International Standard

ISO 21068-2

Second edition
2024-06

Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon —

Part 2: Determination of volatile components, total carbon, free carbon, silicon carbide, total and free silicon, free and surface silica

Analyse chimique des matières premières et des produits réfractaires contenant du carbure de silicium, du nitrure de silicium, de l'oxynitrure de silicium et du SiAlON —

Partie 2: Dosage des composés volatils, du carbone total, du carbone libre, du carbure de silicium, du silicium total et libre et de la silice libre et superficielle

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Foreword

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This document was prepared by Technical Committee ISO/TC 33, *Refractories,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 187, *Refractory products and materials,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 21068-2:2008), which has been technically revised.

The main changes are as follows:

— methods described in ISO 12698-1:2007 for the determination of free carbon, silicon carbide and free silica have been included in this document;

— methods that are no longer used in practice have been removed;

— normative references and bibliography have been updated;

— document has been editorially revised.

A list of all parts in the ISO 21068 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The ISO 21068 series has been developed from the combination of EN 12698-1:2007[1] and EN 12698-2:2007[2] and ISO 21068-1:2008,[3] ISO 21068-2:2008[4] and ISO 21068-3:2008.[5] The last three standards have been originally developed from the combination of Japanese standard JIS R 2011:2007[6] and work items developed within CEN. Because there is a wide variety of laboratory equipment in use, the most commonly used methods are described.

ISO 21068-4 is derived from EN 12698-2:2007[2] describing XRD methods for the determination of mineralogical phases typically apparent in nitride and oxy-nitride bonded silicon carbide refractory products using a Bragg-Brentano diffractometer.

The ISO 21068 series is applicable to the analysis of all refractory products as classified in ISO 10081-1,[7] ISO 10081-2,[8] ISO 10081-3 [9] and ISO 10081-4[10] (shaped) and ISO 1927-1[11] (unshaped) and for raw materials containing carbon and/or silicon carbide. Therefore, the ISO 21068 series covers the full range of analysis from pure silicon carbide to oxide refractory composition with low-content silicon carbide and/or nitrides. Primarily, the ISO 21068 series 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. ISO 21068-4 includes details of sample preparation and general principles for qualitative and quantitative analysis of mineralogical phase composition. Quantitative determination of α-Si_3N_4, β-Si_3N_4, Si_2ON_2, AlN, and sialon are described.

If free carbon is present, ISO 21068-2 includes different temperature treatments to determine the mass changes gravimetrically. Frequently, the resulting residue is used for other determinations.

The determination of other groups of analytes described in the ISO 21068 series are free metals, free silicon (Si_{free}), free aluminium (Al_{free}), free magnesium (Mg_{free}), free iron (Fe_{free}) and the group of oxides from main to trace components.

The ISO 21068 series also describes the determination of silicon dioxide, total silicon, oxygen and nitrogen and other oxide bound metals that typically occur in the materials.

It represents a listing of analytical methods which is generally 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 species independent. For carbon-containing ceramic raw materials and compositions, the ISO 21068 series provides analytical methods for the determination of free carbon, and SiC in the presence of oxide compounds in particular SiO_2.

Due to the diversity of laboratory equipment, the ISO 21068 series summarizes broadly used analytical techniques which lead to equivalent results. For example, the determination of carbon is based on all described methods on the reaction of carbon with oxygen at elevated temperatures to CO_2. Thus, carbon is analysed as CO_2.

As well as carbon and carbide compounds, metallic silicon, aluminium and magnesium are considered. While metallic silicon is mainly 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 oxide bound components, such as Al_2O_3, CaO, MgO, TiO_2, Cr_2O_3, ZrO_2 and alkalis, can be determined by XRF, ICP-OES or wet chemical methods (see ISO 12677[13], ISO 26845[23], ISO 21587-1[20], ISO 21587-2[21] and ISO 21587-3[22]). These results can be corrected by formulae provided by the ISO 21068 series, in consideration of the values obtained by the determination of carbon, SiC, and metallic components.

The ISO 21068 series also provides 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.

The ISO 21068 series also provides methods to distinguish quantitatively between different varieties of nitrides like silicon nitride, silicon oxy-nitride and sialon.

Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon —

Part 2:
Determination of volatile components, total carbon, free carbon, silicon carbide, total and free silicon, free and surface silica

1 Scope

This document specifies analytical techniques for the determination of volatile components by thermal treatment at specified temperatures, and methods for the determination of the total carbon, free carbon, silicon carbide, total and free silicon and free and surface silica content of silicon-carbide, silicon-nitride and silicon-oxynitride containing raw materials and refractory products.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

ISO 9286:2021, *Abrasive grains and crude — Chemical analysis of silicon carbide*

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

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Determination of volatile components by gravimetric methods

4.1 General

The determination of volatile components is defined as change in mass caused by heat treatment of the sample at a defined temperature. The change in mass is measured by weighing.

Table 1 gives an overview of methods for determination of volatile components.

Table 1 — Methods for determination of volatile components

Title of method	Temperature	Subclause	Application
Loss on drying (w_{LOD250})	250 °C	4.2	Attached water and chemically combined water are removed, for example, in clay containing plastic formulations.
Loss on ignition in argon (w_{LOIAr})	750 °C	4.3	All volatile compounds from pitch- or resin-bonded formulations are removed.

4.2 Determination of the loss on drying at 250 °C (w_{LOD250})

4.2.1 Principle

The test sample is heated at 250 °C ± 10 °C and the change in mass is determined gravimetrically.

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.

4.2.2.2 Analytical balance, capable of measuring to the nearest 0,01 g.

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 100 g to 600 g of the sample into the container and spread it out evenly. 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 air 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, w_{LOD250}, as a percentage by mass, using Formula (1).

$$w_{LOD250} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \quad (1)$$

where

w_{LOD250} is the loss on drying at 250 °C, in mass percent;

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

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

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

4.3 Determination of the loss on ignition in argon (w_{LOIAr})

4.3.1 Principle

The sample is heated in an argon atmosphere at 750 °C to remove volatile matter. The change in mass is determined gravimetrically.

NOTE The residue can be used for determination of C_{total}, SiC and C_{free} in organic matter containing materials.

The change in mass during heating in argon must be considered for the calculation of C_{total}, SiC and C_{free}.

4.3.2 Apparatus

Ordinary laboratory apparatus and the following.

4.3.2.1 Analytical balance, capable of measuring to the nearest 0,001 g.

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

4.3.2.3 Resistance furnace, capable of reaching (750 ± 25) °C, in the centre of the heating zone.

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

4.3.2.5 Ceramic tube, with cones or other gastight connector, of suitable diameter, made from porcelain, sillimanite, quartz or other suitable material.

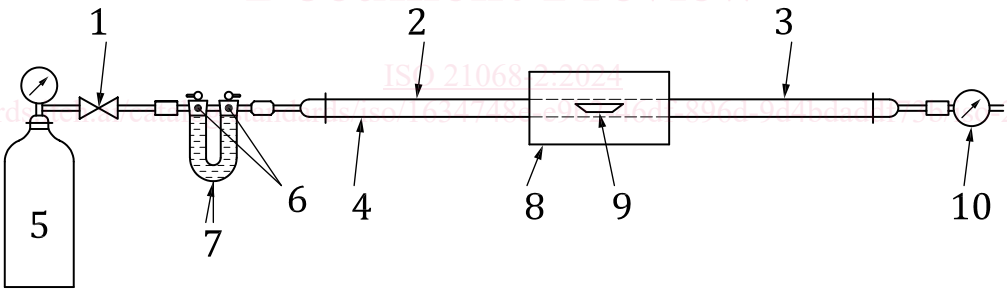
4.3.2.6 Open combustion boats, of unglazed ceramic material, the length of which matches the oven's zone of constant temperature. The boats shall be broad enough to accommodate the amount of sample required for the determination.

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

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

4.3.3 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

4.3.4 Reagents

4.3.4.1 Argon, 99,997 %.

4.3.5 Procedure

4.3.5.1 Check of test assembly, blank value determination

To check a newly set up test assembly or to carry out routine checks, at least two samples of known volatile-matter content shall be calcined as described in 4.3.5.2 before determining the analytical sample.

The difference between the result found in accordance with 4.3.5.2 and the known volatile-matter content shall be considered as the blank value.

4.3.5.2 Determination

Carry out at least two determinations.

Before use, flush the apparatus for at least 15 min with argon (4.3.4.1).

Weigh the empty combustion boat that has previously been heated at (750 ± 25) °C and cooled down to room temperature and record the mass m_0. Weigh approximately 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 200 °C. Pass argon through it at a rate that ensures at least five changes of gas in the tube within 15 min.

NOTE 1 The required argon flow rate can be estimated according to Formula (2):

$$F_{\mathrm{Ar}} = \frac{\pi \times D^2 \times l}{200\ 000} \tag{2}$$

where

F_{Ar} is the argon flow rate, in litres per hour;

D is the tube inner diameter, in millimetres;

l is the tube length, in millimetres.

Place the sample in the centre of the heating zone and heat 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 200 °C.

NOTE 2 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, that means, 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.

4.3.6 Calculation

Calculate the loss on ignition in argon at 750 °C, w_{LOIAr}, as a percentage by mass, using Formula (3).

$$w_{\mathrm{LOIAr}} = \frac{m_1 - m_2}{m_1 - m_0} \times 100 \tag{3}$$