INTERNATIONAL STANDARD

ISO 21068-1

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Chemical analysis of silicon-carbide-containing raw materials and refractory products —

Part 1: General information and sample preparation

Analyse chimique des matières premières et des produits réfractaires contenant du carbure de silicium —

Partie 1: Informations générales et préparation des échantillons

Reference number
ISO 21068-1:2008(E)

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Foreword

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

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

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 21068-1 was prepared by Technical Committee ISO/TC 33, *Refractories*

ISO 21068 consists of the following parts, under the general title *Chemical analysis of silicon-carbide-containing raw materials and refractory products*:

— *Part 1: General information and sample preparation*

— *Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon*

— *Part 3: Determination of nitrogen, oxygen and metallic and oxidic constituents*

Introduction

ISO 21068, Parts 1 to 3, have been developed from the combination of a Japanese standard JIS 2011 [2] and work items originally developed within CEN. As there is a wide variety of laboratory equipment in use, the most commonly used methods are described.

ISO 21068, Parts 1 to 3, are applicable to the analysis of all refractory products as classified in ISO 10081 [10] to [13] (shaped) and ISO 1927 [3] (unshaped) and raw materials containing carbon and/or silicon carbide. Therefore, ISO 21068, Parts 1 to 3, covers the full range of analysis from pure silicon carbide to oxidic refractory composition with low-content silicon carbide and/or nitrides. Primarily, ISO 21068, Parts 1 to 3, provides methods to distinguish between different carbon bound types like total carbon (C_{total}) and free carbon (C_{free}) and derives from these two the silicon carbide content.

If free carbon is present, the standard includes different types of temperature treatment in order to determine the mass changes gravimetrically. Frequently, the resulting residue is used for other determinations.

The determination of other groups of analytes described in ISO 21068, Parts 1 to 3, are free metals, free silicon (S_{ifree}), free aluminum (Al_{free}), free magnesium (Mg_{free}), free iron (Fe_{free}) and the group of oxides from main to trace components.

ISO 21068, Parts 1 to 3, also describe the chemical analysis of silicon dioxide, total silicon, oxygen and nitrogen and other oxidic bound metals that typically occur in the materials.

It represents a listing of analytical methods which is approximately structured according to material composition. However, it is still the user who should prove the applicability of the method depending on the material and analytical requirements.

The most broadly used analytical techniques such as X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma-optical emission spectrometry (ICP-OES) suffer from the disadvantage that the analytical results are chemical bond independent. For carbon-containing ceramic raw materials and compositions ISO 21068, Parts 1 to 3, provide analytical methods for the determination of free carbon, and SiC in the presence of oxidic compounds in particular SiO_2.

Because of the diversity of laboratory equipment, the three parts of ISO 21068 summarize broadly used analytical techniques which lead to equivalent results. In principle, the determination of carbon is based in all itemized methods on the oxygen extraction method, where carbon is oxidized at elevated temperatures. Thereafter carbon is analysed as CO_2.

As well as carbon and carbidic compounds, metallic silicon, aluminium and magnesium are considered. While metallic silicon is in majority a precursor material which remains after the production process of SiC in the raw material, metallic aluminium is added as an antioxidant in carbon-containing refractory formulations.

Mostly oxidic bound components, such as Al_2O_3, CaO, MgO, TiO_2, Cr_2O_3, ZrO_2 and alkalines, can be determined by XRF as described in ISO 12677, ICP-AES or wet chemical methods (see ISO 26845 [25], ISO 21587-1 [22] and ISO 21587-3 [24]). These results can be corrected by formulas provided by ISO 21068, Parts 1 to 3, in consideration of the values obtained by the determination of carbon, SiC, and metallic components.

ISO 21068, Parts 1 to 3, also provide methods for qualitative and quantitative determinations of the nitrogen content and the determination of oxygen. Thereby only the total content of nitrogen and oxygen is given; a precise determination of non-carbide components (oxides and nitrides) is not possible in this way.

ISO 21068, Parts 1 to 3, do not provide methods to distinguish quantitatively between different varieties of nitrides like silicon nitride, silicon oxy-nitride and sialon. For further information about the determination of this group of compounds, see EN 12698-2.

Chemical analysis of silicon-carbide-containing raw materials and refractory products —

Part 1: General information and sample preparation

1 Scope

This part of ISO 21068 gives definitions and specifies techniques for the preparation of samples for the chemical analysis of silicon-carbide-containing raw materials and refractory products including:

a) graphite brick containing silicon carbide;

b) silicon carbide brick (includes the bricks containing silicon nitride);

c) refractories containing carbon and/or silicon carbide mixed with clay;

d) refractories containing carbon and/or silicon carbide mixed with silica (and fused silica);

e) refractories containing carbon and/or silicon carbide mixed with high alumina material;

f) refractories containing carbon and/or silicon carbide mixed with magnesia (and dolomite);

g) refractories containing carbon and/or silicon carbide mixed with chrome mineral or magnesia-chrome materials;

h) refractories containing carbon and/or silicon carbide except those described in a) to g) above.

The items of chemical analysis described in ISO 21068, Parts 1 to 3 are as follows:

1) loss on drying (LOD);

2) loss on ignition (LOI);

3) total carbon, C_{total};

4) free carbon, C_{free};

5) silicon carbide, SiC;

6) free silicon (Si_{free});

7) free aluminium (Al_{free});

8) free magnesium (Mg_{free});

9) free iron (Fe_{free});

10) silicon(IV) oxide (SiO_2);

11) aluminium oxide (Al_2O_3);

12) iron(III) oxide (total iron oxide calculated as Fe_2O_3);

13) titanium(IV) oxide (TiO_2);

14) calcium oxide (CaO);

15) magnesium oxide (MgO);

16) sodium oxide (Na_2O);

17) potassium oxide (K_2O);

18) chromium(III) oxide (Cr_2O_3);

19) zirconium oxide (ZrO_2);

20) boron oxide (total boron calculated as B_2O_3);

21) nitrogen;

22) oxygen;

23) nitrides (undifferentiated: Si_3N_4, AlN, BN, sialon, oxy-nitrides, etc.).

The range of determination specified in this part of ISO 21068 is given in Table 1.

Table 1 — Range of determination

Component	Range % by mass
LOI	–10 to 99
C_{total}	0,01 to 99
C_{free}	0,01 to 99
SiC	3 to 99
Si_{free}	0,1 to 10
Al_{free}	0,1 to 10
Mg_{free}	0,1 to 10
Fe_{free}	0,1 to 10
SiO_2	0,1 to 95
Al_2O_3	0,1 to 95
Fe_2O_3	0,1 to 15
TiO_2	0,1 to 5
CaO	0,1 to 60
MgO	0,1 to 95
Na_2O	0,1 to 5
K_2O	0,1 to 5
Cr_2O_3	0,1 to 40
ZrO_2	0,1 to 1
B_2O_3	0,1 to 5
Si_3N_4	0,1 to 35

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 31-0, *Quantities and units — Part 0: General principles*

ISO 5022, *Shaped refractory products — Sampling and acceptance testing*

ISO 8656-1, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

ISO 12677:2003, *Chemical analysis of refractory products by XRF — Fused cast bead method*

EN 12698-2, *Chemical analysis of nitride bonded silicon carbide refractories — Part 2: XRD methods*

ISO 21068-2:2008, *Chemical analysis of silicon-carbide-containing raw materials and refractory products — Part 2: Determination of loss on ignition, total carbon, free carbon and silicon carbide, total and free silica and total and free silicon*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
unshaped refractory materials
mixtures consisting of an aggregate and a bond or bonds, prepared ready for use either directly in the condition in which they are supplied or after the addition of one or more suitable liquids

NOTE 1 Unshaped refractory materials can contain metallic, organic or ceramic fibre material.

NOTE 2 These mixtures are either dense or insulating. Insulating mixtures are those whose true porosity is not less than 45 % when determined in accordance with EN 1094-4 [1] using a test piece fired to specified conditions.

3.2
dense shaped refractory materials
preshaped and burned or tempered refractory compositions to obtain a ceramic or a carbon-based bond

NOTE Dense shaped refractory materials are classified in accordance with ISO 10081 [10] to [13].

3.3
moisture
water which is not chemically bound in refractory raw materials and products, from moisture absorption during storage, or residual water used for the preparation of a refractory castable mix

3.4
volatile components
components which are evaporated at 750 °C under an argon atmosphere

NOTE In general, chemically bound water (hydraulic and phosphate-bond unshaped refractories), hydroxyl groups and organic components with low vapour pressure, as present in pitch, tar, resin or other organic binder, are removed.

3.5
refractories containing carbon and/or silicon-carbide
formulations containing refractory components provided as shaped or unshaped products containing SiC and/or carbon

NOTE Whereas carbon can be available as graphite, organic binder (e.g. pitch, tar, resin, carbon black), the SiC content in refractory material can vary from less than 1 % by mass to almost 100 % by mass.

3.6
free carbon
carbon species such as graphite, amorphous carbon (carbon black) and organic carbon (pitch, tar or resin)

3.7
free metallic components
metallic species which are added into refractories or appear as residual components in raw materials as a result of their production process, including treatment

EXAMPLE Si in SiC.

NOTE This includes metallic components which are formed in, and remain through, the combustion process (e.g. free silicon, free aluminium, and free magnesium).

3.8
oxidic bond components
metal oxide species which are added as a compound into refractory admixtures or occur as residual components in raw materials due to their production process

EXAMPLE SiO_2 in SiC.

NOTE SiO_2 has to be differentiated concerning free and/or combined silica content, free silica and surface silicon dioxide.

3.9
loss on ignition at 850 ºC
mass change when 5 g of the test sample or the residue after drying at 110 °C is heated in an open-air electric oven at 850 °C for 3 h

NOTE 1 Drying at 110 °C is described in 4.2.3.

NOTE 2 This value is used for the determinations of silicon(IV) oxide, aluminium oxide, iron(III) oxide, titanium(IV) oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide, chromium(III) oxide, zirconium oxide, and boron oxide.

4 Sampling and preparation of the test sample

4.1 General

Sampling shall be carried out in accordance with ISO 5022 for shaped refractory products and ISO 8656-1 for unshaped refractory products unless otherwise agreed by the user and the producer.

NOTE Information on sampling procedures for the analysis of bulk particulate materials is given in ISO 11648-2 [14].

4.2 Sample pretreatment

4.2.1 General

In order to avoid preparation-dependent inaccuracy for the results, the samples shall be prepared as described in 4.2.2 to 4.2.4.

4.2.2 Crushing

With the exception of raw materials, samples are generally in large pieces that require jaw crushing prior to the fine grinding stage. Because of contamination, particularly by iron, it is essential that size reduction in jaw crushing is the minimum possible, commensurate with obtaining a representative sample and achieving the maximum size that can be tolerated at the subsequent fine grinding stage.

If free iron or total iron is required, a separate sample should be crushed in an iron-free device.

In the fine grinding stage, it is essential to use the minimum amount of grinding, as excessive grinding will oxidize silicon carbide to silica.

NOTE As an example, grinding a sample to < 75 µm rather than < 125 µm could increase the free silica by between 0,06 % and 0,4 % and decrease the SiC by between 0,04 % and 0,25 %.

To produce a test sample with the minimum of oxidation, carefully grind and sieve the material through a 150 µm sieve. Because of the hardness of these materials, it is preferable to fine grind (in such a manner as to reduce the size to < 150 µm) using a tungsten carbide vial in a swing mill, or alternative mills lined with tungsten carbide or lined with any material that does not contaminate the sample with any of the analytes to be determined. The grinding process will inevitably generate contamination due to abrasion of the vial material, and, if excessive contamination is to be expected, corrections shall be made to the analysis, in terms of dilution of the sample by the grinding media, to the loss on ignition due to the gain in weight on oxidizing tungsten carbide. These corrections require a factor to allow for the cobalt or nickel binder in the grinding material, in accordance with Annex B of ISO 12677:2003.

Similarly, in the case of free carbon and total carbon determinations, 0,051 8 % of carbon shall be subtracted for each 1 % of tungsten oxide found in the analytical sample, the carbon figure shall then in turn be corrected for the dilution factor above. When tungsten carbide grinding media are not available, prepare two analytical samples, one using an alumina mortar or vial and the other using an iron percussion mortar. Use the sample prepared in the iron mortar for determinations except for total iron and free iron. Use the alumina ground sample for total iron, free iron and free silicon.

4.2.3 Drying

For chemical analysis, the sample shall be in a dry state. Dry the sample at 110 °C ± 10 °C to constant mass.

NOTE 1 Drying overnight is usually sufficient.

NOTE 2 Chemically bonded water and volatiles in pitch and resin can be already affected by this sample treatment, but they are not removed quantitatively at 110 °C. In this case, special heat pretreatments are required (see 7.1.3 of ISO 21068-2:2008).

4.2.4 Weighing (only general procedure)

The specified quantity of test sample for chemical analysis and all weighing procedures, such as changes in mass, shall be weighed using chemical balances as follows:

a) for weighing the test sample for the determination of total carbon, free carbon, silicon carbide and silicon nitride by fusion-thermal conductivity method (in an inert gas) and the test sample for calibration, a chemical balance capable of weighing to the nearest 0,01 mg shall be used;

b) for weighing the test sample for the other determinations, a chemical balance capable of weighing to the nearest 0,1 mg shall be used.

5 Preliminary analyses

Normally the composition of the sample is known approximately. If not, a preliminary analysis is necessary.

If the nature of the material is unknown, the presence of other silicon species besides SiC or SiO_2 in the sample (e.g. silicon, silicon nitride, sialon, silicon oxy-nitride), shall be checked by carrying out a semi-quantitative analysis by X-ray diffraction (XRD) in accordance with EN 12698-2.

NOTE 1 The presence of free aluminium can be determined with this method.

NOTE 2 With XRD, the detection limits can vary because of the crystal structure (approximately between 0,1 % and 1 % by mass).

In addition to a preliminary XRD analysis, a qualitative test for nitrogen can be carried out by placing 0,5 g of the powder sample in a dry boiling tube, adding a few pellets of NaOH and heating over a Bunsen burner until the pellets fuse. Test for any ammonia evolved with a wet pH indicator paper. If no significant quantity of ammonia is detected, the nitrogen determination may be omitted.

6 Expression of results

Calculate the test results as a percentage composition (mass fraction) and express the result as the mean of two determinations, in accordance with ISO 31-0, as follows:

a) if an integer part of the mass fraction is two digits, express the result to one decimal place;

b) if an integer part of the mass fraction is one digit, express the result to two decimal places.

7 Test report

The test report shall contain as a minimum the following information:

a) all information necessary for identification of the sample tested;

b) a reference to this International Standard (ISO 21068-1:2008);

c) the International Standard and method used for sampling;

d) the chemical components determined;

e) the specific details of the methods used;

f) the results of the tests, including the results of the individual determinations and their mean, calculated as specified in each part and expressed in accordance with Clause 6;

g) if available,

   1) possible bias from sample preparation, and

   2) the precision and bias of measurement;

h) any deviations from the procedure specified;

i) any unusual features (anomalies) observed during the test;

j) the date of the test;

k) the name of the testing establishment.

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[9] ISO 10060, *Dense, shaped refractory products — Test methods for products containing carbon*

[10] ISO 10081-1, *Classification of dense shaped refractory products — Part 1: Alumina-silica*

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[12] ISO 10081-3, *Classification of dense shaped refractory products — Part 3: Basic products containing from 7 % to 50 % residual carbon*

[13] ISO 10081-4, *Classification of dense shaped refractory products — Part 4: Special products*

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[20] ISO 21079-2, *Chemical analysis of refractories containing alumina, zirconia, and silica — Refractories containing 5 % to 45 % of ZrO_2 (alternative to the X-ray fluorescence method) — Part 2: Wet chemical analysis*

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[22] ISO 21587-1, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and gravimetric silica*

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[24] ISO 21587-3, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) — Part 3: Inductively coupled plasma and atomic absorption spectrometry methods*

[25] 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*

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