SLOVENSKI STANDARD
SIST EN ISO 12677:2003

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Kemijska analiza ognjevzdržnih izdelkov z XRF – Metoda z vlito talino (ISO 12677:2003)

Chemical analysis of refractory products by XRF - Fused cast bead method (ISO 12677:2003)

Chemische Analyse von feuerfesten Erzeugnissen durch Röntgenflureßenz - Schmelzaufschluss-Verfahren (ISO 12677:2003)

Analyse chimique des matériaux réfractaires par fluorescence de rayons X - Méthode de la perle fondue (ISO 12677:2003)

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Chemical analysis of refractory products by XRF - Fused cast bead method (ISO 12677:2003)

Analyse chimique des matériaux réfractaires par fluorescence de rayons X - Méthode de la perle fondue (ISO 12677:2003)

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (EN ISO 12677:2003) has been prepared by Technical Committee ISO/TC 33 "Refractories" in collaboration with Technical Committee CEN/TC 187 "Refractory products and materials", the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2003, and conflicting national standards shall be withdrawn at the latest by November 2003.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

Endorsement notice

The text of ISO 12677:2003 has been approved by CEN as EN ISO 12677:2003 without any modifications.

NOTE Normative references to International Standards are listed in Annex ZA (normative).

Annex ZA
(normative)

Normative references to international publications with their relevant European publications

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

NOTE Where an International Publication has been modified by common modifications, indicated by (mod.), the relevant EN/HD applies.

Publication	Year	Title	EN	Year
ISO 10058	1992	Magnesites and dolomites - Chemical analysis	EN ISO 10058	1996

INTERNATIONAL STANDARD

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

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

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Contents

Page

Foreword

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

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*.

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

1 Scope

This International Standard specifies a method for chemical analysis of refractory products and materials, and technical ceramics composed of oxides, including the determination of oxide at levels between 0,01 % and 99 % by means of the XRF fused cast bead method.

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

2 Normative references

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

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

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

ISO 10058, *Magnesites and dolomites — Chemical analysis*

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

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

3 Types of material

High alumina $\geqslant$ 45 % Al_2O_3

Alumino-silicate 7 % to 45 % Al_2O_3

Silica $\geqslant$ 93 % SiO_2

Zircon

Zirconia and zirconates

Magnesia

Magnesia/alumina spinel (~ 70/30)

Dolomite

Limestone

Magnesia/chromic oxide

Chrome ore

Chrome alumina

Alumina/magnesia spinel (~ 70/30)

Zirconia-alumina-silica cast material (AZS)

Calcium silicates

Calcium aluminates

Magnesium silicates

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

4 Principle

The powdered sample is fused with a suitable flux to destroy its mineralogical and particulate composition. The resultant melt is cast into the shape of a glass bead which is then introduced into an XRF spectrometer. The intensities of the fluorescent X-rays of the required elements in the bead are measured and the chemical composition of the sample is analysed by reference to previously determined calibration graphs or equations and applying corrections for inter-element effects. The calibration equations and inter-element corrections are established from beads produced using pure reagents and/or series reference materials (SeRMs), prepared in the same way as the samples. Certified Reference Materials (CRMs) can be used providing they meet all the requirements of 10.2.2 and 10.4.1.

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

5 Sample grinding

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

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

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

Two methods of obtaining the required particle size are permissible:

a) For mechanical grinding devices, establish what grinding times are sufficient to grind the various samples analysed to the correct fineness and thereafter apply these minimum times for grinding. When grinding hard materials, such as chromite, sieving is used, but this may induce segregation.

b) After hand grinding for 20 s, sieve the ground powder through a sieve of 100 μm aperture in accordance with ISO 565. Regrind any material remaining on the sieve for a further 20 s, sieve and repeat this procedure until the whole of the sample passes through the sieve. Transfer the sample to a suitable container and mix for 1 min, using a mechanical mixer such as a vertical linear mixer.

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

6 Apparatus

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

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

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

6.3 Heat reservoir for casting mould, (optional) required in special circumstances when using moulds of small sizes, so that the mould does not cool too rapidly when removed from the furnace. A small piece of flat refractory material is suitable, e.g. a piece of sillimanite batt with dimensions 10 mm × 50 mm × 50 mm.

6.4 Air jet, (optional) required to cool the mould rapidly. This can be any device whereon a narrow jet of air can be directed to the centre of the base of the casting dish. A convenient way of doing this is to use the base of a bunsen burner without a barrel to serve as an air jet.

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

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

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

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

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

7 Loss on ignition (and/or drying)

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

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

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

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

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

8 Flux

8.1 Choice of flux and ratio of flux to sample

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

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

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

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

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

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

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 $3RD$,

where

R is the ratio of flux to sample;

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

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

8.2 Compensations for moisture in flux

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

a) Calcine the entire quantity of flux required overnight at 700 °C immediately before it is used for analysis and afterwards store it in a desiccator.

b) Carry out duplicate losses on ignition on 1 g portions of well-mixed flux for each kilogram of flux used. Carry out the calcining at the normal fusion temperature for 10 min, or the normal fusion time, whichever is the greater [see 9.2.2 f)]. Store the flux in a tightly sealed container except when in use. The loss on ignition, expressed as a percentage, L, is then used to calculate a factor, F [see equation (1)], which is in turn used to calculate the mass of the unignited flux needed to produce the required mass of flux on the ignited basis (F times required mass of ignited flux = required mass of unignited flux). Carry out this loss on ignition, at weekly intervals or for each kilogram of flux used, whichever is the more frequent.

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

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

9 Fusion casting procedures

9.1 General

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

9.2 Fusion of samples and casting of beads

9.2.1 Choice of procedure

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

9.2.2 Requirements

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

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

b) The total mass of sample and flux shall be chosen for the particular casting mould type used, and this mass shall always be the same.

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

d) The melts produced shall be visually homogeneous.

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

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

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

h) Beads produced shall be free from blemishes on the chosen measuring surface.