INTERNATIONAL STANDARD

**ISO 21068-3**

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

## 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 —*

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



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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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 21068-3 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 [8] 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 as classified in ISO 10081 (all parts) [3], [4], [5], [6] (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 3:
# Determination of nitrogen, oxygen and metallic and oxidic constituents

## 1 Scope

This part of ISO 21068 specifies methods for the determination of total nitrogen and nitrogen calculated as silicon nitride, total oxygen, and free metallic and oxidic components in silicon carbide raw materials and refractory products.

It applies only to silicon carbide materials that are not bonded with nitrogen. Nitride-bonded silicon carbide refractories are covered in EN 12698-1.



## 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 10058-1, *Chemical analysis of magnesite and dolomite refractory products (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents, dissolution and 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 spectrometry (FAAS) and inductively coupled plasma emission spectrometry (ICP-AES)*

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

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 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 emission spectrometry (ICP-AES)*

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

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

ISO 21079-1, *Chemical analysis of refractories containing alumina, zirconia and silica — Refractories containing 5 % to 45 % of $ZrO_2$ (alternative to the X-ray fluorescence method) — Part 1: Apparatus, reagents and dissolution*

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

ISO 21079-3, *Chemical analysis of refractories containing alumina, zirconia and silica — Refractories containing 5 % to 45 % of $ZrO_2$ (alternative to the X-ray fluorescence method) — Part 3: Flame atomic absorption spectrometry (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*

ISO 26845, *Chemical analysis of refractories — General requirements for wet chemical analysis, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) methods*



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 nitrogen and oxygen

### 4.1 General

For oxygen only, the IR detection method is given; for nitrogen, several different methods are described, calculated nominally as $Si_3N_4$.

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 (CR) and infrared absorption (IR) detection

#### 4.2.1 Principle

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

NOTE 1 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 rare-earth copper catalyst, which converts carbon monoxide to carbon dioxide, and then to an infrared 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 or other suitable analyser to quantify the nitrogen.

NOTE 2 A method for the determination of oxygen contents less than 3 % is given in EN 725-3 [7].

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

When materials with dissociation temperatures higher than 2 400 °C ± 25 °C are being analysed, it is recommended that a fluxing agent is also included with the sample. A suitable agent would be a nickel wire basket.

### 4.2.2 Reagents

**4.2.2.1** **Nickel or tin capsule**, of suitable dimensions and oxygen and nitrogen free.

**4.2.2.2** **Nickel basket**, of suitable dimensions and oxygen and nitrogen free.

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

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

**4.2.2.5** **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.

### 4.2.4 Calibration

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

a) using certified reference materials (preferably primary);

b) by injection of known volumes of pure carbon dioxide and nitrogen into the detection system.

If b) is used, it is recommended that a standard reference material be analysed to verify the performance of the electrode furnace, associated chemicals and detection system.

For both methods, a minimum of three calibration points and a zero shall be used to establish the calibration.

### 4.2.5 Procedure

#### 4.2.5.1 General

Operate the instrument in accordance with the instrument operation manual.

#### 4.2.5.2 Determination

Dry and grind the sample (see Clause 4 of ISO 21068-1:2008). Weigh it, to the nearest 0,1 mg, into the nickel capsule and seal it, taking care to expel any air present.

NOTE A typical sample mass is approximately 50 mg ± 1 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.

Put the nickel capsule into the loading-mechanism analyser.

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, for a period of time sufficient to allow any entrapped oxygen and nitrogen to be expelled;

b) drop the sample into the graphite crucible and perform the analysis.

Because of the sample masses involved, report results as the mean of at least three determinations.

#### 4.2.5.3 Blank determinations

Although any oxygen and nitrogen present in the graphite crucible is removed prior to the analysis being carried out [see 4.2.5.2 a)], there may still be oxygen and nitrogen present in the tin capsule and nickel basket. Make blank determinations and subtract them from subsequent analyses. The blank shall be the mean of at least three determinations.



Prepare a solution containing approximately 75 ml of acetic acid, 25 ml of nitric acid and 1,5 ml of hydrochloric acid. In a well-ventilated fume cupboard, heat the solution to a temperature of 55 °C ± 5 °C, immerse the nickel basket in the heated solution for 30 s to 60 s, remove the nickel basket from the solution and rinse immediately in running water. Immerse the nickel basket in chemically pure acetone, dry thoroughly and place the cleaned nickel basket in a desiccator.



#### 4.2.5.4 Calculation

Calculate the mass fraction of nitrogen or oxygen, $w_a$, expressed as a percentage, using Equation (1).

$$w_a = w_m - b \tag{1}$$

where

$w_m$ is the mass fraction of nitrogen or oxygen, respectively, measured in the sample, expressed as a percentage;

$b$ is the average blank determination of nitrogen or oxygen respectively, expressed as a percentage by mass.

Report the results as the mean of three determinations.

## 5 Determination of nitrogen calculated as $Si_3N_4$

### 5.1 General

The nitrogen determined is calculated as silicon nitride. The determination of silicon nitride is carried out using one of the following methods:

a) acid decomposition with pressurization/separation by the steam distillation/neutralization titration method;

b) acid decomposition with pressurization/separation by steam distillation/indophenol blue absorption spectroscopy; this method should be used for samples containing silicon nitride whose percentage is less than 2 % by mass;

c) inert-gas fusion-thermal conductivity method.

The calculation of $Si_3N_4$ by using the measured nitrogen content is only justified and expedient if nitrogen is chemically bonded as silicon nitride quantitatively. The methods described in Clause 4 are, in principle, applicable for the determination of total nitrogen. When method 5.2 or 5.3 is used for determining total nitrogen, the obtained result should be verified by a method as described in Clause 4 or 5.4. This is because of the high chemical resistance of nitrides, particularly with regard to unknown nitrides, besides $Si_3N_4$, contained in the sample.

## 5.2 Acid decomposition — Titration method

### 5.2.1 Principle

A sample is decomposed with sulfuric acid and hydrofluoric acid in a pressurization container, so that silicon nitride changes to ammonium salt, and boric acid is then added to it. The resulting solution is transferred into a distillation flask. Sodium hydroxide is added to the flask and steam distillation is carried out, and the ammonia distillate is absorbed into an appropriate amidosulfonic acid. The remaining amidosulfonic acid is titrated with sodium hydroxide.

### 5.2.2 Reagents



Solutions 5.2.2.1, 5.2.2.2 and 5.2.2.7 shall be stored in plastics bottles.



**5.2.2.1 Hydrofluoric acid**.



**5.2.2.2 Sulfuric acid** (1+1).



**5.2.2.3 Boric acid**.

**5.2.2.4 Sodium hydroxide** (500 g/l).

**5.2.2.5 Ammonium sulfate**, purity more than 99,9 % by mass. Heat at 110 °C ± 10 °C for 3 h and cool in a desiccator.

**5.2.2.6 Amidosulfuric acid solution**, 0,1 mol/l.

Weigh 10,0 g, to the nearest 0,1 mg, of amidosulfuric acid (reference material for volumetric analysis, or high-purity reagent above 99,99 % by mass). Dissolve in water, transfer to a 1 000 ml volumetric flask, and dilute to the mark with water.

Calculate the factor, $F$, for the 0,1 mol/l amidosulfuric acid solution using Equation (2).

$$F = \frac{m_a \times P}{9{,}709\,5 \times 100} \tag{2}$$

where

$m_a$ is the mass of amidosulfuric acid, in grams;

$P$ is the purity of amidosulfuric acid, expressed as a percentage by mass.

**5.2.2.7 Sodium hydroxide solution**, 1 mol/l.

Weigh 165 g of sodium hydroxide in a 500 ml polyethylene airtight container, add 150 ml of carbon-dioxide-free water to dissolve it, and allow it to stand for 4 to 5 days with shielding from carbon dioxide. Take 54 ml of its supernatant liquid in a 1 l polyethylene airtight container, add carbon-dioxide-free water to it to make a total 1 l, mix well, and store it with a soda-lime tube attachment.

**5.2.2.8 Sodium hydroxide solution**, 0,1 mol/l.

Pipette 100 ml of 1 mol/l sodium hydroxide solution into a 1 000 ml volumetric flask, dilute with carbon-dioxide-free water to 1 000 ml, mix well, put it in an airtight polyethylene container, and store it with a soda-lime tube attachment.

Transfer precisely 50 ml of 0,1 mol/l amidosulfuric acid solution (5.2.2.6) to a 200 ml beaker, dilute to about 100 ml with water, and titrate with 0,1 mol/l sodium hydroxide solution using a pH meter equipped with a glassy electrode. Determine the titration volume of 0,1 mol/l sodium hydroxide solution at the end point of which the pH is 5,5.

Calculate the factor, $F'$, of this 0,1 mol/l sodium hydroxide solution using Equation (3).

$$F' = \frac{F \times 50{,}00}{V} \tag{3}$$

where,

$F$ is the factor of 0,1 mol/l amidosulfuric acid solution;

$V$ is the volume of titration of 0,1 mol/l sodium hydroxide, in millilitres.



**5.2.3 Apparatus**



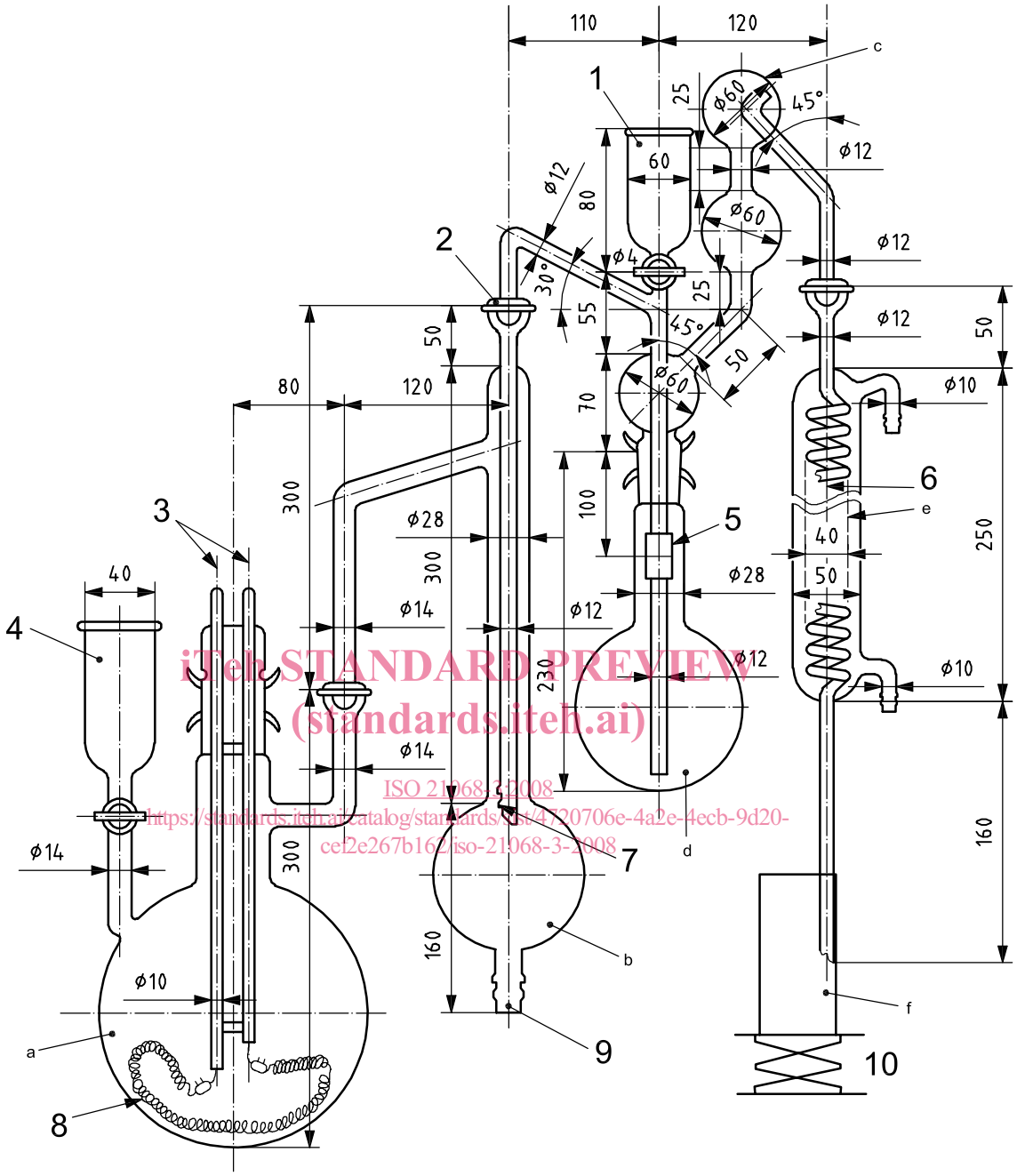
**5.2.3.1 Pressurization vessel**, for decomposition, the inner cap and the vessel are made of ethylene 4-fluoride resin and outer cap and pressure-resistant container are made of stainless steel.

To avoid cross-contamination by nitrogen from other uses of the vessel, reserve pressure vessels solely for the determination of silicon nitride.

**5.2.3.2 Steam distillation apparatus**, consisting of the elements listed in 5.2.3.2.1 to 5.2.3.2.6.

NOTE An example of the steam distillation apparatus is given in Figure 1. Each component is made of borosilicate glass and they are connected with common ground-glass joints and fixed with springs or clamps.

Dimensions in millimetres






**Key**

| | | | | | |
|---|---|---|---|---|---|
| 1 | funnel | 5 | rubber tube | 9 | connection of rubber tube with pinchcock |
| 2 | ball joint | 6 | 13 to15 coils | 10 | jack |
| 3 | Dumet wire | 7 | small holes | | |
| 4 | funnel with stopcock | 8 | electric heater | | |

| | | | | | |
|---|---|---|---|---|---|
| a | Flask (2,5 l) for generation of steam. | c | Sphere and tube. | e | Graham condenser. |
| b | Trap (500 ml). | d | Distillation flask (750 ml). | f | Collecting vessel. |

**Figure 1 — Example of the steam distillation apparatus**