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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

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

Partie 2: Détermination de la perte au feu, du carbone total, du carbone libre et du carbure de silicium, de la silice totale et libre, et du silicium total et libre

Reference number
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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.

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 21068-2 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 [6] and work items originally developed within CEN. Because there is a wide variety of laboratory equipment in use, the most commonly used methods are described.

This part of ISO 21068 is applicable to the analysis of all refractory products classified in ISO 10081 [2] to [5] (shaped) and ISO 1927 [1] (unshaped) and raw materials containing carbon and/or silicon carbide. Therefore, this part of ISO 21068 covers the full range of analysis from pure silicon carbide to oxidic refractory composition with a low content of silicon carbide and/or nitrides. Primarily, this part of ISO 21068 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, this part of ISO 21068 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 this part of ISO 21068 are free metals, free silicon (Si_{free}), free aluminum (Al_{free}), free magnesium (Mg_{free}), free iron (Fe_{free}) and the group of oxides from main to trace components.

This part of ISO 21068 also describes the chemical analysis of SiO_2, total Si, oxygen and nitrogen and other oxidic-bound metals which typically occur in the materials.

This part of ISO 21068 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.

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

1 Scope

This part of ISO 21068 specifies analytical techniques for the determination of change in mass by thermal treatment at specified temperatures, and methods for the determination of the total carbon content, free carbon, silicon carbide, silicon, total silica and free silica content of silicon-carbide-containing raw materials and refractory products.

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 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 9286:1997, *Abrasive grains and crude — Chemical analysis of silicon carbide*

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

ISO 21068-1:2008, *Chemical analysis of silicon-carbide-containing raw materials and refractory products — Part 1: General information and sample preparation*

EN 12698-1:2007, *Chemical analysis of nitride bonded silicon carbide refractories — Part 1: Chemical methods*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21068-1 apply.

4 Determination of change in mass

4.1 General

The determination of change in mass is defined as a loss or increase in mass caused by heat treatment. Several methods are distinguished based on the sample material, temperature and atmosphere. The determination of change in mass is carried out by a gravimetric method. Heat treatments in air will lead to a loss of volatile matter and carbon and an increase of mass due to oxidation, whereas a heat treatment in argon will only lead to a loss of volatile matter.

Normally, the residue is used for other determinations. Therefore, the change in mass is considered for the calculation of the analytical result. The analytical method which is applied to the residue depends on the matrix and the parameters to be determined. It is up to the user to select the appropriate analytical method.

Table 1 gives an overview of methods of determination of change in mass by heat pretreatments and their different applications.

Table 1 — Methods and application purpose of determination of change in mass

Short title of method	Temperature	Subclause	Application
Loss on drying (LOD_{250})	250 °C	4.2	Attached water and chemically combined water are removed, e.g. in clay containing plastic formulations
Loss on calcination in argon (LOI_{Ar})	750 °C	4.3	All volatile compounds out of pitch- or resin-bonded formulations are removed
Change in mass in air	200 °C	4.4	Volatile compounds are removed from resin-bonded formulations
	400 °C	4.4	Volatile compounds are removed from pitch-bonded formulations
Change in mass (LOI_{750})	750 °C	4.5	Both procedures are suitable to remove carbon (e.g. graphite) from refractory formulations. If fine-grained SiC is present, care should be taken because SiC may be oxidised as well.
Loss on ignition (LOI_{850})	850 °C	4.6	
Loss on ignition ($LOI_{1\,050}$)	1 050 °C	4.7	Loss or gain of mass; attached water, chemically combined water, carbon, organic compounds (e.g. pitch, resin), silicon carbide, and metals are removed

4.2 Determination of the loss on drying at 250 °C (LOD_{250}) gravimetric method

4.2.1 Principle

The test sample is heated at 250 °C ± 10 °C and the loss of mass from attached water is determined.

4.2.2 Apparatus

4.2.2.1 Heat-resistant container, for example with dimensions 200 mm × 150 mm × 30 mm and made from stainless steel.

4.2.3 Procedure

Heat the heat-resistant container at 250 °C ± 10 °C for 30 min. Cool in a desiccator, weigh and record its empty mass , m_0, to the nearest 0,01 g.

Transfer the sample into the container and spread it out flat. Then weigh and record the mass, m_1, of the container and sample to the nearest 0,01 g.

Place the container without a lid in an air bath and heat it at 250 °C ± 10 °C for 16 h. Allow to cool in a desiccator. Weigh and record the mass, m_2, of the container plus the dried sample to the nearest 0,01 g.

4.2.4 Calculation

Calculate the loss on drying at 250 °C, LOD_{250}, as a percentage by mass, using Equation (1).

$$\text{LOD}_{250} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \qquad (1)$$

where

m_0 is the mass of the empty container, in grams;

m_1 is the mass of the container plus the sample before drying, in grams;

m_2 is the mass of the container plus the sample after drying, in grams.

4.3 Determination of the loss on calcination in argon (LOI_{Ar})

4.3.1 Principle

Pretreatment under argon at 750 °C to remove volatile matter. The loss of volatile matter is determined by a gravimetric method.

The residue (R_{Ar}) is normally used for determination of C_{total}, SiC and C_{free} (therefore these parameters will be additionally indexed with $_{\text{Ar}}$), and the change in mass has to be considered for the calculation of the result.

4.3.2 Apparatus

Ordinary laboratory apparatus and the following.

4.3.2.1 U-tube, with ground stoppers and filled with magnesium perchlorate.

4.3.2.2 Resistance furnace, heatable and adjustable at (750 ± 25) °C, in the centre of the heating zone.

4.3.2.3 Thermocouple with display, registering up to 1 200 °C.

4.3.2.4 Ceramic tube, with cones or other gastight connector, with an inner diameter ⩾ 16 mm, made from porcelain, sillimanite, quartz or other suitable material.

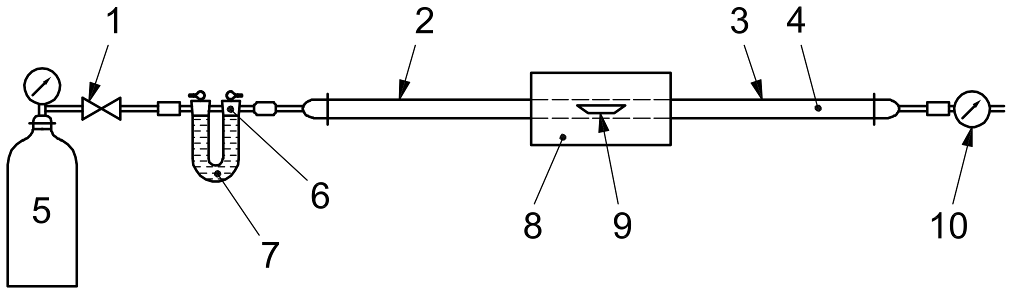
4.3.2.5 Open combustion boats, of unglazed ceramic material, the length of which is adapted to the oven's zone of constant temperature. The boats shall be broad enough to accommodate the amount of sample required for the determination.

4.3.2.6 Gas flowmeter, with an upper scale reading of around 20 l/h.

The argon-conducting parts, such as tubes and connections, should be made of material proofed against oxygen diffusion. Preferable materials are glass and copper. Silicone is unsuitable.

4.3.2.7 Test assembly

The test assembly is set up as shown in Figure 1.



Key

1	valve for pressure control	5	argon cylinder	9	combustion boat
2	cold zone B	6	glass wool	10	gas flowmeter
3	cold zone A	7	magnesium perchlorate		
4	ceramic tube	8	resistance furnace		

Figure 1 — Apparatus set-up for determination of loss on calcination in argon

4.3.3 Reagents

4.3.3.1 Argon, 99,997 %.

4.3.4 Procedure

4.3.4.1 Check of test assembly, blank value determination

To check a newly set up test assembly or to carry out routine checks, a few samples of known volatile-matter content shall be calcined as described in 4.3.4.2 before examining the analytical sample.

The difference between the result found in accordance with 4.3.4.2 and the known volatile-matter content shall be taken into account as the blank value.

4.3.4.2 Determination

Carry out at least two determinations.

Before use, flush the apparatus for at least 15 min with argon.

Weigh the empty combustion boat that has previously been heated at (750 ± 25) °C and record the mass m_0. Weigh 2 g of the sample to the nearest 0,001 g into the combustion boat and record the mass m_1.

Place the combustion boat and sample in cold zone A of the apparatus at $\leqslant$ 200 °C. Pass argon through it at a rate that ensures five changes of gas in the tube within 15 min.

Place the sample in the centre of the heating zone and calcine for 20 min at (750 ± 25) °C, without interruption of the argon stream.

Move the combustion boat into cold zone B and cool in the argon stream at $\leqslant$ 200 °C.

NOTE A period of 20 min is usually required to cool the sample.

Allow the boat to cool to room temperature in a desiccator, weigh to the nearest 0,001 g and record the final mass, m_2.

Repeat the calcination in the argon stream at (750 ± 25) °C until constant mass is obtained, i.e. when two measurements taken at an interval of 30 min do not differ by more than 5 mg.

If the residue is required for the determination of other components, homogenize it and keep it in a closed weighing bottle in a desiccator.

4.3.5 Calculation

Calculate the loss on calcination in argon at 750 °C, $\mathrm{LOI}_{\mathrm{Ar}}$, as a percentage by mass, using Equation (2).

$$\mathrm{LOI}_{\mathrm{Ar}} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{2}$$

where

m_0 is the mass of the empty combustion boat, in grams;

m_1 is the mass of the combustion boat plus sample before ignition, in grams;

m_2 is the mass of the combustion boat plus sample after ignition, in grams.

NOTE The decrease in mass is denoted by a minus sign.

4.4 Determination of the change in mass by heat pretreatment in air

For resin- and pitch-bonded materials, a sample pretreatment shall be performed in accordance with ISO 10060, or the following procedure shall be followed.

Usually before crushing and grinding, subject a sample of approximately 1 kg to heat treatment as follows:

a) resin-bonded materials: 200 °C for 18 h in air;

b) pitch-bonded materials: 400 °C for 18 h in air.

Calculate the change in mass at 200 °C/400 °C, D, as a percentage by mass, using Equation (3).

$$D = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{3}$$

where

m_0 is the mass of the empty container, in grams;

m_1 is the mass of the container plus sample before heat pretreatment, in grams;

m_2 is the mass of the container plus sample after ignition, in grams.

Report the result to the nearest 0,1 %.

When the nature of free carbon is not known, first carry out thermogravimetric analysis to determine the temperature of the heat treatment.

4.5 Determination of the change in mass at 750 °C (LOI_{750})

4.5.1 Principle

Determination of the change in mass as a function of time by ignition at 750 °C in an electric muffle furnace. The loss or increase of mass is determined by a gravimetric method.

4.5.2 Apparatus

4.5.2.1 **Muffle furnace**, with a temperature control from 100 °C to 1 000 °C.

4.5.2.2 **Fused silica dish**, porcelain, or platinum, approximately 60 mm long and 35 mm wide.

4.5.2.3 **Balance**, capable of weighing to 0,1 mg.

4.5.3 Procedure

Weigh the empty dish that has previously been heated at (750 ± 25) °C and record the mass m_0. Weigh 2,5 to 3,5 g of the sample, dried at 110 °C, to the nearest 0,001 g into the combustion boat and record the mass m_1.

Place the dish and the sample in the muffle furnace at 500 °C for 20 min.

Increase the furnace temperature to 750 °C and ignite the sample for a further 1 h 30 min when the furnace has reached the test temperature.

Take the dish out of the furnace and allow it to cool down to room temperature in a desiccator.

Weigh the dish and sample. Record the mass m_2.

Replace the dish and sample in the furnace for a further 30 min and check whether there is a further loss in mass. If so, repeat the whole procedure.

NOTE If a mass increase is observed after the second ignition, do not carry out further ignition because it can indicate possible oxidation of some elements.

4.5.4 Calculation

Calculate the loss on ignition at 750 °C, LOI_{750}, as a percentage by mass, using Equation (4).

$$\mathrm{LOI}_{750} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \qquad (4)$$

where

m_0 is the mass of the empty dish, in grams;

m_1 is the mass of the dish plus sample before ignition, in grams;

m_2 is the mass of the dish plus sample after ignition, in grams.

NOTE The result obtained in this way cannot be considered as the free carbon content.

4.6 Determination of loss on ignition at 850 °C (LOI$_{850}$)

4.6.1 Apparatus

4.6.1.1 Platinum dish, platinum or porcelain (e.g. Type B 20 ml).

4.6.2 Procedure

Heat the platinum dish at 850 °C ± 25 °C for 15 min, cool it in a desiccator, and then weigh the platinum dish. Record the mass of the empty dish m_0.

Weigh 5,0 g of a sample, to the nearest 0,1 g, into the platinum dish and spread it widely and thinly. Record the mass of the dish plus sample m_1.

Put the platinum dish without a cover into an electric furnace and raise the temperature from room temperature to 850 °C ± 25 °C, and keep heating for 3 h. Put the lid on the platinum dish, cool in a desiccator, weigh it and record the mass m_2.

In the case of fusion of the sample containing silicon carbide, silicon nitride and metal silicon, several hours should be spent on a rise of temperature to the 700 °C to 850 °C region. There is a risk of eroding a platinum dish with a rapid rise of temperature to above 850 °C.

4.6.3 Calculation

Calculate the loss on ignition at 850 °C ± 25 °C, R, expressed as a percentage by mass using Equation (5).

$$R = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{5}$$

where

m_0 is the mass of the empty dish, in grams;

m_1 is the mass of the dish plus sample before ignition, in grams;

m_2 is the mass of the dish plus sample after ignition, in grams.

Transfer the residue, after measurement, to an agate mortar, grind and mix lightly to be homogeneously, transfer to a flat weighing bottle (50 mm × 30 mm), and keep in a desiccator. Use it for determination of each component.

4.7 Determination of loss on ignition at 1 050 °C (LOI$_{1\,050}$)

4.7.1 Principle

A sample is heated at 1 050 °C ± 25 °C and loss or gain of mass from loss of attached water, water of crystallization, carbon, organic compounds, silicon carbide, and metals is determined by a gravimetric method.

4.7.2 Apparatus

4.7.2.1 Crucible, platinum or porcelain (e.g. Type B 20 ml).

4.7.3 Procedure

Heat the crucible to 1 050 °C ± 25 °C for a specified time, cool in a desiccator and weigh the empty platinum or porcelain crucible and record the mass m_0.

A platinum crucible should be heated for about 15 min and a porcelain crucible should be heated for about 60 min.

Weigh 1,0 g of the dry sample into the platinum or porcelain crucible to the nearest 0,1 mg, spread thinly and weigh the mass of the crucible and sample and record the mass m_1.

Place the crucible without a lid in an electric muffle furnace and slowly raise the temperature to 1 050 °C ± 25 °C. Maintain this temperature for about 60 min and allow to cool with a lid. Weigh the crucible plus the ignited sample and record the mass m_2.

4.7.4 Calculation

Calculate the loss on ignition, $\mathrm{LOI}_{1\,050}$, as a percentage by mass, using Equation (6).

$$\mathrm{LOI}_{1\,050} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{6}$$

where:

m_0 is the mass of the empty crucible, in grams;

m_1 is the mass of the crucible plus sample before ignition, in grams;

m_2 is the mass of the crucible plus sample after ignition, in grams.

If a gain on ignition is observed, a minus sign should be added in front of the numerical value.

5 Determination of the total carbon content

NOTE Suitable certified reference materials (CRMs) for the calibration of a carbon analyser are given in Annex A.

5.1 General

The total carbon content, w_{Ctotal}, can be determined using the following methods:

- combustion with oxygen, using either
  - a resistance furnace (RF), with lead borate fusion or tin powder as accelerator/decomposition agent, or
  - an induction furnace (IF), with metal fusion as accelerator;
- detection methods using
  - coulometry,
  - gravimetry,
  - conductometry,
  - infrared absorption,
  - thermal conductivity.

Usual combinations of available equipment are shown in Table 2.

Table 2 — Usual combinations of equipment for carbon determination

Equipment	Coulometry	Conductivity	Gravimetry	IR absorption	Thermal conductivity
Resistance furnace	+	+	+	+	
Induction furnace			+	+	+

The procedures for the determination of total carbon are therefore structured as combustion techniques, detection techniques and detection methods constituting the laboratory procedure.

5.2 Combustion techniques

5.2.1 General

Two different combustion techniques with different decomposing agents/accelerators can be used.

5.2.2 Resistance furnace in oxygen and lead borate as decomposing agent

5.2.2.1 Principle

The sample is heated together with lead borate in a stream of oxygen in a resistance tube furnace to convert the carbon to carbon dioxide by combustion. The sample mass and the details of the combustion depend on the method of determination used. The combustion gases are conducted through a tube containing percarbamide to absorb the oxidation products of the sulfur contained in the sample. The carbon dioxide is absorbed in an alkaline medium and determined either coulometrically, gravimetrically, conductometrically or by infrared absorption.

5.2.2.2 Reagents

Use only reagents of analytical grade.

5.2.2.2.1 Oxygen, 99,99 % or 99,5 %.

NOTE Oxygen 99,99 % is used if the instrument does not have an oxygen-refining capability. Oxygen 99,5 % is used if the instrument has oxygen-refining ability.

5.2.2.2.2 Lead borate, $2\,PbO{\cdot}B_2O_3$, prepared by melting 45 g of analytical grade lead oxide, PbO, together with 7 g of analytical grade boron trioxide, B_2O_3, for 10 min at (950 °C ± 25) °C, cooling the melt by pouring it onto a clean aluminium plate and then pulverizing it.

5.2.2.3 Apparatus

Ordinary laboratory apparatus and the following.

5.2.2.3.1 Resistance furnace with ceramic tube, capable of being used up to 1 200 °C. The furnace shall be capable of being maintained at a temperature of (1 050 ± 25) °C in the centre of the heating zone. The furnace shall be fitted with a thermocouple connected to a device permitting measurement of the furnace temperature.

Allowance should be made for the fact that, frequently, the temperature indicated on the built-in temperature control display of the furnace deviates from the actual temperature in the ceramic tube. It should be adjusted using an external thermocouple device, measuring the temperature of the heating zone inside the tube.

5.2.2.3.2 Open combustion boats of unglazed ceramic material, the length of which is adapted to the heating zone of the furnace, and which are broad enough to accommodate the amount of sample required for the determination. Before use, the boats shall be heated in a laboratory furnace at 1 000 °C for 1 h and stored in a desiccator after cooling.