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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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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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 21068-2:2008), 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.

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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.

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

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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

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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.

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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.

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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.

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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.

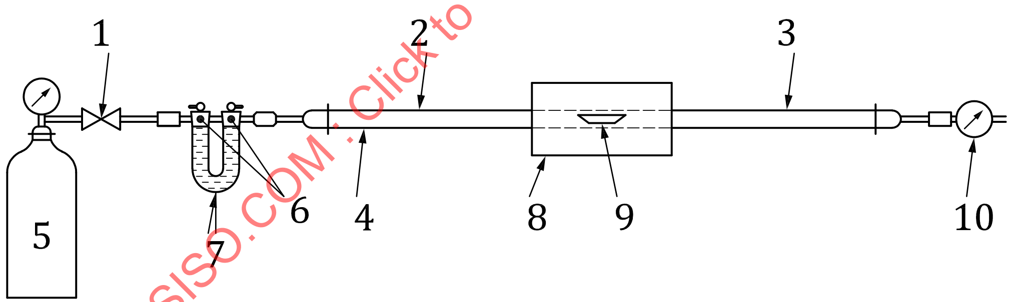
4.3.2.6 Open combustion boats, of unglazed ceramic material, the length of which matches the oven's zone of constant temperature. The boats shall be broad enough to accommodate the amount of sample required for the determination.

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

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

4.3.4 Reagents

4.3.4.1 Argon, 99,997 %.

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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).

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

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where

w_{LOIAr} is the loss on ignition in argon at 750 °C, in mass percent;

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

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

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

5 Determination of the total carbon content

5.1 Scope

This clause describes a quantitative analysis of the total carbon content by combustion in a resistance or an induction furnace. In both cases the sample is combusted in an oxygen stream whereby CO_2 and CO are formed. Remaining CO is catalytically oxidised to CO_2 prior to the measurement. Thereafter, CO_2 is measured by coulometric, infrared absorption or thermal conductivity methods.

5.2 Combustion techniques

For sample combustion with oxygen, one of the listed techniques shall be used:

— a resistance furnace (RF) with lead borate or tin fusion as accelerator/decomposition agent,

— an induction furnace (IF) with metal fusion as accelerator.

5.2.1 Combustion in a resistance furnace with lead borate or tin as decomposing agent

5.2.1.1 Principle

The sample is heated together with lead borate or tin in a stream of oxygen in a resistance tube furnace to convert the carbon to carbon dioxide by combustion. The sample mass and the details of the combustion depend on the method of determination used.

5.2.1.2 Reagents

Use only reagents of analytical grade.

5.2.1.2.1 Oxygen, 99,99 %.

5.2.1.2.2 Lead borate, 2 $PbO \cdot B_2O_3$.

If not commercially available, prepare lead borate by melting 45 g of analytical grade lead oxide, PbO, together with 7 g of analytical grade boron trioxide, B2O3, for 10 min at (950 °C ± 25) °C, cooling the melt by pouring it onto a clean aluminium plate and then pulverizing it.

5.2.1.2.3 Tin powder, grain size < 100 µm.

5.2.1.3 Apparatus

Ordinary laboratory apparatus and the following.

5.2.1.3.1 Analytical balance, capable of measuring to the nearest 0,000 01 g (0,01 mg).

5.2.1.3.2 Resistance furnace with ceramic tube, capable of being maintained at a temperature of (1 050 ± 25) °C if lead borate is used as the accelerator or (1 350 ± 25) °C if tin is used as the accelerator

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in the centre of the heating zone. The furnace shall be fitted with a thermocouple connected to a device permitting measurement of the furnace temperature.

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

5.2.1.4 Setting up of test assembly

Set up the test assembly in accordance with the manufacturer's instructions.

5.2.1.5 Procedure for RF combustion with lead borate or tin

Adjust the oxygen (5.2.1.2.1) flow rate to prevent the risk of air being sucked in from the outside. Preheat the furnace to a temperature of (1 050 ± 25) °C if lead borate is used as the accelerator or (1 350 ± 25) °C if tin is used as the accelerator.

Weigh the required sample mass to the nearest 0,000 01 g into the combustion boat and spread it uniformly in the combustion boat. Cover the sample with 1,5 g of lead borate (5.2.1.2.2) or, alternatively, 2,0 g of tin powder (5.2.1.2.3) and place the combustion boat in the centre of the heating zone.

NOTE Combustion is usually complete after 5 min.

The carbon dioxide gas formed is supplied by the oxygen carrier gas to the detection unit (5.3).

5.2.1.6 Precision

Precision data for the determination of total carbon by combustion in a resistance furnace with tin as decomposing agent and detection by infrared absorption is given in A.1.2.

5.2.2 Combustion in an induction furnace (IF) with metallic powder as decomposing agent

5.2.2.1 Principle

The sample is heated together with a metal additive in a stream of oxygen using a high-frequency induction furnace. The carbon dioxide released is transferred by carrier gas to the detection unit.

5.2.2.2 Reagents

Use only reagents of at least analytical grade.

5.2.2.2.1 Granulated iron accelerator, for example as supplied by the supplier of the furnace.

5.2.2.2.2 Granulated tungsten accelerator, for example as supplied by the supplier of the furnace.

5.2.2.2.3 Granulated copper accelerator, for example as supplied by the supplier of the furnace.

5.2.2.2.4 Oxygen, 99,99 %

5.2.2.3 Apparatus

5.2.2.3.1 Analytical balance, capable of measuring to the nearest 0,000 01 g (0,01 mg).

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5.2.2.3.2 Combustion crucibles, of ceramic material with covers and holders as recommended by the apparatus provider.

Before use, the combustion crucibles and covers should be fired at a minimum temperature of 1 000 °C.

5.2.2.4 Procedure

Weigh the required sample mass to the nearest 0,000 01 g into the combustion crucible and add the metal accelerator. Suitable accelerators include: copper/iron (1 g each), copper/tungsten (1 g each), iron/tungsten (1 g / 2 g). Then the ceramic cover is placed on the crucible. The crucible is placed in the furnace.

Perform the combustion of the sample according to the operating instructions of the analysis system.

The carbon dioxide gas formed during combustion is supplied by the oxygen carrier gas to the detection unit (5.3).

5.2.2.5 Precision

Precision data for the determination of total carbon by combustion in an induction furnace with metal additives as decomposing agent and detection by infrared absorption is given in A.2.

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5.3 Detection techniques

Usually, combustion and detection techniques are commercially available in combined systems.

For quantitative measurements, carbon oxidized with oxygen to CO_2 shall be measured by either using:

— coulometry (5.3.1),

— infrared absorption (IR) (5.3.2) or

— thermal conductivity (TC) method 5.3.3).

5.3.1 Coulometry

The carbon present in the sample is combusted in a stream of oxygen in a furnace to produce carbon dioxide. Together with the oxygen, the combustion gases are drawn off by a pump through a tube containing percarbamide ($CO(NH_2)_2 \bullet H_2O_2$), which absorbs the oxidation products of the sulfur contained in the sample. The carbon dioxide is transferred to a titration cell filled with alkaline barium perchlorate, $Ba(ClO_4)_2$, solution where it is absorbed with a consequent reduction of the alkalinity of the solution. Automatic back titration to the initial pH value of the solution is carried out using electrolytically generated barium hydroxide. The charge Q which flowed during back titration is directly proportional to the absorbed carbon dioxide and, thus, to the total carbon content of the sample.

Set up and operate the test assembly in accordance with the manufacturer's instructions.

To verify the accuracy of the procedure reference materials with known total carbon content shall be used.

NOTE Suitable certified reference materials (CRMs) for the verification of the method are given in Annex B.

5.3.2 Detection of the released carbon dioxide, CO_2, by infrared absorption (IR)

The sample gas is transferred into an infrared analysis apparatus. The infrared absorbance change is measured. The detector shall be calibrated with at least two reference materials with known total carbon content.

NOTE Suitable certified reference materials (CRMs) for the calibration of the detector are given in Annex B.

Set up and operate the test assembly in accordance with the manufacturer's instructions.

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5.3.3 Thermal conductivity (TC) method

The sample gas is transferred into a thermal conductivity measurement cell. The change in thermal conductivity is measured.

The detector shall be calibrated with at least two reference materials with known total carbon content.

NOTE Suitable certified reference materials (CRMs) for the calibration of the detector are given in Annex B.

Set up and operate the test assembly in accordance with the manufacturer's instructions.

5.4 Expression of results

The measured mass of CO_2 is recalculated using Formula (4) to mass fraction of total carbon in the sample and is reported as w_{Ctotal}. Results should be reported to at least 1 decimal place.

$$w_{Ctotal} = \frac{0{,}272\,9 \times m_{CO2}}{m_E} \times 100 \quad (4)$$

where:

w_{Ctotal} is the content of total carbon in the sample, in mass percent;

m_{CO2} is the mass of carbon dioxide released during sample combustion, in milligrams;

m_E is the initial sample mass, in milligrams.

0,272 9 is the stoichiometric factor for converting CO_2 to carbon.

6 Determination of free carbon content

6.1 General

For the determination of free carbon, direct and indirect methods are used.

Direct methods:

— combustion of free carbon at 850 °C followed by coulometric, infrared absorption or thermal conductivity detection;

— wet chemical oxidation of free carbon (hot chromic sulfuric iodic acid method) followed by coulometric detection.

Indirect methods:

— determination of the free carbon by change in mass during calcination in air;

— determination of free carbon by calculation.

NOTE Suitable certified reference materials (CRMs) for the verification of the methods are given in Annex B.

6.1.1 Direct methods

6.1.1.1 Combustion of free carbon at 850 °C followed by coulometric, infrared absorption or thermal conductivity detection

6.1.1.1.1 Principle

For direct determination of free carbon, combustion in a resistance furnace as described in 5.2.1 is performed at 850 °C without adding lead borate or tin as decomposing agent. Under these conditions, the

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oxidation of silicon carbide can be neglected and only free carbon will be oxidized to carbon dioxide. The quantification of released carbon dioxide shall be performed by using optionally coulometry, infrared absorption or thermal conductivity.

NOTE This direct method for the determination of free carbon is only applicable if oxidation of silicon carbide can be neglected. This is the case, for example, with α-SiC containing not less than 95 % of silicon carbide, SiC, and not more than 2 % of free carbon, C.

If partial oxidation of SiC during combustion cannot be excluded, a correction of the measured free carbon content shall be applied according to Annex C.

6.1.1.1.2 Apparatus

Ordinary laboratory apparatus and the test assembly for total carbon determination as described in 5.2.1. The furnace shall be capable of being maintained at a temperature of (850 ± 20) °C in the centre of the heating zone.

6.1.1.1.3 Coulometric detection

Use the method described in 5.3.1.

6.1.1.1.4 Infrared absorption detection

Use the method described in 5.3.2.

6.1.1.1.5 Thermal conductivity detection

Use the method described in 5.3.3.

6.1.1.1.6 Results

Report the free carbon content w_{Cfree} in mass percent to the nearest 0,01 %.

6.1.1.1.7 Precision

Precision data for the determination of free carbon by combustion at 850 °C and infrared absorption or thermal conductivity detection is given in A.1.3.

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6.1.1.2 Direct determination of free carbon by wet oxidation (hot chromic sulfuric iodic acid method)

6.1.1.2.1 Principle

This method defines the wet-chemical procedure for oxidation of free carbon to carbon dioxide (CO_2). Methods for measurement of released CO_2 are not defined.

The free carbon of the sample is oxidized to carbon dioxide by chromic sulfuric iodic acid at 120 °C. The formed CO_2 is transported with an inert carrier gas stream to a detection system of choice.

This method is applicable to free carbon contents of 0,01 % m/m to 5 % m/m. At higher concentrations, incomplete recovery is possible.

This method also considers possible oxidation of silicon carbide which may occur if the silicon carbide powder sample contains fine grained silicon carbide (grain size less than 10 µm).

The method also releases organic carbon and carbonate carbon as CO_2.

Unless otherwise specified, solutions are aqueous.

NOTE Coulometric, conductometric or infrared absorption CO_2 detection systems can be used.

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6.1.1.2.2 Reagents

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

6.1.1.2.2.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water).

6.1.1.2.2.2 Drying agent, for example phosphorus pentoxide, P_2O_5.

6.1.1.2.2.3 Sodium dichromate, $Na_2Cr_2O_7 \cdot 2H_2O$.

6.1.1.2.2.4 Potassium iodate, KIO_3.

6.1.1.2.2.5 Calcium carbonate, $CaCO_3$.

6.1.1.2.2.6 Sulfuric acid H_2SO_4, ρ = 1,84 g/ml.

6.1.1.2.2.7 Argon Ar, or nitrogen N_2, 99,998 % pure**.**

6.1.1.2.2.8 Chromic sulfuric iodic acid solution, prepared by dissolving 22 g of sodium dichromate (see 6.1.1.2.2.3) in 300 ml H_2O, and adding 700 ml sulfuric acid (see 6.1.1.2.2.6). The solution is heated for 30 min at (150 ± 10) °C, then 10 g of potassium iodate is added (see 6.1.1.2.2.4). After cooling, the solution is stored in a glass bottle.

WARNING — Chromic sulfuric iodic acid should be handled with care, be aware of local safety regulations.

6.1.1.2.3 Apparatus

Ordinary laboratory apparatus and the following:

6.1.1.2.3.1 Drying cupboard, with heating and temperature control up to (110 ± 5) °C.

6.1.1.2.3.2 Suitable crushing device, for example hard material mortar or mill with hard metal milling tools such as tungsten carbide.

6.1.1.2.3.3 Analytical balance, capable of measuring to the nearest 0,05 mg.

6.1.1.2.3.4 Aluminium heating-block, with temperature control to (120 ± 5) °C.

6.1.1.2.3.5 Aluminium capsules, for example diameter 6 mm, length 15 mm, prepared from aluminium foil.

6.1.1.2.3.6 Analytical sieve, mesh size 32 µm complying with the requirements of ISO 3310-1.

6.1.1.2.3.7 Reaction vessel, with cooling device and drying trap (see Figure 2).

6.1.1.2.4 Sample preparation

For the wet chemical oxidation of sintered material, grain sizes of less than 32 µm are required. Crushing devices which consist of materials with high free carbon content shall not be used. Crush a piece of the sintered body in the crushing device (see 6.1.1.2.3.2). Sieve the crushed sample through the analytical sieve (see 6.1.1.2.3.6). Dry the test sample (sampled as described in ISO 21068-1) in the drying cupboard (6.1.1.2.3.1) to constant mass at (110 ± 5) °C for a minimum of 2 h prior to analysis.

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6.1.1.2.5 Procedure

Insert the reaction vessel into the heating block (see 6.1.1.2.3.4) and connect it via a cooler and drying trap with the chosen detection system. Adjust the carrier gas flow as required by the detection system used. Units with a sucking pump usually work with a surplus of carrier gas and pressure compensation. Optimize the gas flow so that no air is sucked into the system.

Adjust the temperature of the heating block to (120 ± 5) °C.

Pipette 30 ml of chromic sulfuric iodic acid (6.1.1.2.2.8) into the reaction vessel. To control the tightness of the system, run a blank measurement of 5 min to 10 min after a heating time of 20 min. Weigh, depending on the sample material and the expected content of free carbon, 20 mg to 200 mg of the dried sample (6.1.1.2.4) to the nearest 0,1 mg into an aluminium capsule (6.1.1.2.3.5). Close the capsule with tweezers. Put the capsule in the sample insertion device of the reaction vessel and drop it into the hot chromic sulfuric iodic acid. At the same time the sample drops into the acid, switch on the measuring mode of the detection unit.

The measurement shall be performed until all free carbon has been detected as CO_2.

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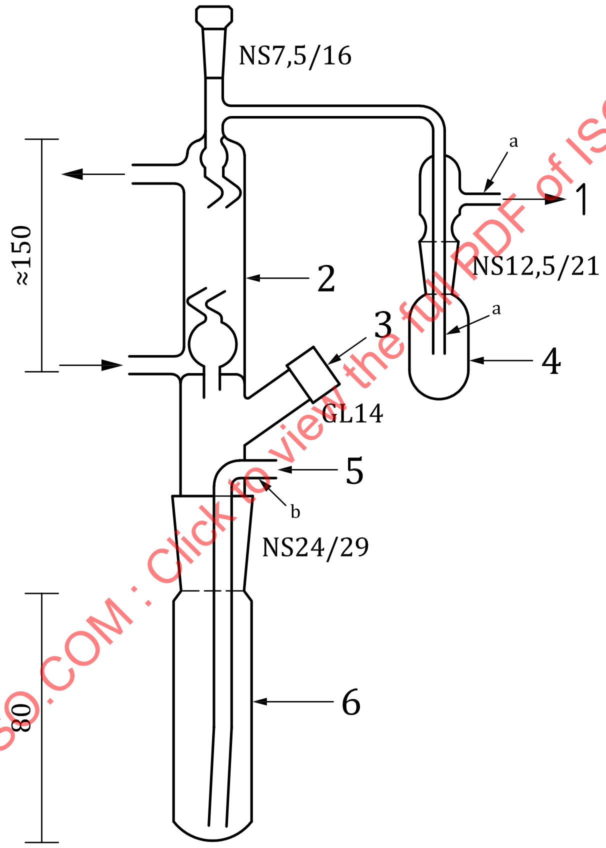

Key

1 to detection unit
2 cooler
3 sample insertion device
4 drying trap
5 carrier gas inlet
6 reaction vessel
a Inner diameter 5 mm.
b Inner diameter 6 mm.

Figure 2 — Example of a reaction vessel (dimensions in millimetres)

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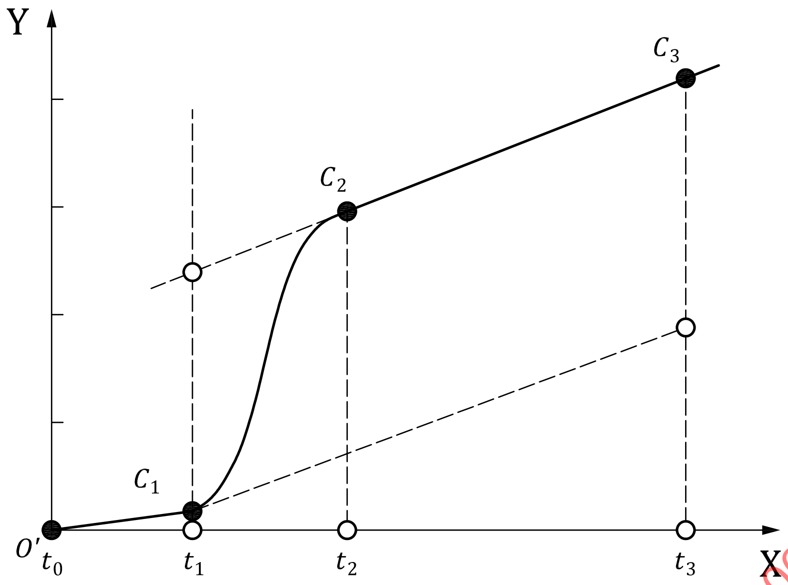

Key

X reaction time for the wet-chemical oxidation of free carbon to carbon dioxide

Y measured carbon dioxide, represented as mass of carbon

Figure 3 — Evaluation of CO_2 release curve

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6.1.1.2.6 Calculation and expression of results

In Figure 3 the typical development of CO_2 release, presented as measured mass of carbon (Y-axis) versus time (X-axis), during wet-chemical oxidation is given. The slight increase between t_0 (start of measurement) and t_1 (start of reaction of free carbon) is caused by residual CO_2 in the carrier gas. At t_2, all free carbon in the sample has reacted to CO_2. The mass of carbon measured between t_1 and t_2, however, also contains carbon originating from carrier gas and possible oxidation of silicon carbide. To compensate this contribution the increase of carbon mass between t_2 (end of reaction of free carbon) and t_3 (end of measurement) is measured and used to calculate the so-called mean drift rate C_{Drift}. Under the assumption that between t_1 and t_3 the contribution rate of carbon originating from carrier gas and oxidation of silicon carbide is constant the correct free carbon content of the sample is calculated using Formulae (5) and (6):

$$C_{Drift} = \frac{m_{C3} - m_{C2}}{t_3 - t_2} \tag{5}$$

$$m_{Cfree} = (m_{C2} - m_{C1}) - C_{Drift} \times (t_2 - t_1) \tag{6}$$

where:

C_{Drift} is the mean carbon drift-rate, in milligrams per minute;

m_{C1} is the mass of carbon at start of reaction of free carbon, in milligrams;

m_{C2} is the mass of carbon at end of reaction of free carbon, in milligrams;

m_{C3} is the mass of carbon at end of measurement, in milligrams;

t_1 is the time at start of reaction of free carbon, in minutes;

t_2 is the time at end of reaction of free carbon, in minutes;

t_3 is the time at end of measurement, in minutes;

m_{Cfree} is the drift-rate corrected mass of free carbon, in milligrams.

The free carbon content w_{Cfree} of the sample shall be calculated under consideration of sample mass using Formula (7). The free carbon content shall be expressed in mass fractions in % and rounded in accordance with the uncertainty of measurement.

$$w_{Cfree} = \frac{100 \times m_{Cfree}}{m_E} \quad (7)$$

where:

w_{Cfree} is the content of free carbon in the sample, in mass percent;

m_{Cfree} is the drift-rate corrected mass of free carbon, in milligrams;

m_E is the sample mass, in milligrams.

Express the result to the nearest 0,01 %.

NOTE To obtain precision data for this method, silicon carbide powder samples with a free carbon content of 0,05 mass percent to 0,5 mass percent were analysed in an interlaboratory study. The results for repeatability standard deviation s_r, repeatability limit r, reproducibility standard deviation, S_R and reproducibility limit R, as defined in ISO 5725-2 [12] are given in mass percent in Table 2.

Table 2 — Precision data for the determination of free carbon

Repeatability		Reproducibility	
s_r	r	S_R	R
0,004	0,01	0,011	0,03

6.1.2 Indirect methods

6.1.2.1 Determination of the free carbon by change in mass during calcination in air

6.1.2.1.1 Principle

Indirect determination of the free carbon content by measurement of total carbon and change in mass during calcination in air at (750 ± 25) °C.

The following determinations shall be carried out:

— total mass fraction of carbon, w_{Ctotal}, of the dried starting material by one of the methods described in Clause 5;

— change in mass on calcination, m_v, in air;

— total mass fraction of carbon of the residue on calcination in air, w_{CR}, by the same method used for w_{Ctotal}.

This method of indirect determination of the free carbon content takes the oxidation of silicon carbide during the ignition at (750 ± 25) °C in air into account.

If there are doubts about using this method, because the substance to be analysed contains volatile constituents, carbonates and/or other reactive additives (Fe, Si, Al), the amounts of these constituents shall be determined and allowed for correction of free carbon content.

This indirect method of free carbon determination is invalid when the sample contains more than 0,6 % vanadium pentoxide, V_2O_5, or boric acid, H_3BO_3.

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Carbon not bound as silicon carbide, SiC, shall not constitute more than 5 %. If the free carbon, C_{free}, content exceeds 5 %, 6.1.2.2 shall be applied. Alkali oxides or alkali carbonates that act as fluxes interfere with the determination.

6.1.2.1.2 Determination of total carbon

6.1.2.1.2.1 Reagents and apparatus

Use the reagents and apparatus given in Clause 5 according to the chosen method.

6.1.2.1.3 Apparatus for calcination in air

Ordinary laboratory apparatus and the following.

6.1.2.1.3.1 Laboratory furnace, capable of being maintained at (750 ± 25) °C.

6.1.2.1.3.2 Agate mortar.

6.1.2.1.3.3 Crucibles, of unglazed ceramic material.

6.1.2.1.3.4 Analytical balance, capable of measuring to the nearest 0,000 1 g (0,1 mg).

6.1.2.1.4 Procedure

6.1.2.1.4.1 Determining the change in mass on calcination in air

Weigh, to the nearest 0,1 mg, about 1 g of the sample prepared and dried as specified in ISO 21068-1, into a crucible which was pre-calcined at (750 ± 25) °C and cooled in a desiccator. Calcine the sample in the laboratory furnace for 60 min at (750 ± 25) °C and then cool in a desiccator. Weigh to the nearest 0,1 mg. Repeat the calcination at least once for 30 min, and weigh the cooled crucible containing the residue again, to the nearest 0,1 mg.

A slight increase in mass during the second calcination is acceptable, but a decrease in mass requires the calcination to be continued until the mass is constant or increases.

Use the sample mass determined after the final calcination to calculate the change in mass, m_V, using Formula (8).

6.1.2.1.4.2 Determining the total carbon content of the residue on ignition

After calcination as described in 6.1.2.1.4.1, place the material in the agate mortar and homogenize without reducing the particle size further. Determine the total carbon content of the residue on ignition, w_{CR}, in accordance with one of the methods described in Clause 5.

6.1.2.1.4.3 Determining the total carbon content of the starting material

Determine the total carbon content, w_{Ctotal}, of the sample prepared and dried as specified in ISO 21068-1, using one of the methods described in Clause 5.

6.1.2.1.4.4 Calculation

Calculate the change in mass on calcination, m_V, as a percentage by mass, to the nearest 0,01 %, using Formula (8).

$$m_V = \frac{m_A - m_E}{m_E} \times 100 \tag{8}$$

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where

m_v is the change in mass on calcination at 750 °C, in mass percent;

m_A is the mass of the residue after calcination at 750 °C, in grams;

m_E is the initial sample mass, in grams.

A loss in mass shall be written with a negative sign in Formula (9) and an increase in mass with a positive sign.

Calculate the mass fraction of free carbon, w_{Cfree}, expressed as a percentage, to the nearest 0,01 %, using Formulae (9) to (11).

$$w_{Cfree} = \frac{w_{Ctotal} - w_{CR}}{f_1} - \frac{m_V \times w_{CR}}{100 \times f_1} - \frac{m_V}{f_2} \quad (9)$$

where

w_{Cfree} is the free carbon content of the sample, in mass percent;

w_{Ctotal} is the total carbon content (6.1.2.1.4.3), in mass percent;

w_{CR} is the total carbon content of the residue on ignition (6.1.2.1.4.2), in mass percent;

m_V is the change in mass on calcination (6.1.2.1.4.4), in mass percent.

The factors f_1 and f_2 used in Formula (9) are calculated using the molar masses of silicon dioxide, M_{SiO2} (60,08 g/mol) silicon carbide, M_{SiC} (40,10 g/mol) and carbon, M_C (12,01 g/mol) according to Formulae (10) and (11).

$$f_1 = \frac{\dfrac{M_{SiO2} - M_{SiC}}{M_C} + 1}{\dfrac{M_{SiO2} - M_{SiC}}{M_C}} = 1{,}601\,1 \quad (10)$$

$$f_2 = \frac{M_{SiO2} - M_{SiC}}{M_C} + 1 = 2{,}663\,6 \quad (11)$$

NOTE To obtain precision data for this method, silicon carbide powder samples with a free carbon content <5 mass percent were analysed in an interlaboratory study. The results for repeatability standard deviation s_r, repeatability limit r, reproducibility standard deviation, S_R and reproducibility limit R, as defined in ISO 5725-2 [12] are given in mass% in Table 3.

Table 3 — Precision data for the determination of free carbon

Repeatability		Reproducibility	
s_r	r	S_R	R
0,07	0,20	0,21	0,59

6.1.2.2 Determination of free carbon by calculation

The determination of free carbon is carried out by calculation using the total carbon content, w_{Ctotal}, and silicon carbon content, w_{SiC}, of the sample. The total carbon content of the dried sample is measured by one of the methods described in Clause 5 and the silicon carbide content of the dried sample is measured according to 7.3 or 7.4. This method for determination of free carbon is only applicable if oxidation of silicon carbide during measurement of the silicon carbide content of the sample can be neglected.

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6.1.2.2.1 Calculation

Calculate the mass fraction of free carbon, w_{Cfree}, expressed as a percentage using Formula (12).

$$w_{Cfree} = w_{Ctotal} - w_{SiC} \times 0{,}299\ 5 \qquad (12)$$

where

w_{Cfree}	is the free carbon content of the sample, in mass percent;
w_{Ctotal}	is the total carbon content of the sample determined according to Clause 5, in mass percent;
w_{SiC}	is the silicon carbide content of the sample determined according to 7.3 or 7.4, in mass percent;
0,299 5	is the stoichiometric factor for converting silicon carbide to carbon.

Report the result to the nearest 0,01 %.

7 Determination of silicon carbide content

7.1 General

The determination of silicon carbide, SiC, is carried out by one of the following methods:

— indirect method (7.2),

— combustion methods (7.3 and 7.4): SiC-bound carbon is determined using samples where free carbon was already removed by previous combustion methods.

NOTE Suitable certified reference materials (CRMs) for the verification of the methods are given in Annex B.

7.2 Determination of silicon carbide, SiC, by indirect method

7.2.1 Principle

The carbon bound in silicon carbide is determined by calculation as the difference between the total carbon content determined as described in Clause 5 and the free carbon content determined as described in 6.1.1 or 6.1.2.1. Since a possible oxidation of silicon carbide is considered for the determination of free carbon, this also applies for the determination of the silicon carbide content by this indirect method.

7.2.2 Calculation

Calculate the mass fraction of silicon carbide, w_{SiC}, expressed as a percentage, using Formula (13).

$$w_{SiC} = (w_{Ctotal} - w_{Cfree}) \times 3{,}338\ 3 \qquad (13)$$

where

w_{SiC}	is the silicon carbide content of the sample, in mass percent;
w_{Ctotal}	is the total mass fraction of carbon determined as described in Clause 5, in mass percent;
w_{Cfree}	is the mass fraction of free carbon determined as described in 6.1.1 or 6.1.2.1, in mass percent;
3,338 3	is a stoichiometric factor used for converting carbon to silicon carbide.

Report the result to the nearest 0,1 %.

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7.2.3 Precision

Precision data for the determination of silicon carbide are given in A.1.4. For calculation of silicon carbide content using Formula (13), total carbon was determined by combustion in a resistance furnace with tin as decomposing agent and infrared absorption detection (5.2.1) and free carbon was determined by combustion at 850 °C and infrared absorption or thermal conductivity detection (6.1.1.1).

7.3 Determination of silicon carbide, SiC, by combustion methods

SiC-bound carbon is determined by combustion of a sample already free from C_{free} by previous combustion. For this method, the residue in the combustion boat after determination of free carbon by combustion at 850 °C (see 6.1.1.1) is used. This method for determination of SiC is only applicable if oxidation of silicon carbide during free carbon measurement can be neglected.

7.3.1 Procedure

After measurement of the content of free carbon, w_{Cfree}, according to 6.1.1.1, weigh the combustion boat to the nearest 0,1 mg, remove the residue and homogenize it with an agate mortar. The total carbon content of the residue, w_{CR}, is then measured using one of the methods described in Clause 5.

7.3.2 Calculation

Calculate the mass fraction of silicon carbide, w_{SiC}, expressed as a percentage, using Formula (14).

$$w_{SiC} = \frac{w_{CR} \times m_A \times 3{,}338\ 3}{m_E} \tag{14}$$

where

w_{SiC}	is the silicon carbide content of the sample, in mass percent;
m_E	is the sample mass used for C_{free} determination according to 6.1.1.1, in grams;
m_A	is the mass of the residue after C_{free} determination according to 6.1.1.1, in grams;
w_{CR}	is the total carbon content of the residue of C_{free} determination, in mass percent;
3,338 3	is the stoichiometric factor used for converting carbon to silicon carbide.

Report the result to the nearest 0,1 %.

7.4 Determination of silicon carbide, SiC, by combustion at 750 °C

7.4.1 Principle

The sample is combusted in air at (750 ± 25) °C to remove free carbon. The residue only contains carbon bound in silicon carbide. The total carbon content of the residue is determined and the corresponding silicon carbide content of the residue is calculated. The silicon carbide content of the sample is then calculated considering the mass change during combustion. This method for determination of SiC is only applicable if oxidation of silicon carbide during combustion can be neglected.

7.4.2 Residue production

Pre-treat a combustion boat (unglazed ceramic material) in a muffle furnace at (750 ± 25) °C for 2 h and record the mass m_0. Weigh approximately 3 g of the sample, dried at 110 °C, to the nearest 0,001 g into the combustion boat and record the mass m_1. Place the combustion boat in the muffle furnace at 500 °C for 20 min. Increase the furnace temperature to (750 ± 25) °C and ignite the sample for a further 1 h 30 min. Take the combustion boat out of the muffle furnace and allow it to cool down to room temperature in a desiccator. Weigh the combustion boat and record the mass m_2. Replace the combustion boat in the muffle

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furnace for a further 30 min and check whether there is a further loss in mass. If so, repeat the ignition until a constant mass m_2 is obtained.

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

The sample mass m_E and the mass of the residue m_A is calculated using Formulae (15) and (16).

$$m_E = m_1 - m_0 \tag{15}$$

$$m_A = m_2 - m_0 \tag{16}$$

where

m_E is the sample mass, in grams;

m_A is the mass of the residue after combustion, in grams;

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

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

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

7.4.3 Determination of the total carbon content of the residue

Remove the residue in the combustion boat and homogenize it with an agate mortar. The total carbon content of the residue, w_{CR}, is then measured using one of the methods described in Clause 5.

7.4.4 Calculation

Calculate the mass fraction of silicon carbide in the residue, $w_{SiC\,R}$, in mass percent, using Formula (17).

$$w_{SiC\,R} = w_{CR} \times 3{,}338\,3 \tag{17}$$

where

$w_{SiC\,R}$ is the silicon carbide content of the residue after combustion, in mass percent;

w_{CR} is the mass fraction of carbon in 7.4.3, in mass percent.

3,338 3 is the stoichiometric factor used for converting carbon to silicon carbide.

Calculate the mass fraction of silicon carbide of the dried sample, w_{SiC}, expressed as a percentage, using Formula (18).

$$w_{SiC} = \frac{w_{SiC\,R} \times m_A}{m_E} \tag{18}$$

where

w_{SiC} is the silicon carbide content of the sample, in mass percent;

$w_{SiC\,R}$ is the silicon carbide content of the residue, in mass percent;

m_A is the mass of the residue after combustion (7.4.2), in grams;

m_E is the mass of the sample (7.4.2), in grams.

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Report the result to the nearest 0,1 %.

8 Determination of total silicon content

The standard procedures for the determination of total silicon are described in the following documents:

— ISO 12677[13];

— ISO 26845[23];

— ISO 21587-1[20], ISO 21587-2[21], ISO 21587-3[22];

— ISO 20565-1[14], ISO 20565-2[15], ISO 20565-3[16];

— ISO 21079-1[17], ISO 21079-2[18], ISO 21079-3[19].

According to these standards, silicon (Si) is determined as silica (SiO_2). The total silicon content, w_{Si}, is then calculated using Formula (19):

$$w_{Si} = 0{,}467\,4 \times w_{SiO2} \tag{19}$$

where

w_{Si}	is the total silicon content of the sample, in mass percent;
w_{SiO2}	is the silica content of the sample, in mass percent;
0,467 4	is the stoichiometric factor for converting silicon dioxide to silicon.

9 Determination of free silicon content

9.1 Principle

The free silicon content, $w_{Si\ free}$, is determined by a gas volumetric method. The silicon carbide sample is boiled in an aqueous sodium hydroxide solution whereby hydrogen is formed as a result of the reaction of free silicon with the alkaline solution. The volume of the evolved hydrogen is measured using a gas burette. Interferences caused by other metals present in the sample are removed in a pretreatment step.

9.2 Pretreatment with hydrochloric acid

When other hydrogen forming metals such as aluminium are present in the sample, pre-treat the sample with hydrochloric acid prior to the determination of free silicon in accordance with 9.3.4.

9.3 Determination of free silicon by hydrogen evolution

9.3.1 Reagents

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

9.3.1.2 Sodium hydroxide solution, c(NaOH) = 250 g/l.

9.3.1.3 Sulfuric acid, H_2SO_4, $c(H_2SO_4)$ = 9 mol/l.

9.3.1.4 Methyl orange, $C_{14}H_{14}N_3NaO_3S$, aqueous solution 1 g/l.

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9.3.1.5 Gas burette indicating liquid.

Add a few drops of sulfuric acid, H_2SO_4, (9.3.1.3) and a few drops of methyl orange solution (9.3.1.4) to 500 ml of water.

9.3.2 Apparatus

9.3.2.1 General

Connect the following equipment as shown in Figure 4. Ensure that the apparatus is airtight before the measurement.

9.3.2.2 Electric heating mantle, 600 W.

9.3.2.3 Flat-bottomed flask, 100 ml (alternatively Erlenmeyer flask, 100 ml).

If a flat-bottomed flask (50 ml) and gas burette (50 ml) are used, use half the mass of test portion and half the added sodium hydroxide solution.

9.3.2.4 Allihn condenser, 400 mm.

9.3.2.5 Connector tube, consisting of a glass tube with outside diameter 8 mm, inside diameter 1 mm, and length 100 mm, bent around the centre part at right angles.

9.3.2.6 Hempel gas burette, 100 ml.

NOTE A water-cooling-style gas burette is preferred.

9.3.2.7 Level bottle, 500 ml, connected to the gas burette with a rubber tube and containing gas burette indicating liquid.

9.3.2.8 Insulation plate, of slate or similar material, placed between the gas burette and the electric heating mantle.

9.3.2.9 Analytical balance, capable of measuring to the nearest 0,000 1 g (0,1 mg).

9.3.3 Mass of test portion

The mass of the test portion depends on the free silicon content as shown in Table 4.

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Table 4 — Mass of test portion

Free silicon content % by mass	Mass of test portion g
below 1	5,0
1 to 2	2,5
2 to 3	1,5
3 to 5	1,0
above 5	0,5

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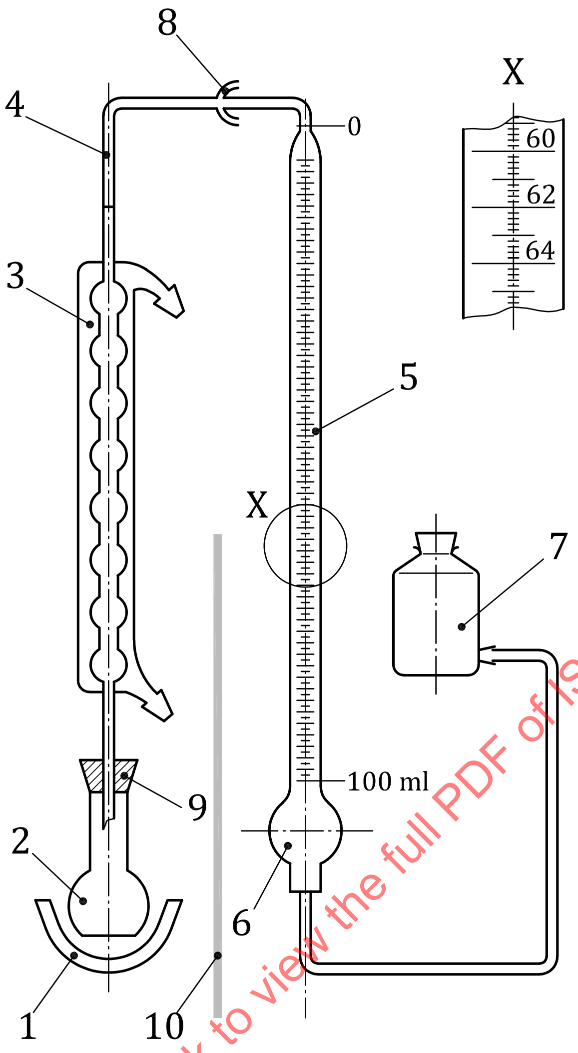

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Key

1 electric heating mantle, 600 W
2 flat-bottomed flask, 100 ml
3 Allihn condenser, 400 mm
4 connector tube
5 Hempel gas burette, 100 ml
6 spherical part of gas burette, 180 ml - 200 ml
7 level bottle, 500 ml
8 spherical joint
9 silicone plug with perforation
10 insulation plate

Figure 4 — Apparatus for determination of free silicon

9.3.4 Procedure

Weigh the sample to the nearest 0,1 mg and transfer to a flat-bottomed flask (9.3.2.3). Add 10 ml of hydrochloric acid, HCl (9.3.1.1), and heat to dryness on a sand bath. After cooling, flow water into the condenser (9.3.2.4), measure the water temperature at the outlet of the condenser and confirm the temperature change within ±1 °C after 10 min. Add 40 ml of sodium hydroxide solution, NaOH (9.3.1.2), to the flat-bottomed flask, connect it to the bottom of the condenser, and put an electric heating mantle (9.3.2.2) under it.

For constant water temperature a cooling and heating circulator is recommended. Place the insulation plate (9.3.2.8) between the electric heating mantle and the gas burette as illustrated in Figure 4 to avoid heating of the gas burette.

Promptly balance the liquid surface of the level bottle to the zero line of gas burette (9.3.2.6) and fix the level bottle (9.3.2.7). Connect the gas burette to the upper part of the condenser by using a connector tube (9.3.2.5) and balance the liquid surface of the level bottle to the liquid surface of the gas burette. Read the scale on the gas burette to the nearest 0,1 ml. Measure the temperature adjacent to the gas burette.

Heat the flat-bottomed flask and lower the level bottle until the liquid surface of the level bottle is matched to the level shown in Figure 4 (spherical part of the gas burette). Keep the solution boiling for 90 min, remove the electric heating mantle and dip the flat-bottomed flask with condenser into cold water. When the temperature reaches the same as that before the reaction, balance the liquid surface of the level bottle to the liquid surface of the gas burette. Then read the scale on the gas burette to the nearest 0,1 ml. The difference to the first reading of the scale of the gas burette corresponds to the volume of hydrogen produced. Measure the temperature and the atmospheric pressure. Do not allow the room temperature to change by more than 3 °C.

9.3.5 Blank test

Carry out the procedure in 9.3.4 without the sample.

9.3.6 Calculation

Calculate the mass fraction of free silicon, $w_{\text{Si free}}$, in the sample, expressed as a percentage, using Formula (20).

$$w_{\text{Si free}} = \frac{(V_1 - V_2) \times f \times 0{,}000\ 627}{m} \times 100 \qquad (20)$$

where

$w_{\text{Si free}}$	is the free silicon content of the sample, in mass percent;
V_1	is the volume of hydrogen produced in 9.3.4, in millilitres;
V_2	is the volume of hydrogen produced in 9.3.5, in millilitres;
f	is the correction coefficient;
m	is the mass of test portion, in grams.

The correction coefficient is calculated using Formula (21).

$$f = \frac{273 \times (p - p')}{(273 + T) \times 101{,}3} \qquad (21)$$

where

f	is the correction coefficient;
T	is room temperature (or temperature of water in thermostat) in degree Celsius;
p	is atmospheric pressure in kilopascals;
p'	the water vapour pressure at T °C, in kilopascals.

Precision data for the determination of free silicon is given in A.1.5.

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10 Determination of free silica content

10.1 Principle

This method is used to determine silica in silicon carbide, silicon nitride and other silica containing materials with a silica content greater than 0,03 %.

The determination of silica is based on the reaction with hydrofluoric acid to hexafluorosilicic acid (H_2SiF_6), separation of H_2SiF_6 by distillation and absorption in aqueous alkaline solution and subsequent determination of silicon in the absorption solution by ICP-OES. This method is not influenced by other silicon compounds, so it is possible to analyse the silica content of materials such as silicon carbide and elemental silicon.

10.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and of known analytical purity. Unless otherwise specified, solutions are aqueous.

10.2.1 Water, distilled or fully demineralized by ion exchange (deionized water).

10.2.2 Sodium hydroxide solution, $c(NaOH)$ = 1 mol/l.

10.2.3 Hydrofluoric acid, concentrated, ρ = 1,13 g/ml, $c(HF)$ 40 % by mass = 22,6 mol/l.

WARNING — Concentrated hydrofluoric acid should be handled with special care, be aware of local safety regulations.

10.2.4 Hydrofluoric acid, diluted, $c(HF)$ = 1 mol/l.

10.2.5 Boric acid, H_3BO_3.

10.2.6 Silicon calibration stock solution, $c(Si)$ = 1 g/l.

10.3 Apparatus

Normal laboratory apparatus and the following.

10.3.1 Analytical balance, capable of measuring to the nearest 0,05 mg.

10.3.2 Reaction vessel, such as a glassy carbon crucible with cover, or PTFE/PFA vessel with a screw cap. The cover or screw cap shall have a gas outlet in the centre and a small hole located off-centre (see Figure 5).

10.3.3 Absorption flask, polyethylene, 100 ml volumetric flask.

10.3.4 Heating-block, with thermocouple and temperature control from 50 °C to 150 °C.

10.3.5 Silicone-tubing, with stopcock.

10.3.6 PTFE-tubing and PTFE-stopper.

10.3.7 Electric suction-pump.

10.3.8 ICP-OES-spectrometer.

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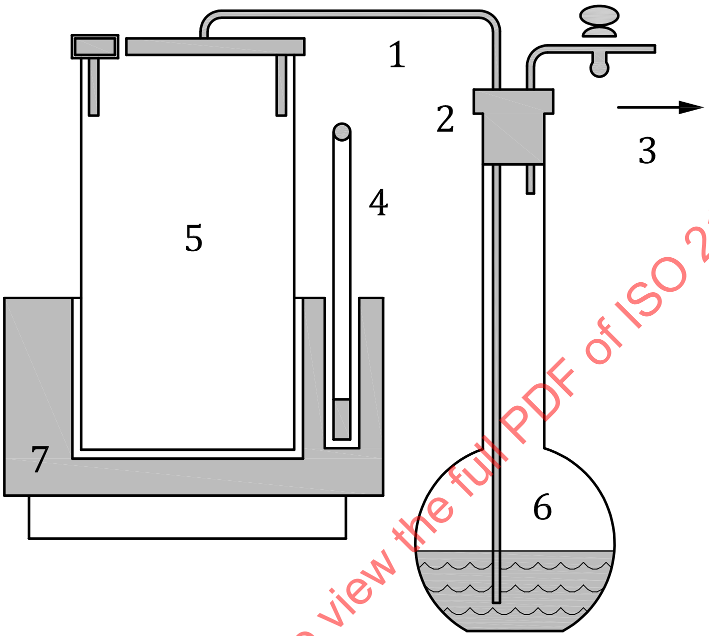
10.4 Sample preparation

Dry the test sample (sampled as described in ISO 21068-1) to constant mass at (110 ± 10) °C for a minimum of 2 h prior to analysis.

10.5 Procedure

Condition the absorption flask (10.3.3) overnight by filling the flasks with diluted HF solution (10.2.4). Depending on the expected SiO_2 concentration, weigh from 20 mg to 2 g, to the nearest 0,1 mg into the reaction vessel (10.3.2). Empty the absorption flask, rinse with water (10.2.1) and fill the absorption flask with 50 ml NaOH solution (10.2.2) and assemble the apparatus as shown in Figure 5.



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Key

1 PTFE tube
2 PTFE stopper
3 silicone tubing with stopcock to suction pump
4 thermocouple
5 reaction vessel
6 absorption flask with absorption solution
7 heating block with temperature control

Figure 5 — Apparatus for determination of free silica

Switch on the suction-pump (10.3.7) and carefully open the stopcock (10.3.5) to provide an air stream in the absorption flask producing about 10 bubbles/s. Take care that the cover of the reaction vessel closes tightly and control the tightness of the whole system.

NOTE A stream of air can enter the reaction vessel through the small hole in the cover of the glassy carbon crucible (or the screw cap of the PTFE/PFA vessel).

Adjust the temperature of the heating-block (10.3.4) to (50 ± 5) °C and pipette 2 ml of concentrated hydrofluoric acid (10.2.3) through the hole in the cover of the glassy carbon crucible (or the screw cap of the PTFE or PFA vessel).

Increase the temperature to (100 ± 5) °C within 15 min and maintain that temperature for 45 min. The hydrofluoric acid in the reaction vessel was then distilled to the absorption flask. To ensure the reaction is complete, heat the reaction vessel to (150 ± 5) °C and switch off the heater 5 min after that temperature is

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attained. Allow the reaction vessel to cool to ambient temperature, remove the cover and rinse the inside of the PTFE tube with water into the absorption flask. Close the stopcock, switch off the pump and remove the PTFE tube from the absorption flask while rinsing the tube with water.

Finally, add 1 g of H_3BO_3 (10.2.5) to the solution in the absorption flask, dilute to volume with water and mix it thoroughly.

For the silicon measurement prepare a blank solution by adding 50 ml NaOH solution, 2 ml concentrated HF, and 1 g H_3BO_3 into a 100 ml polyethylene volumetric flask, dilute to volume with water and mix thoroughly.

Prepare a calibration solution by adding 50 ml NaOH solution, 2 ml concentrated HF and 1 g H_3BO_3 into a 100 ml polyethylene volumetric flask. Depending on the expected silicon concentration of the sample solution in the absorption flask, pipette an appropriate volume of the silicon calibration stock solution (10.2.6) into the volumetric flask. Dilute to volume with water and mix thoroughly. The silicon concentration of the calibration solution should be higher than the silicon concentration of the sample solution. Blank solution and calibration solution are used to establish a 2-point calibration of the ICP-OES.

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10.5.1 Determination

Determine the silicon concentration of the sample solution by ICP-OES following the manufacturer's instructions.

10.5.2 Calculation and expression of SiO_2 content

Calculate the SiO_2 content, w_{SiO2}, as a percentage by mass using Formula (22):

$$w_{SiO2} = \frac{C_{Si} \times V \times f}{10 \times m_E} \quad (22)$$

where

w_{SiO2} is the silica content of the sample, in mass percent;

C_{Si} is the silicon concentration in the sample solution, in milligrams per liter;

V is the volume of the absorption flask, in millilitres;

m_E is the mass of the sample, in milligrams;

f is the stoichiometric factor for converting Si to SiO_2 = 2,139 3.

Express the result to the nearest 0,01 %.

NOTE To obtain precision data for this method, a silicon carbide powder sample with a SiO_2 content of 0,5 mass percent was analysed in an interlaboratory study. The results for repeatability standard deviation s_r, repeatability limit r, reproducibility standard deviation, S_R and reproducibility limit R, as defined in ISO 5725-2 [12] are given in mass percent in Table 5.

Table 5 — Precision data for the determination of free silica

Repeatability		Reproducibility	
s_r	r	S_R	R
0,007	0,02	0,018	0,05

11 Determination of surface silica content

If required, determine the surface silica content as described in ISO 9286:2021, 4.5.

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12 Expression of results

The test results shall be expressed in accordance with ISO 21068-1.

13 Test report

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

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Annex A
(informative)

Precision data

A.1 Precision data obtained for the analysis of refractories containing carbon and/or silicon carbide

NOTE For evaluation of precision data an interlaboratory study was carried out. Based on the results of the participating laboratories precision data was calculated according to ISO 5725-2 [12].

A.1.1 Samples

a) R001: ACS, Alumina-carbon-silicon carbide brick

b) R002: MC, Magnesia-carbon brick

c) R003: SC, Silicon carbide brick

d) R004: ACS, Alumina-carbon-silicon carbide brick

e) R006: ACS, Alumina-carbon-silicon carbide brick

f) R007: AC, Alumina-silicon carbide brick

g) R008: TC, Taphole clay

h) R009: SC, Silicon carbide raw material

i) R010: AC, Alumina carbon brick

A.1.2 Precision data for the determination of total carbon content

The interlaboratory study was carried out on eight materials. The results are given in Tables A.1 and A.2.

NOTE Total carbon was determined by combustion in a resistance furnace with tin as decomposing agent and infrared absorption detection (5.2.1).

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Table A.1 — Precision data for total carbon

Sample	p_j	n_j	m	s_r	r	v_r	S_R	R	V_R
R001 ACS	9	18	12,64	0,06	0,15	0,44	0,18	0,51	1,44
R002 MC	9	18	15,55	0,13	0,36	0,82	0,26	0,74	1,70
R003 SC	8	16	19,46	0,06	0,18	0,33	0,14	0,41	0,74
R004 ACS	9	18	37,34	0,07	0,20	0,19	0,33	0,94	0,90
R006 ACS	9	18	9,88	0,04	0,12	0,42	0,19	0,54	1,97
R007 AC	9	18	4,90	0,02	0,06	0,45	0,20	0,55	4,03
R008 TC	9	18	53,76	0,27	0,76	0,50	0,29	0,81	0,54
R009 SC	9	18	29,92	0,09	0,26	0,31	0,35	0,98	1,17

Key

p_j Number of participating laboratories

n_j Number of accepted single values of all laboratories

m Mean value, in percentage by mass

s_r Repeatability standard deviation, in percentage by mass

r Repeatability limit: $r = 2,8 \times s_r$, in percentage by mass

v_r Variation coefficient of the repeatability standard deviation, in percentage relative

S_R Reproducibility standard deviation, in percentage by mass

R Reproducibility limit: $R = 2,8 \times S_R$, in percentage by mass

V_R Variation coefficient of the reproducibility standard deviation, in percentage relative

Table A.2 — Single values for total carbon, percentage by mass

Laboratory		R001	R002	R003	R004	R006	R007	R008	R009
		ACS	MC	SC	ACS	ACS	AC	TC	SC
L_1	n_1	12,78	15,65	—	37,17	10,07	4,88	53,51	30,82
	n_2	12,81	15,88	—	37,32	10,12	4,87	53,52	30,70
L_2	n_1	12,68	15,57	19,25	37,29	9,76	4,79	53,90	29,80
	n_2	12,61	15,81	19,19	37,29	9,79	4,82	53,55	29,65
L_3	n_1	12,48	15,72	19,41	37,11	9,71	4,71	53,56	29,73
	n_2	12,40	15,82	19,57	36,98	9,70	4,75	53,19	29,68
L_4	n_1	12,49	15,06	19,40	37,02	9,71	4,80	54,22	30,14
	n_2	12,48	15,26	19,29	37,08	9,69	4,85	53,55	30,05
L_5	n_1	12,69	15,77	19,51	37,37	9,84	5,07	53,98	29,78
	n_2	12,76	15,54	19,60	37,44	9,93	5,08	54,15	29,82
L_6	n_1	12,91	15,21	19,64	38,10	10,26	5,35	53,99	29,45
	n_2	13,06	15,04	19,59	38,13	10,30	5,33	53,59	29,75
L_7	n_1	12,69	15,63	19,49	37,07	9,87	4,82	54,15	29,84
	n_2	12,57	15,64	19,42	37,27	9,74	4,79	53,68	29,92
L_8	n_1	12,45	15,57	19,35	37,24	9,78	4,71	53,70	29,84
	n_2	12,48	15,35	19,41	37,21	9,74	4,74	54,15	29,79
L_9	n_1	12,54	15,67	19,57	37,53	9,86	4,93	53,67	29,90
	n_2	12,55	15,72	19,64	37,58	9,84	4,94	53,70	29,96

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