



FINAL DRAFT International Standard

ISO/FDIS 21068-3

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

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

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

*Partie 3: Dosage de l'azote, de l'oxygène et des constituants
métalliques et oxydés*

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Contents

Page

Foreword	v
Introduction	vi
1 Scope	1
2 Normative references	1
3 Terms and definitions	2
4 Determination of nitrogen and oxygen	2
4.1 General.....	2
4.2 Combined determination of nitrogen and oxygen by an analyser with thermal conductivity (TC) and infrared (IR) absorption detection.....	2
4.2.1 Principle.....	2
4.2.2 Reagents.....	3
4.2.3 Apparatus.....	3
4.2.4 Nickel pre-treatment.....	3
4.2.5 Calibration.....	4
4.2.6 Procedure.....	4
4.2.7 Precision.....	5
4.3 Determination of total nitrogen content by fusion decomposition.....	5
4.3.1 General.....	5
4.3.2 Principle.....	5
4.3.3 Reagents.....	5
4.3.4 Apparatus.....	5
4.3.5 Sample preparation.....	6
4.3.6 Procedure.....	7
4.3.7 Calculation and expression of results.....	7
4.3.8 Precision.....	8
4.4 Determination of total nitrogen content by Kjeldahl distillation.....	8
4.4.1 Principle.....	8
4.4.2 Reagents.....	8
4.4.3 Apparatus.....	9
4.4.4 Sample preparation.....	9
4.4.5 Procedure.....	9
4.4.6 Calculation and expression of results.....	10
4.4.7 Precision.....	10
4.5 Calculation of Si ₃ N ₄ content using total nitrogen content.....	10
4.5.1 Calculation.....	10
5 Determination of soluble iron by extraction with hydrochloric acid followed by inductively coupled plasma-optical emission spectrometry (ICP-OES)	11
5.1 General.....	11
5.2 Principle.....	11
5.3 Apparatus.....	11
5.4 Reagents.....	11
5.5 Sample preparation.....	11
5.6 Procedure.....	11
5.7 Measurement.....	12
5.8 Calculation.....	12
6 Determination of metallic (free) aluminium by the hydrogen generating method	12
6.1 Principle.....	12
6.2 Reagents.....	12
6.3 Apparatus.....	13
6.4 Sample preparation.....	13
6.5 Procedure.....	13
6.6 Calculation and expression of results.....	13

ISO/FDIS 21068-3:2024(en)

7	Determination of acid soluble aluminium and magnesium	14
7.1	General.....	14
7.2	Reagents.....	14
7.3	Procedure.....	14
7.4	Measurement.....	14
7.5	Precision.....	14
8	Determination of elemental impurities in SiC raw materials	15
8.1	General.....	15
8.1.1	Alkaline melt fusion.....	15
8.1.2	Acid pressure decomposition.....	17
8.2	Determination of impurities by XRF (fused bead method).....	18
8.3	Determination of impurities by DC-Arc-OES (direct solid sampling method).....	18
9	Expression of results	18
10	Test report	18
Annex A (informative) Precision data		19
Bibliography		24

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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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 21068-3:2008), which has been technically revised.

The main changes are as follows:

- methods described in ISO 12698-1:2007 for the determination of free aluminium, total nitrogen and free alumina 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 latter has 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.

This document is also applicable to the analysis of SiC raw materials.

Except the XRD method specified in ISO 21068-4, all chemical methods specified in this document are only validated for SiC raw materials. For refractory products 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 raw materials containing carbon and/or silicon carbide this document applies after appropriate verification for any matrix composition.

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

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

1 Scope

This document specifies analytical techniques for the determination of total nitrogen and nitrogen calculated as silicon nitride, total oxygen, and metallic and oxidic components in silicon carbide 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 10058-1, *Chemical analysis of magnesite and dolomite refractory products (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and determination of gravimetric silica*

ISO 10058-2, *Chemical analysis of magnesite and dolomite refractory products (alternative to the X-ray fluorescence method) — Part 2: Wet chemical analysis*

ISO 10058-3, *Chemical analysis of magnesite and dolomite refractory products (alternative to the X-ray fluorescence method) — Part 3: Flame atomic absorption spectrophotometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES)*

ISO 12677, *Chemical analysis of refractory products by X-ray fluorescence (XRF) — Fused cast-bead method*

ISO 16169, *Preparation of silicon carbide and similar materials for analysis by ISO 12677*

ISO 20565-1, *Chemical analysis of chrome-bearing refractory products and chrome-bearing raw materials (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and determination of gravimetric silica*

ISO 20565-2, *Chemical analysis of chrome-bearing refractory products and chrome-bearing raw materials (alternative to the X-ray fluorescence method) — Part 2: Wet chemical analysis*

ISO 20565-3, *Chemical analysis of chrome-bearing refractory products and chrome-bearing raw materials (alternative to the X-ray fluorescence method) — Part 3: Flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES)*

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

ISO 21079-1, *Chemical analysis of refractories containing alumina, zirconia and silica — Refractories containing 5 percent to 45 percent of ZrO₂ (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents and dissolution*

ISO 21079-2, *Chemical analysis of refractories containing alumina, zirconia, and silica — Refractories containing 5 percent to 45 percent of ZrO₂ (alternative to the X-ray fluorescence method) — Part 2: Wet chemical analysis*

ISO 21079-3, *Chemical analysis of refractories containing alumina, zirconia, and silica — Refractories containing 5 percent to 45 percent of ZrO₂ (alternative to the X-ray fluorescence method) — Part 3: Flame atomic absorption spectrophotometry (FAAS) and inductively coupled plasma emission spectrometry (ICP -AES)*

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

ISO 21587-2, *Chemical analysis of aluminosilicate refractory products (alternative to the X-ray fluorescence method) — Part 2: Wet chemical analysis*

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*

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 nitrogen and oxygen

4.1 General

For oxygen only the inert-gas fusion method is given; for nitrogen, calculated usually as Si₃N₄, several different methods are described.

NOTE The calculation of nitrogen as Si₃N₄ is only applicable in the case where other nitride species are absent or too low to detect by XRD, see ISO 21068-1. Otherwise, nitrogen is reported as total nitrogen.

4.2 Combined determination of nitrogen and oxygen by an analyser with thermal conductivity (TC) and infrared (IR) absorption detection

4.2.1 Principle

The method uses inert-gas fusion analysis. A pre-weighed sample is placed in a graphite crucible positioned between the electrodes of an impulse furnace. Typically, 5 kW of power is passed through the crucible generating a temperature of approximately 2 800 °C.

NOTE Furnace temperatures can be varied by increasing and decreasing current/voltage.

The sample decomposes, releasing any oxygen and nitrogen present. The nitrogen released remains as elemental nitrogen, while oxygen combines with the carbon of the graphite crucible to form carbon monoxide. The sample gases are carried on a helium carrier gas either to a copper oxide catalyst, which converts carbon monoxide to carbon dioxide, and then to an infrared absorption cell which measures the carbon dioxide present or are measured directly without catalyst as carbon monoxide. The gas stream is then passed through sodium hydroxide to remove carbon dioxide, and magnesium perchlorate to remove any moisture present, and finally through a thermal conductivity cell to quantify the nitrogen.

Because the sample will invariably be in the form of a powder, it should be enclosed in a small tin capsule before placing it in the graphite crucible to prevent any loss of sample during analysis.

For materials difficult to decompose, a fluxing agent shall be added to the sample. A suitable agent is oxygen free nickel capsule or nickel wire basket.

4.2.2 Reagents

Only chemicals with a known and sufficient analytical purity for the analytical purpose shall be used. Distilled water or water which has been completely deionized by means of an ion exchange process shall be used.

WARNING — Concentrated acids used are to be handled with care, be aware of local safety regulations.

4.2.2.1 **Tin capsule**, of suitable dimensions and oxygen and nitrogen free.

4.2.2.2 **High temperature graphite crucibles**, of suitable size, recommended by the instrument producer.

4.2.2.3 **Nickel capsules or basket**, of suitable dimensions and oxygen and nitrogen free.

4.2.2.4 **Acetic acid**, 96 % mass fraction.

4.2.2.5 **Nitric acid**, 65 % mass fraction.

4.2.2.6 **Hydrochloric acid**, 32 % mass fraction.

4.2.2.7 **Acetone**.

4.2.2.8 **Carbon dioxide**, 99,998 % pure.

4.2.2.9 **Nitrogen**, 99,998 % pure.

4.2.2.10 **Helium**, 99,998 % pure.

4.2.3 Apparatus

Ordinary laboratory apparatus and the following.

4.2.3.1 **Combined nitrogen/oxygen analyser**, commercially available.

NOTE If no combined analyser for nitrogen and oxygen is available, a separate nitrogen and/or oxygen analyser can be used.

4.2.3.2 **Analytical balance**, with a resolution of at least 0,01 mg.

4.2.4 Nickel pre-treatment

If nickel capsules or baskets are used, surface oxygen shall be removed by the following cleaning procedure.

Prepare a solution containing approximately 75 ml of acetic acid (4.2.2.4), 25 ml of nitric acid (4.2.2.5) and 1,5 ml of hydrochloric acid (4.2.2.6). In a well-ventilated fume cupboard, heat the solution to a temperature of $55\text{ °C} \pm 5\text{ °C}$, immerse the nickel capsule or basket in the heated solution for 30 s to 60 s, remove the nickel capsule or basket from the solution and rinse immediately in running water. Immerse the nickel capsule or basket in chemically pure acetone (4.2.2.7), dry thoroughly and place the cleaned nickel capsules or basket in a desiccator.

4.2.5 Calibration

Referring to the instrument operation manual, the calibration can be achieved by two methods:

- a) using primary standards or certified reference materials;
- b) by injection of known volumes of pure carbon dioxide (4.2.2.8) and nitrogen (4.2.2.9) into the detection system.

If b) is used, it is recommended to additionally analyse a certified reference material to verify the performance of the electrode furnace, associated chemicals and detection system.

4.2.6 Procedure

4.2.6.1 General

Operate the instrument in accordance with the instrument operation manual.

4.2.6.2 Determination

Prepare and dry the sample as specified in ISO 21068-1. Weigh it, to the nearest 0,01 mg, into the capsule (4.2.2.1) and seal it, taking care to expel any air present.

NOTE A typical sample mass is approximately 50 mg. However, in practice, the sample mass is determined by a combination of the dynamic range of the analyser and the magnitude of the concentration of oxygen and nitrogen present in the sample.

Place the tin capsule including the sample into the loading-mechanism of the analyser. If nickel is used, the tin capsule is firstly put into the nickel capsule or basket.

Carry out the analysis in two stages:

- a) heat the graphite crucible to a temperature at least as high as that used for the analysis, until any entrapped oxygen and nitrogen is expelled;
- b) drop the sample into the graphite crucible and perform the analysis.

At least three determinations per sample shall be carried out.

4.2.6.3 Blank determinations

Carry out the blank determination as described in 4.2.6.2, but without a sample. The blank shall be the mean of at least three determinations.

4.2.6.4 Calculation

Calculate the mass fraction of nitrogen or oxygen, w_a , expressed as a percentage, using [Formula \(1\)](#).

$$w_a = w_m - b \quad (1)$$

where

w_a is the content of nitrogen or oxygen in the sample, in mass percent;

w_m is the measured content of nitrogen or oxygen in the sample, in mass percent;

b is the measured blank of nitrogen or oxygen, in mass percent.

Report the results as the mean of three determinations.

4.2.7 Precision

The precision data for the determination of total nitrogen and total oxygen in a silicon carbide powder sample by inert-gas fusion is given in [A.1](#).

4.3 Determination of total nitrogen content by fusion decomposition

4.3.1 General

This method is used to determine nitrogen in silicon nitride, Si_3N_4 , and other compounds in the form of nitrides and oxynitrides by fusion decomposition. Analogous methods may be used to determine nitrogen in materials containing not less than 5 % by mass of nitrogen bound in the form of nitrides and oxynitrides.

4.3.2 Principle

The sample is fused with lithium hydroxide at 700 °C to convert the nitrogen into ammonia. A stream of inert gas is used to transfer the ammonia to an absorption vessel containing boric acid solution. The amount of absorbed ammonia is determined by titration with an acid of known concentration.

4.3.3 Reagents

Only chemicals with a known and sufficient analytical purity for the analytical purpose shall be used.

4.3.3.1 Water, distilled or fully demineralized by ion exchange.

4.3.3.2 Powdered lithium hydroxide, LiOH .

4.3.3.3 Sulfuric acid, $\rho = 1,84$ g/ml.

4.3.3.4 Titration acid, 0,1 mol/l hydrochloric or sulfuric acid of known standardization for titration.

4.3.3.5 Boric acid solution, prepared by dissolving 40 g of boric acid, H_3BO_3 , in 1 l of hot water.

4.3.3.6 Inert gas, argon or nitrogen, with a purity of 99,99 %.

4.3.3.7 Sodium carbonate, Na_2CO_3 , with a purity of at least 99,95 %.

4.3.3.8 Calcium chloride, CaCl_2 , dried.

4.3.4 Apparatus

4.3.4.1 Analytical balance, with a resolution of at least 0,01 mg.

4.3.4.2 Measurement device, apparatus for releasing, carrying over and absorbing ammonia (see [Figure 1](#)), comprised of:

- a) flow meter;
- b) gas washing bottles;
- c) vitreous silica reaction tube with ground joints, stoppers and gas inlet;
- d) unglazed porcelain boats;
- e) tube furnace, e.g. heated by infrared radiation, capable of being heated to, and maintained at, (700 ± 10) °C;