0{,}006\ 77\ W_{\mathrm{Cr_2O_3}}) = 13{,}758\ (1 + 0{,}006\ 77 \times 35{,}488) = 17{,}063$$

$$C_{\mathrm{Cr_2O_3}} = 35{,}886\ (1 - 0{,}000\ 65\ W_{\mathrm{Fe_2O_3}}) = 35{,}886\ (1 - 0{,}000\ 65 \times 17{,}063) = 35{,}488$$

($C_{\mathrm{Fe_2O_3}}$ is confirmed to converge at the third iteration calculation.)

Convergent calculation using a personal computer is needed in the multi-component system during actual measurements.

b) Multiple regression method

This method eliminates the need for presumed basic calibration curves, and determines directly the calibration curve coefficients a, b and c using the theoretical matrix coefficients in Tables H.5 to H.12. The non-linear multiple regression programme is usually available.

Table H.5 — Example of the theoretical matrix correction coefficients for fireclay refractory products

Case 1

Correcting component	Analysis component to be corrected								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
Al_2O_3			–0,000 38	–0,000 33	–0,000 37	–0,000 30	–0,000 10	–0,000 10	–0,000 27
Fe_2O_3	–0,000 38	–0,001 15		–0,001 77	0,000 92	–0,001 52	0,001 15	0,001 12	–0,001 40
TiO_2	–0,001 05	–0,000 41	0,007 15		0,006 88	–0,001 69	0,000 46	0,000 48	–0,001 69
MnO	–0,000 51	–0,001 00	0,001 81	–0,001 80		–0,001 66	0,001 01	0,000 99	–0,001 55
CaO	–0,001 21	–0,000 24	0,007 27	–0,006 28	–0,007 05		0,000 30	0,000 33	–0,001 47
MgO	–0,000 19	–0,001 48	–0,000 60	–0,000 52	–0,000 58	–0,000 47		–0,000 20	–0,000 44
Na_2O	–0,000 34	–0,001 24	–0,000 91	–0,000 79	–0,000 89	–0,000 72	0,001 27		–0,000 67
K_2O	–0,001 36	–0,000 09	–0,007 17	0,006 02	0,006 92	0,005 33	0,000 15	0,000 18	

Conditions: Rh end-window; 50 kV; $Li_2B_4O_7$ flux at 10:1; base component SiO_2 with second main component Al_2O_3.

Case 2

Correcting component	Analysis component to be corrected								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
Al_2O_3			–0,000 38	–0,000 33	–0,000 37	–0,000 30	–0,000 09	–0,000 09	–0,000 28
Fe_2O_3	–0,000 39	0,001 32		–0,000 77	0,001 07	–0,000 73	0,001 25	0,001 18	–0,000 70
TiO_2	–0,001 41	0,000 13	0,007 17		0,006 89	–0,001 12	0,000 10	0,000 06	–0,001 31
MnO	–0,000 51	0,001 17	0,001 98	–0,000 94		–0,000 91	0,001 12	0,001 05	–0,000 87
CaO	–0,001 50	0,000 05	0,007 28	0,006 29	0,007 06		0,000 01	–0,000 03	–0,001 22
MgO	–0,000 20	0,001 68	–0,000 60	–0,000 52	–0,000 59	–0,000 47		–0,000 19	–0,000 44
Na_2O	–0,000 35	0,001 43	–0,000 91	–0,000 80	–0,000 89	–0,000 72	0,001 40		–0,000 68
K_2O	–0,001 58	–0,000 05	0,007 18	0,006 04	0,006 93	0,005 39	–0,000 09	–0,000 12	

Conditions: Cr side-window; 50 kV; scan type; sample: $Li_2B_4O_7$ = 1:10; base component SiO_2; second base component Al_2O_3.

Case 3

Correcting component	Analysis component to be corrected								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
Al_2O_3			–0,000 38	–0,000 33	–0,000 37	–0,000 29	–0,000 10	–0,000 09	–0,000 27
Fe_2O_3	–0,000 36	0,001 20		–0,001 71	0,000 68	–0,001 41	0,001 19	0,001 15	–0,001 27
TiO_2	–0,001 04	0,000 45	0,007 13		0,006 85	–0,001 73	0,000 49	0,000 51	–0,001 70
MnO	–0,000 49	0,001 05	0,001 54	–0,001 80		–0,001 58	0,001 05	0,001 02	–0,001 46
CaO	–0,001 21	0,000 28	0,007 25	0,006 26	0,007 03		0,000 33	0,000 35	–0,001 54
MgO	–0,000 19	0,001 52	–0,000 60	–0,000 52	–0,000 58	–0,000 46		–0,000 20	–0,000 43
Na_2O	–0,000 34	0,001 27	–0,000 91	–0,000 79	–0,000 88	–0,000 71	0,001 19		–0,000 67
K_2O	–0,001 35	0,000 13	0,007 15	0,006 00	0,006 90	0,005 30	0,000 17	0,000 20	

Conditions: Rh end-window; 40 kV; simultaneous type; sample: $Li_2B_4O_7$ = 1:10; base component SiO_2; second base component Al_2O_3.

Table H.6 — Example of the theoretical matrix correction coefficients for silica refractory products

Case 1

Correcting component	Analysis component to be corrected								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
Al_2O_3			−0,000 38	−0,000 33	−0,000 37	−0,000 30	−0,000 09	−0,000 09	−0,000 27
Fe_2O_3	−0,000 36	0,00115		−0,001 78	0,000 92	−0,001 52	0,001 16	0,001 13	−0,001 39
TiO_2	−0,001 03	0,000 41	0,007 15		0,006 88	−0,001 68	0,000 46	0,000 49	−0,001 68
MnO	−0,000 49	0,001 00	0,001 81	−0,001 81		−0,001 66	0,001 02	0,000 99	−0,001 55
CaO	−0,001 20	0,000 25	0,007 27	0,006 28	0,007 05		0,000 30	0,000 33	−0,001 48
MgO	−0,000 18	0,001 48	−0,000 60	−0,000 52	−0,000 58	−0,000 47		−0,000 20	−0,000 44
Na_2O	−0,000 33	0,001 24	−0,000 91	−0,000 79	−0,000 89	−0,000 72	0,001 27		−0,000 67
K_2O	−0,001 34	0,000 09	0,007 17	0,006 02	0,006 92	0,005 33	0,000 15	0,000 18	
Conditions: Rh end-window; 50 kV; scan type; sample: $Li_2B_4O_7$ = 1:10; base component SiO_2; second base component Al_2O_3.									

Case 2

Correcting component	Analysis component to be corrected								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
Al_2O_3			−0,000 38	−0,000 33	−0,000 37	−0,000 30	−0,000 09	−0,000 08	−0,000 28
Fe_2O_3	−0,000 37	0,001 32		−0,000 77	0,001 07	−0,000 73	0,001 26	0,001 18	−0,000 70
TiO_2	−0,001 37	0,000 15	0,007 17		0,006 89	−0,001 11	0,000 11	0,000 07	−0,001 30
MnO	−0,000 50	0,001 17	0,001 98	−0,000 94		−0,000 90	0,001 12	0,001 05	−0,000 87
CaO	−0,001 48	0,000 05	0,007 28	0,006 29	0,007 06		0,000 00	−0,000 03	−0,001 23
MgO	−0,000 19	0,001 68	−0,000 60	−0,000 52	−0,000 59	−0,000 47		−0,000 19	−0,000 44
Na_2O	−0,000 34	0,001 44	−0,000 91	−0,000 80	−0,000 89	−0,000 72	0,001 40		−0,000 68
K_2O	−0,001 55	−0,000 04	0,007 18	0,006 04	0,006 93	0,005 39	−0,000 08	−0,000 12	
Conditions: Cr side-window; 50 kV; scan type; sample: $Li_2B_4O_7$ = 1:10; base component SiO_2; second base component Al_2O_3.									

Case 3

Correcting component	Analysis component to be corrected								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O
Al_2O_3			−0,000 38	−0,000 33	−0,000 37	−0,000 29	−0,000 09	−0,000 09	−0,000 27
Fe_2O_3	−0,000 35	0,001 20		−0,001 72	0,000 68	−0,001 40	0,001 19	0,001 16	−0,001 27
TiO_2	−0,001 03	0,000 45	0,007 13		0,006 85	−0,001 72	0,000 49	0,000 51	−0,001 70
MnO	−0,000 48	0,001 05	0,001 54	−0,001 81		−0,001 58	0,001 06	0,001 02	−0,001 45
CaO	−0,001 20	0,000 29	0,007 25	0,006 26	0,007 03		0,000 33	0,000 35	−0,001 55
MgO	−0,000 18	0,001 52	−0,000 60	−0,000 52	−0,000 58	−0,000 46		−0,000 20	−0,000 43
Na_2O	−0,000 33	0,001 28	−0,000 91	−0,000 79	−0,000 88	−0,000 71	0,001 30		−0,000 67
K_2O	−0,001 34	0,000 13	0,007 15	0,006 00	0,006 90	0,005 30	0,000 18	0,000 20	
Conditions: Rh end-window; 40 kV; simultaneous type; sample: $Li_2B_4O_7$ = 1:10; base component SiO_2; second base component Al_2O_3.									