International
Standard

ISO 21068-3

Second edition
2024-06

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'oxynitrure de silicium et du SiAlON —

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

Reference number
ISO 21068-3:2024(en)

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Published in Switzerland

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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 dosage 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 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.

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.

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 Si_3N_4, several different methods are described.

NOTE The calculation of nitrogen as Si_3N_4 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 °C ± 5 °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).

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

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 a 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, ρ = 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;

f) vitreous silica wool;

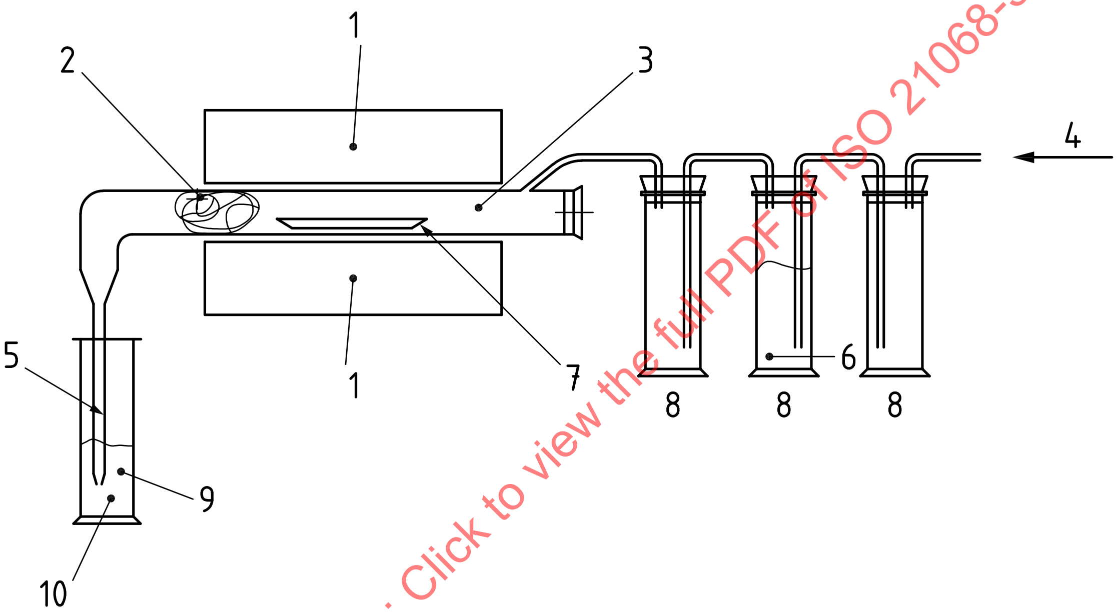
g) gas inlet tube with ground joint and capillary tip or frit.

The inert gas from a pressurized gas cylinder passes through a gas washing bottle filled with sulfuric acid (4.3.3.3), preceded and followed by an empty washing bottle for safety reasons.

NOTE No gas purification is necessary if the ammonia content of the inert gas does not exceed 0,005 % by volume.

The inert gas is then passed through a flow meter and into the vitreous silica reaction tube at the side gas inlet. The ground joint through which the sample is inserted is also located at this point. The other end of the reaction tube is connected by a ground joint to a gas inlet tube with capillary tip or frit which extends almost to the bottom of a narrow absorption vessel.

The reaction tube shall be heated by a tubular furnace which can be maintained at (700 ± 10) °C. The still hot part of the tube outside the tubular furnace and adjacent to the absorption vessel is packed with loose vitreous silica wool which is capable of condensing any lithium hydroxide which evaporates.



Key

1	tubular furnace
2	vitreous silica wool
3	vitreous silica tube with connections
4	inert gas (Ar or N_2)
5	gas inlet tube with capillary tip or frit
6	sulfuric acid
7	porcelain boat
8	washing bottles
9	boric acid solution
10	absorption vessel

Figure 1 — Nitrogen determination apparatus for fusion decomposition

4.3.4.3 **Potentiometric titrator,** with a metering volume of 50 ml and a maximum relative tolerance of 0,1 %.

4.3.5 Sample preparation

Prepare and dry the sample as specified in ISO 21068-1.

4.3.6 Procedure

4.3.6.1 Decomposition by fusion

The time for complete reaction should be established before the method is applied.

Coat the entire inside of the porcelain boats with 500 mg of lithium hydroxide (4.3.3.2) at 600 °C and store the boats in a desiccator. Weigh 100 mg of the sample to the nearest 0,01 mg, into a coated porcelain boat and mix thoroughly with 1,5 g of lithium hydroxide. Flush the apparatus with inert gas (4.3.3.6) and pour 40 ml of boric acid solution (4.3.3.5) into the absorption vessel and immerse the gas inlet tube in it. Set the inert gas flow to 70 ml/min to 100 ml/min, open the ground joint closure and push the porcelain boat into the centre of the reaction tube to the point where the thermocouple is located. After closing the tube again, slowly heat the tube furnace to (700 ± 10) °C in stages to prevent the melt from spattering. For tube furnaces that heat up rapidly, the heating phase shall not be less than 15 min. After 30 min at (700 ± 10) °C, the nitride nitrogen will have been quantitatively converted into ammonia. Ensure the furnace temperature does not, under any circumstances exceed 730 °C, as lithium hydroxide will start to evaporate above that temperature.

4.3.6.2 Standardization of titration acid

Dry the sodium carbonate (4.3.3.7) at 270 °C to 300 °C for 1 h, stirring occasionally, and store it in a desiccator over calcium chloride (4.3.3.8).

Weigh 200 mg of dried sodium carbonate to the nearest 0,01 mg in a sealable weighing bottle.

Dissolve the sodium carbonate in 50 ml of water (4.3.3.1) and add the titration acid (4.3.3.4) to be standardized using a potentiometric titrator (4.3.4.3) until the equivalent point in the pH range 4,6 ± 0,2 is reached. Take the mean value of not less than three titrations. The coefficient of variation shall not exceed 0,001.

4.3.6.3 Titrating the absorption solution

When the reaction is complete, remove the gas inlet tube from the absorption vessel and rinse its inside and outside with water. Titrate the amount of absorbed ammonia to the equivalence point which is generally a pH value of 4,6 ± 0,2 with the standardized titration acid using the potentiometric titrator.

4.3.6.4 Blank value

Carry out a blank determination as described in 4.3.6.1 and 4.3.6.3, without a test sample.

4.3.7 Calculation and expression of results

4.3.7.1 General

When calculating the results, the titration correction factor (see 4.3.7.2) shall be included.

Report the result to the nearest 0,1 %.

4.3.7.2 Calculation of titration correction factor

Calculate the titration correction factor, *t*, of the acid using Formula (2):

$$t = \frac{m_{\mathrm{Na}}}{5{,}299\,4 \cdot V_1} \tag{2}$$

where

t is the titration correction factor;

m_{Na} is the sample mass of sodium carbonate, in milligrams;

V_1 is the volume used of the 0,1 mol/l acid to be standardized, in millilitres;

5,299 4 is the titrimetric factor, in milligrams per millilitres.

4.3.7.3 Calculation of nitrogen content

Calculate the nitrogen content, M_N, as a percentage by mass using Formula (3):

$$M_N = \frac{(V_2 - V_3) \times t \times 1{,}4007 \times 100}{m} \tag{3}$$

where

M_N	is the total nitrogen of the sample, in mass percent;
V_2	is the volume of titration acid used for the sample, in millilitres;
V_3	is the volume of titration acid used for the blank value, in millilitres;
t	is the titration correction factor of the acid;
m	is the sample mass, in milligrams;
1,400 7	is the titrimetric factor, in milligrams per millilitres.

4.3.8 Precision

The precision data for the determination of total nitrogen in a silicon nitride powder sample by fusion decomposition is given in A.2.

4.4 Determination of total nitrogen content by Kjeldahl distillation

4.4.1 Principle

The nitrogen in silicon nitride, Si_3N_4, and other compounds in the form of nitrides and oxynitrides are determined using high pressure acid decomposition.

The sample is dissolved in hydrofluoric acid under pressure and the nitrogen is distilled over as ammonia into an absorption vessel containing boric acid solution, using an ammonia distillation apparatus. The amount of absorbed ammonia is determined by titration with an acid of known concentration.

4.4.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and of known analytical purity.

4.4.2.1 Water, distilled or fully demineralized by ion exchange.

Unless otherwise specified, solutions are aqueous.

4.4.2.2 Hydrofluoric acid, HF, ρ = 1,13 g/ml.

4.4.2.3 Boric acid, H_3BO_3.

4.4.2.4 Boric acid solution, to be prepared by dissolving 40 g of boric acid in 1 l of hot water (temperature approx. 60 °C).

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

4.4.2.6 Titration acid, hydrochloric acid, or sulfuric acid solution, $c(HCl)$ = 0,1 mol/l or $c(H_2SO_4)$ = 0,05 mol/l.

4.4.2.7 Sodium hydroxide solution, to be prepared by dissolving 400 g of sodium hydroxide in 1 l of water.

4.4.3 Apparatus

Ordinary laboratory apparatus and the following:

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

4.4.3.2 Laboratory oven or microwave oven, suitable for temperatures up to 230 °C.

4.4.3.3 Apparatus for the determination of ammonia, e.g. by the Parnas-Wagner method, with a steam generator.

4.4.3.4 Digestion apparatus to be used under pressure, with polytetrafluoroethylene inserts with a capacity of 100 ml and suitable for use at temperatures up to 200 °C.

4.4.3.5 Potentiometric titrator, comprised of a pH measuring cell, a metered volume of 50 ml and a resolution of at least ±0,025 ml.

4.4.4 Sample preparation

Prepare and dry the sample as specified in ISO 21068-1 .

4.4.5 Procedure

4.4.5.1 Decomposition of sample under pressure

Weigh 500 mg of the test sample, pre-treated as specified in 4.4.4, to the nearest 0,01 mg. Transfer this quantitatively to the polytetrafluoroethylene insert of the pressurized digestion apparatus (4.4.3.4) and add 5 ml of water (4.4.2.1) and 10 ml of hydrofluoric acid (4.4.2.2). Seal the apparatus as directed by the manufacturer and heat (4.4.3.2) the solution and sample to (200 ± 5) °C for 4 h to 6 h. After cooling and opening the apparatus, bind the excess hydrofluoric acid by adding 4,7 g of boric acid (4.4.2.3). Ignore any dark particles which are occasionally left behind. Transfer the solution to a 250 ml volumetric flask and make up to the mark with water.

4.4.5.2 Standardization of titration acid

Dry the sodium carbonate at 270 °C to 300 °C for 1 h, stirring occasionally, and store it over calcium chloride in a desiccator.

Weigh 200 mg of sodium carbonate (4.4.2.5) to the nearest 0,01 mg into a sealable weighing bottle.

Dissolve the sodium carbonate in 50 ml of water and add the titration acid (4.4.2.6) using a potentiometric titrator apparatus (4.4.3.5) until the equivalence point in the pH range of 4,6 ± 0,2 is reached. Take the mean of not less than three titrations. The coefficient of variation shall not exceed 0,001.

4.4.5.3 Distillation and potentiometric titration

Use a one-mark bulb pipette to pipette a 50 ml aliquot portion of the solution prepared as described in 4.4.5.1 into an ammonia determination apparatus (4.4.3.3) which has been steamed out. Pour 20 ml of boric acid solution (4.4.2.4) into the absorption vessel of the still and immerse the condenser outlet in the solution. After adding 50 ml of sodium hydroxide solution (4.4.2.7) to the digestion solution, distil over the ammonia into the absorption vessel by passing steam through the heated solution until 200 ml to 250 ml has been collected. The reaction is complete when there is no change in the pH value of the boric acid solution.

Determine the amount of ammonia absorbed in the boric acid solution by potentiometric titration using the standardized titration acid. The equivalence point is in the pH range of 4,6 ± 0,2.

The time for complete reaction should be established before the method is applied.

4.4.5.4 Blank value

To determine the blank value, carry out the analysis procedures described in 4.4.5.1 and 4.4.5.3, but without sample.

4.4.6 Calculation and expression of results

4.4.6.1 General

For calculation of results the titration correction factor (4.4.6.2) shall be included.

Report the result to the nearest 0,1 %.

4.4.6.2 Calculation of the titration correction factor

Calculate the titration correction factor, *t*, of the acid using Formula (2).

4.4.6.3 Calculation of nitrogen content

Calculate the nitrogen content, M_N, as a percentage by mass using Formula (3).

4.4.7 Precision

The precision data for the determination of total nitrogen in a silicon nitride powder sample by Kjeldahl distillation is given in A.3.

4.5 Calculation of Si_3N_4 content using total nitrogen content

4.5.1 Calculation

Calculate the mass fraction of silicon nitride in the sample, $w_{Si_3N_4}$, expressed as a percentage using Formula (4):

$$w_{si_3N_4} = w_N \times 2{,}504 \tag{4}$$

where

$w_{si_3N_4}$ is the silicon nitride content of the sample, in mass percent;

w_N is the mass fraction of total nitrogen in the sample measured according to sections 4.2, 4.3 or 4.4, in percent;

2,504 stoichiometric factor for converting nitrogen to silicon nitride.

5 Determination of soluble iron by extraction with hydrochloric acid followed by inductively coupled plasma-optical emission spectrometry (ICP-OES)

5.1 General

The determination of hydrochloric acid soluble iron on the finished product is an important parameter for process and quality control. Iron can be introduced to materials during manufacture and into powdered samples using a milling apparatus that has iron-containing components in its construction. The content of soluble iron determined by the described method is highly dependent upon the extraction method used.

5.2 Principle

The powdered silicon carbide sample is extracted with hydrochloric acid by boiling under reflux. After cooling down to room temperature and sedimentation of silicon carbide, the clear supernatant is used for measurement of iron concentration by ICP-OES.

5.3 Apparatus

Ordinary laboratory apparatus and the following:

5.3.1 Analytical balance, with a resolution of at least 1 mg.

5.3.2 Extraction apparatus, glass, consisting of an 100 ml Erlenmeyer flask with ground joint and matching reflux condenser.

5.3.3 Hot plate, suited to bring the content of the Erlenmeyer flask (5.3.2) to a boil.

5.3.4 Volumetric flask, at least 100 ml, glass.

5.3.5 ICP-OES, inductively coupled plasma - optical emission spectrometer (ICP-OES), sequential or simultaneous.

5.4 Reagents

Fully deionized water and reagents of known analytical grade shall be used. Ensure that the reagents are of sufficiently high purity so that they can be used without affecting the accuracy of the determination.

5.4.1 Hydrochloric acid, HCl, $c(\mathrm{HCl}) = 5$ mol/l.

5.5 Sample preparation

Prepare and dry the sample as specified in ISO 21068-1 .

5.6 Procedure

WARNING — There is a risk of release of acid fumes during the extraction process.

A sub-sample mass suited for the analytical purpose is weighed to the nearest 1 mg into the Erlenmeyer flask (5.3.2) and 25 ml hydrochloric acid (5.4.1) is added.

NOTE A sub-sample mass of 1 g has been shown to be appropriate.

Place the Erlenmeyer flask onto the hot plate (5.3.3) and fix the reflux condenser to the Erlenmeyer flask. Turn on the hot plate and boil the content of the Erlenmeyer flask under reflux for 30 min. Turn off the hot plate and rinse the reflux condenser from the top with water. Remove the reflux condenser from the Erlenmeyer flask. Remove the Erlenmeyer flask from the hot plate and let it cool down to room temperature. Transfer the content of the Erlenmeyer flask to the volumetric flask (5.3.4). Thoroughly rinse the Erlenmeyer flask with water and transfer the washings into the volumetric flask. After this, the volumetric flask is filled up to volume with water. After sedimentation of silicon carbide, the clear supernatant is used to measure the iron concentration. For each sample at least two extractions should be carried out. For blank correction, at least two extractions according to the described procedure and without using sample material should be carried out.

5.7 Measurement

The sample solution and blank solution obtained in 5.6 is analysed for iron using ICP-OES. The analysis of aqueous sample solutions by ICP-OES is a common standard procedure whose execution can be assumed to be known. Therefore, a detailed description of the procedure for the analysis of the sample solution by ICP-OES is not given. Recommended iron emission lines are: 241,331 nm, 262,567 nm, 275,573 nm and 373,486 nm.

5.8 Calculation

The content of hydrochloric acid soluble iron w_{Fe} of the sample shall be calculated under consideration of sample mass and blank values. The soluble iron content as the mean of the blank corrected single values of the multiple determinations shall be expressed in mass fractions in percentage and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of soluble iron using Formula (5):

$$w_{Fe} = \frac{(C_M - C_B) \times V_S}{10 \times m_E} \quad (5)$$

where

w_{Fe}	is the content of hydrochloric acid soluble iron in the sample, in mass percent;
C_M	is the measured iron concentration in sample solution, milligrams per litres;
C_B	is the measured iron concentration in blank solution, milligrams per litres;
V_S	is the volume of sample solution, millilitres;
m_E	is the sample mass, milligrams.

6 Determination of metallic (free) aluminium by the hydrogen generating method

6.1 Principle

The volume of hydrogen generated by the reaction of diluted hydrochloric acid with any free aluminium in the sample is measured.

NOTE Any other elements or compounds which evolve with diluted hydrochloric acid hydrogen or other gases (e.g. CO_2 from carbonates) can interfere and will deliver increased values for free aluminium.

The free aluminium content can also be determined by the evolution of hydrogen using sodium hydroxide. In this case, the volume of hydrogen evolved is corrected for the free silicon content (ISO 21068-2:2024, Clause 9).

6.2 Reagents

Only analytical grade chemicals of which the analytical purity is known, and distilled water or water which has been completely deionized by means of an ion exchange process shall be used.

6.2.1 **Hydrochloric acid,** HCl, $c(HCl) = 5$ mol/l.

6.3 Apparatus

6.3.1 Gas volumetric apparatus

NOTE The gas volumetric apparatus is as given in ISO 21068-2:2024, Figure 4, whereby the electric heating mantle and the insulation plate are not required.

6.3.2 Magnetic stirrer

6.3.3 Analytical balance, with a resolution of at least 0,1 mg.

6.4 Sample preparation

Prepare and dry the sample as specified in ISO 21068-1.

6.5 Procedure

Weigh (0,5 ± 0,01) g of sample and transfer to a clean, dry flat-bottomed flask. Balance the liquid surface of the level bottle to the zero line of gas burette and fix the level bottle. Add 40 ml of hydrochloric acid (6.2.1), to the flat-bottomed flask and connect it to the bottom of the condenser.

Connect the gas burette to the upper part of the condenser by using a connector tube and balance the liquid surface of the level bottle to the liquid surface of the gas burette. Read the scale to the nearest 0,1 ml. Measure the temperature adjacent to the gas burette.

Keep the suspension stirring until the level in the gas burette is constant. Balance the liquid surface of the level bottle to the liquid surface of the gas burette. Read the scale to the nearest 0,1 ml. Measure the temperature and the atmospheric pressure. Do not allow the room temperature to change by more than 3 °C.

NOTE Typical reaction times lie between 20 min and 25 min.

6.6 Calculation and expression of results

Correct the volume reading to the gas volume at standard temperature, $V_{(STP)}$, using Formula (6):

$$V_{(STP)} = V_1 \times \frac{(p - p_{H2O})}{1\,013,25} \times \frac{273}{(273 + T)} \qquad (6)$$

where

$V_{(STP)}$ is the gas volume at standard temperature, in millilitres;

V_1 is the measured volume (difference between start and end reading of the gas burette), in millilitres;

p is the atmospheric pressure, at time of measurement, in hectopascals;

p_{H2O} is the partial pressure of water vapour at the measured temperature, in hectopascals;

T is the measured temperature, in degree Celsius.

Calculate the percentage of free aluminium in the sample, A, using Formula (7):

$$A = V_{(STP)} \times 0,000\,804 \times \frac{100}{m} \qquad (7)$$

where

A is the content of free aluminium in the sample, in mass percent;

$V_{(STP)}$ is the gas volume at standard temperature, in millilitres;

m is the sample mass, in grams.

Report the result to the nearest 0,1 %.

7 Determination of acid soluble aluminium and magnesium

7.1 General

The determination of acid soluble (free) aluminium and acid soluble (free) magnesium is carried out using one of the following methods:

a) acid decomposition followed by inductively coupled plasma – optical emission spectrometry (ICP-OES) detection;

b) acid decomposition followed by atomic absorption spectrometry (AAS) detection;

c) acid decomposition followed by inductively coupled plasma – mass spectrometry (ICP-MS) detection.

7.2 Reagents

Only analytical grade chemicals of which the analytical purity is known, and distilled water or water which has been completely deionized by means of an ion exchange process shall be used.

7.2.1 Hydrochloric acid, HCl, c(HCl) = 5 mol/l.

7.3 Procedure

Weigh (0,5 - 1,0) g sample to the nearest 0,01 g into a 100 ml beaker, add 30 ml of hydrochloric acid (7.2.1), stir well, cover with a watch glass, and allow to stand at room temperature.

After 16 h, filter the suspension with a filter paper (type 5 B, particle retention 2,5 µm). Wash the beaker with hydrochloric acid (7.2.1) and filter the washing. Wash filter with residue thoroughly with hydrochloric acid (7.2.1). Transfer the filtrate and washings into a 200 ml volumetric flask and dilute to the mark with water.

If the solution becomes cloudy, centrifuge a portion of the sample solution to separate out particles and use the top clear layer as the sample solution.

7.4 Measurement

The obtained sample solutions shall be analysed using the common analytical methods for liquid sample solutions (see, for example, ISO 26845 [12]) such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS). Sample masses and dilutions shall be adapted for the appropriate technique.

7.5 Precision

The precision data for the determination of acid soluble (free) aluminium and acid soluble (free) magnesium by acid decomposition / ICP-OES in refractories containing carbon is given in A.4.

8 Determination of elemental impurities in SiC raw materials

This clause describes two commonly used sample digestion methods for SiC raw materials. For other SiC containing refractory material groups, X-ray fluorescence (XRF) shall be used in accordance with ISO 12677 or wet chemical analysis methods shall be used as specified in Table 1.

Table 1 — Selection of method of determination according to materials

Classification of refractories	Method of determination
Graphite bricks containing silicon carbide	ISO 21587-1, ISO 21587-2 and ISO 21587-3
Silicon carbide bricks (including those containing silicon nitride)	
Clay-based refractories containing silicon carbide and silicon nitride	
Silica-based refractories containing silicon carbide and silicon nitride	
High-alumina-based refractories containing silicon carbide and silicon nitride	
Magnesia- and dolomite-based refractories containing silicon carbide and silicon nitride	ISO 10058-1, ISO 10058-2 and ISO 10058-3
Chrome-magnesite-based refractories containing silicon carbide and silicon nitride	ISO 20565-1, ISO 20565-2 and ISO 20565-3
Zircon-zirconia-based refractories containing silicon carbide and silicon nitride	ISO 21079-1, ISO 21079-2 and ISO 21079-3
Alumina-zirconia-silica-based refractories containing silicon carbide and silicon nitride	
Alumina-magnesia-based refractories containing silicon carbide and silicon nitride	ISO 21587-1, ISO 21587-2 and ISO 21587-3 and/or ISO 10058-1, ISO 10058-2 and ISO 10058-3
Refractories containing silicon carbide and silicon nitride except those given above	ISO 21587-1, ISO 21587-2 and ISO 21587-3

8.1 General

For the determination of elemental impurities in SiC raw materials by spectrometric methods the following sample decomposition procedures shall be used:

- alkaline melt fusion;
- acid pressure decomposition.

8.1.1 Alkaline melt fusion

8.1.1.1 Principle

The powdered silicon carbide sample is decomposed in a platinum crucible using a melt of a mixture of Na_2CO_3 and K_2CO_3. After dissolution of the melt-cake with nitric acid the concentration of elemental impurities in the sample solution is measured using an appropriate spectrometric method.

8.1.1.2 Reagents

Fully deionized water and reagents of known analytical grade shall be used. Ensure that the reagents are of sufficiently high purity so that they can be used without affecting the accuracy of the determination.

8.1.1.2.1 Mixture of sodium carbonate and potassium carbonate, Na_2CO_3 / K_2CO_3, 1:1 by mass.

8.1.1.2.2 Sodium nitrate, $NaNO_3$.

8.1.1.2.3 Nitric acid, HNO_3, concentrated (ρ = 1,40 kg/l), $c(HNO_3)$ approximately 14,5 mol/l.

8.1.1.3 Apparatus

Ordinary laboratory apparatus and the following:

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

8.1.1.3.2 Platinum crucible, 30 ml, standard form with close-fitting lid.

8.1.1.3.3 Burner, Bunsen type.

8.1.1.3.4 Volumetric flask, glass, 250 ml.

8.1.1.3.5 Beaker, glass, 250 ml.

8.1.1.3.6 Ultrasonic bath.

8.1.1.4 Sample preparation

Prepare and dry the sample as specified in ISO 21068-1. The sample material shall have a particle size of ≤50 µm. Inhomogeneous sample material shall be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which reduces the accuracy of the determination.

8.1.1.5 Procedure

Weigh approximately 200 mg of the silicon carbide powder sample to the nearest 0,01 mg into the platinum crucible (8.1.1.3.2), add 4 g of Na_2CO_3/K_2CO_3 (8.1.1.2.1) mixture, mix thoroughly and place the platinum lid onto the crucible. Heat the crucible with the Bunsen burner and melt the Na_2CO_3/K_2CO_3 mixture using a low temperature flame. Gradually increase the temperature of the flame until the sample is completely decomposed. Add 50 mg to 100 mg of $NaNO_3$ (8.1.1.2.2) to the hot melt and heat the covered crucible with maximum flame temperature for 5 min. After cooling down to room temperature place platinum crucible and lid in the beaker (8.1.1.3.5), add 100 ml water, place the beaker in the ultrasonic bath and dissolve the melt-cake. After complete dissolution of the melt-cake, add 10 ml HNO_3 (8.1.1.2.3). Thoroughly rinse platinum crucible and lid with water and transfer the washings into the beaker. Transfer the content of the beaker to the volumetric flask (8.1.1.3.4). Thoroughly rinse the beaker with water and transfer the washings into the volumetric flask. After this, the volumetric flask is filled up to volume with water.

For each sample at least two decompositions should be carried out. For blank correction, at least two decompositions according to the described procedure and without using sample material should be carried out.

Before re-use of platinum crucible and lid, a cleaning step according to the described procedure above but and without any sample material should be carried out.

8.1.1.6 Measurement

The obtained sample solutions shall be analysed using the common analytical methods for liquid sample solutions (see, for example, ISO 26845 [12]) such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS). Sample masses and dilutions shall be adapted to the analytical purpose.

8.1.2 Acid pressure decomposition

8.1.2.1 Principle

The powdered silicon carbide sample is decomposed at high pressure and temperature using a mixture of concentrated nitric acid, hydrofluoric acid and sulfuric acid. The resulting sample solution is measured using appropriate methods.

8.1.2.2 Reagents

Fully deionized water and reagents of known analytical grade shall be used. Ensure that the reagents are of sufficiently high purity so that they can be used without affecting the accuracy of the determination.

8.1.2.2.1 Nitric acid, HNO_3, concentrated (ρ = 1,40 kg/l), $c(HNO_3)$ approximately 14,5 mol/l.

8.1.2.2.2 Hydrofluoric acid, HF, concentrated (ρ = 1,13 kg/l), $c(HF)$ approximately 23 mol/l.

8.1.2.2.3 Sulfuric acid, H_2SO_4, concentrated (ρ = 1,83 kg/l), $c(H_2SO_4)$ approximately 18 mol/l.

8.1.2.3 Apparatus

Ordinary laboratory apparatus and the following:

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

8.1.2.3.2 Acid/pressure sample decomposition system, capable of being heated to 250 °C ± 5 °C, pressure vessels with suited decomposition vessels resistant against the acids used and a volume up to 250 ml.

NOTE A drying cabinet with fume extractor is suited for heating the pressure vessels. Heating can also be performed using microwave radiation. With these commercially available microwave sample decomposition systems a significant reduction of the time required for complete sample decomposition can be achieved.

8.1.2.3.3 Volumetric flask, at least 100 ml, resistant against the acids used.

8.1.2.4 Sample preparation

Prepare and dry the sample as specified in ISO 21068-1. The sample material shall have a particle size of ≤50 µm. Inhomogeneous sample material shall be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

8.1.2.5 Procedure

A sub-sample mass suited for the analytical purpose but not more than 300 mg is weighed to the nearest 0,01 mg into the decomposition vessel (8.1.2.3.2). Add 4 ml of HNO_3 (8.1.2.2.1), 4 ml of HF (8.1.2.2.2) and 4 ml of H_2SO_4 (8.1.2.2.3). Place the decomposition vessel in the pressure vessel (8.1.2.3.2) and close it according to the manufacturer's instructions. Place the pressure vessel in the heating device and heat to 250 °C ± 5 °C for at least 14 h.

NOTE The heating time is significantly reduced if a microwave sample decomposition system is used.

After the heating step, the pressure vessel is removed from the heating device and, after cooling down, opened according to the manufacturer's instructions. Transfer the content of the decomposition vessel to the volumetric flask (8.1.2.3.3). Thoroughly rinse the decomposition vessel with water and transfer the washings into the volumetric flask. After this, the volumetric flask is filled up to volume with water.

For each sample at least two decompositions should be carried out. For blank correction, at least two decompositions according to the described procedure and without using sample material should be carried out.

Before re-use, the decomposition vessel shall be cleaned with 10 ml HNO_3 (8.1.2.2.1) at a temperature of 100 °C for 4 h. When a microwave sample decomposition system is used a similar cleaning step shall be performed according to the manufacturer's instructions.

8.1.2.6 Measurement

The obtained sample solutions shall be analysed using the common analytical methods for liquid sample solutions (see, for example, ISO 26845 [12]) such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS). Sample masses and dilutions shall be adapted for the specific method.

8.2 Determination of impurities by XRF (fused bead method)

As an alternative method for the determination of elemental impurities, the XRF method as specified in ISO 12677 can be applied. For silicon carbide and similar materials, sample preparation for XRF shall be performed according to ISO 16169.

8.3 Determination of impurities by DCArc-OES (direct solid sampling method)

As an alternative method for the determination of elemental impurities, the DCArc-OES method as specified in EN 15979[14] can be applied. For the DCArc-OES method, no sample decomposition prior to the measurement is required. The combustion and evaporation of the powdered sample material takes place in a direct current arc in an atmosphere of oxygen, an argon/oxygen mixture or in air. The metallic traces in the arc plasma are excited to emission of light. The emitted light is guided into the optical system of a simultaneous emission spectrometer (for example, by coupling via fibre-optics or directly) where it is split in its spectral lines and measured. The mass fractions of elements in the sample are calculated by comparison of the intensities of the element-specific spectral line with those of calibration samples of identical material.

9 Expression of results

Express the test results in accordance with ISO 21068-1.

10 Test report

The test report shall be presented in accordance with ISO 21068-1.

Annex A
(informative)

Precision data

A.1 Precision data for the determination of total nitrogen and total oxygen by inert-gas fusion (4.2) in a silicon carbide powder sample

The results of the interlaboratory study for the determination of total nitrogen by inert-gas fusion are given in Tables A.1 and A.2. and the results for the determination of total oxygen are given in Tables A.3 and A.4.

NOTE The precision data was obtained in the frame of the certification of the reference material BAM-S003 Silicon Carbide Powder (green micro F 800). Based on the results of the participating laboratories, precision data was calculated according to ISO 5725-2 [13].

Table A.1 — Precision data for total nitrogen by inert-gas fusion

Designation	**Precision data**
Number of participating laboratories, p_j	11
Number of accepted single values of all laboratories, n_j	66
Mean value, m, in mg/kg	92,2
Repeatability standard deviation, s_r, in mg/kg	6,7
Repeatability limit: $r = 2{,}8 \text{ x } s_r$, in mg/kg	18,7
Variation coefficient of the repeatability standard deviation, v_r, in percentage relative	7,2
Reproducibility standard deviation, S_R, in mg/kg	31,2
Reproducibility limit: $R = 2{,}8 \text{ x } S_R$, in mg/kg	87,4
Variation coefficient of the reproducibility standard deviation, V_R, in percentage relative	33,9

Table A.2 — Single values for total nitrogen, mg/kg

Laboratory	***m***	***s***	**s_{rel}**	**Measurement**					
				#1	**#2**	**#3**	**#4**	**#5**	**#6**
1	46,7	5,6	12,0	42,0	45,7	43,1	55,2	51,9	42,0
2	59,2	7,7	13,1	55,0	64,0	67,0	67,0	52,0	50,0
3	64,2	3,7	5,8	61,1	60,1	67,6	61,3	67,6	67,6
4	80,0	11,0	13,7	70,0	70,0	80,0	80,0	80,0	100,0
5	88,8	4,3	4,8	84,3	93,1	87,5	88,2	94,7	84,8
6	89,2	3,5	4,0	93,0	84,0	86,0	92,0	91,0	89,0
7	93,8	6,3	6,7	95,0	98,0	103,0	88,0	86,0	93,0
8	99,0	5,3	5,4	95,0	95,0	106,0	105,0	94,0	99,0
9	114,5	2,9	2,5	111,0	116,0	117,0	112,0	118,0	113,0
10	127,8	4,6	3,6	134,0	128,0	132,0	122,0	124,0	127,0
11	150,8	11,6	7,7	135,0	146,0	162,0	142,0	156,0	164,0

Key

m mean value in mg/kg

s standard deviation in mg/kg

s_{rel} standard deviation in percentage relative