INTERNATIONAL STANDARD

ISO 21068-3

First edition
2008-08-01

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

Reference number
ISO 21068-3:2008(E)

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

Published in Switzerland

Contents

Page

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).

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

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

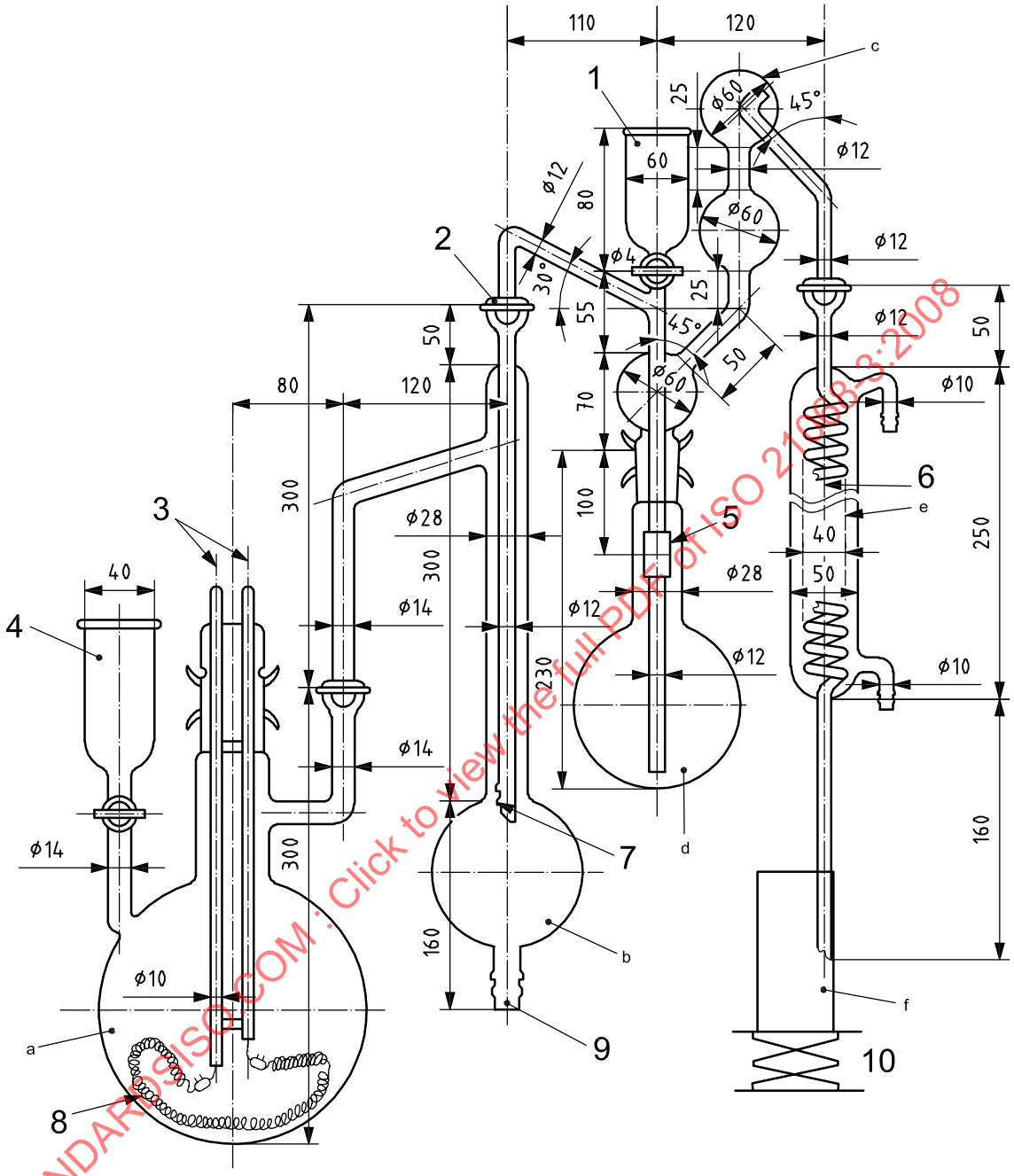
5.2.3.1 Pressurization vessel, for decomposition; the inner cap and the vessel are made of ethylene 4-fluoride resin and outer cap and pressure-resistant container are made of stainless steel.

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

5.2.3.2.1 **Flask**, 2,5 l, for generation of steam, attached to a funnel with a stopcock and an outlet tube for the steam, and an electric heater (using 1 kW Nichrome wire).

5.2.3.2.2 **Trap**, having a rubber tube with pinchcock connected to the bottom tube on the sphere. The nozzle of the inner tube for steam has several small holes.

5.2.3.2.3 **Sphere and tube**, with an inlet tube for steam, a funnel with a stopcock and a trap guarding against splashing. The inlet tube from the trap (see Figure 1, footnote b) is cut to size and connected by a rubber tube to the lower inlet tube inside of the distillation flask (see Figure 1, footnote d). This allows rapid changing over of the lower inlet tube which dips into the NaOH solution. Replace both the inlet and rubber tubes when they show signs of being attacked.

5.2.3.2.4 **Distillation flask**, 750 ml.

5.2.3.2.5 **Graham condenser**.

5.2.3.2.6 **Collecting vessel**, 300 ml tall beaker.

5.2.4 Mass of test portion

The mass of test portion depends on the silicon nitride content, as shown in Table 1.

Table 1 — Mass of test portion

Silicon nitride content % by mass	Mass of test portion g
below 10	1,0
10 to 20	0,5
above 20	0,3

5.2.5 Procedure

Weigh the sample into a platinum crucible (No. 20), put it in a resin vessel, add 5 ml of sulfuric acid (1+1) and 10 ml of hydrofluoric acid. Put the vessel into a pressure-resistant container with an inner cap, fasten an inner cap tightly, and heat at 160 °C ± 5 °C in an air bath for about 16 h.

After cooling, remove the outer and inner caps, pick up the platinum crucible using a pair of plastic tweezers, and transfer the solution into a 100 ml plastic beaker. Wash the platinum crucible, the tweezers, the inner cap, and the resin vessel with a small amount of water, add the washings to the beaker, add 5 g of boric acid and dissolve.

Transfer the solution into a distillation flask. Set up the distillation apparatus, add 50 ml of 0,1 mol/l amidosulfonic acid to a collecting vessel and immerse the end of the Graham condenser in the solution in the collecting vessel. Pour in 50 ml of sodium hydroxide solution (500 g/l) from the funnel of the distillation flask, wash the funnel with water until there is a total of about 150 ml of liquid and then close the stopcock to the funnel.

When a new distillation apparatus is used or when a distillation apparatus has not been used for a long period, the apparatus should be washed in advance by distillation without cooling water at the Graham condenser.

Commence steam distillation. When the liquid volume in the collecting vessel reaches 170 ml, lower the collecting vessel so that it is level with the top of the Graham condenser rather than the surface of liquid, and continue the steam distillation until 200 ml of the liquid volume is collected.

Open the pinchcock on the bottom tube of the trap when steam starts to be generated, and close it when the steam flow maintains 4,5 to 5,0 ml per minute after adjustment of the heater.

Wash the ends of the outer and inner sides of the Graham condenser, and the inner side of the ball joint attached to it, with a small amount of water.

Titrate the distillate with 0,1 mol/l sodium hydroxide solution, using a pH meter equipped with a glassy electrode until pH 5,5 as end point and calculate the volume of 0,1 mol/l sodium hydroxide solution used.

5.2.6 Measurement of recovery rate

Weigh 0,280 g of ammonium sulfate (5.2.2.5), to the nearest 0,1 mg, into a platinum crucible (No. 20), and carry out the procedure given in 5.2.5.

Calculate the recovery, R, as a percentage using Equation (4).

$$R = \frac{(50{,}00 \times F - V \times F') \times 0{,}001\,400\,7}{m_s \times 0{,}212\,0} \times 100 \tag{4}$$

where

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

V is the used volume of 0,1 mol/l sodium hydroxide solution, in millilitres;

F' is the factor of 0,1 mol/l sodium hydroxide solution;

m_s is the mass of ammonium sulfate weighed, in grams.

5.2.7 Calculation

Calculate the mass fraction of silicon nitride, $w_{Si_3N_4}$, expressed as a percentage, using Equation (5).

$$w_{Si_3N_4} = \frac{(50{,}00 \times F - V \times F') \times 0{,}003\,507\,2}{m} \times \frac{100}{R} \times 100 \tag{5}$$

where

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

V is the volume of 0,1 mol/l sodium hydroxide solution used (see 5.2.2.8), in millilitres;

F' is the factor of 0,1 mol/l sodium hydroxide solution;

R is the recovery rate in 5.2.6, in percent;

m is the mass of test portion weighed, in grams.

5.3 Acid decomposition — Photometry method

5.3.1 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 added to it. The resulting solution is transferred into a distillation flask. Sodium hydroxide is added to the flask, steam distillation is carried out and the ammonia distillate is absorbed into sulfuric acid. Sodium hypochlorite and sodium phenolate are added to a portion of the absorbed solution and the absorbance of the developed indo-phenol blue is measured.

5.3.2 Reagents

5.3.2.1 Sulfuric acid, 0,05 mol/l.

5.3.2.2 Sodium hydroxide solution, 200 g/l.

Dissolve 20 g of sodium hydroxide in water and dilute to 100 ml with water. The reagent should be prepared freshly as required.

5.3.2.3 Sodium phenolate solution.

Dissolve 25 g of phenol in 55 ml of sodium hydroxide solution (200 g/l), cool to room temperature, add 6ml of acetone, and dilute to 200 ml with water. The reagent should be freshly prepared on each occasion.

5.3.2.4 Sodium thiosulfate solution, 0,1 mol/l.

Transfer 26 g of sodium thiosulfate pentahydrate and 0,2 g of sodium carbonate into a 1 l volumetric flask, add 1 l of oxygen-free water to dissolve it, and store in an airtight container. Allow to stand for 2 days before use.

Heat the required amount of potassium iodate (reference material for volumetric analysis or high-purity reagent above 99,99 % by mass) at 130 °C for a minimum of 2 h, and cool in a desiccator. Weigh 0,9 g to 1,1 g of potassium iodate and transfer, to the nearest 0,1 mg, into a 250 ml volumetric flask. Add the minimum amount of water required to dissolve it, and further dilute with water to 250 ml. Pipette 25 ml from the volumetric flask into a 200 ml interchangeable ground Erlenmeyer flask. Add 2 g of potassium iodide and 2 ml of sulfuric acid (1+1) to the Erlenmeyer flask. After immediately stoppering, shake it gently, and allow to stand for 5 min in a dark place. As an indicator, add starch solution, and titrate it with the 0,1 mol/l sodium thiosulfate solution. Then add about 0,5 ml of starch solution when the colour of the solution fades to a faint yellow which shows the end point is near. The end point is when the blue colour of the solution has just disappeared.

Separately, transfer 25 ml of water and 2 g of potassium iodide into a 200 ml interchangeable ground Erlenmeyer flask. Add 2 ml of sulfuric acid (1+1). After immediately stoppering, shake gently until completely disolved, and allow to stand for 5 min in a dark place. Carry out the blank test under the same conditions as above, and correct the volume needed for titration.

Calculate the factor, F, of the 0,1 mol/l sodium thiosulfate solution using Equation (6).

$$F = \frac{m_{\mathrm{p}} \times \frac{25}{250}}{0{,}003\,566\,7 \times V} \cdot \frac{A}{100} \tag{6}$$

where

m_{p} is the mass of potassium iodate weighed out, in grams;

A is the purity of potassium iodate, expressed as a percentage by mass;

0,003 566 7 is the mass of potassium iodate equivalent to 1 ml of 0,1 mol/l sodium thiosulfate solution, in grams;

V is the volume of 0,1 mol/l sodium thiosulfate solution needed for titration, in millilitres.

5.3.2.5 Sodium hypochlorite solution, effective chlorine 10 g/l.

Determine the effective chlorine of the sodium hypochlorite solution (effective chlorine 5 % to 12 %) and dilute to 10 g/l of effective chlorine with water. The reagent should be prepared freshly as required.

Determine the effective chlorine of the sodium hypochlorite solution as follows.

Transfer 10 ml of sodium hypochlorite solution to a 200 ml volumetric flask and dilute to the mark with water. Transfer precisely 10 ml to a 300 ml Erlenmeyer flask with stopper and dilute to 100 ml with water. Add 1 g to 2 g of potassium iodide and 6 ml of acetic acid (1+1) to it, stopper, shake well, keep it in the dark for 5 min, and titrate with 0,1 mol/l sodium thiosulfate solution. When the yellow colour of the solution becomes fainter, add 2 ml of starch solution as an indicator and titrate until the resulting blue colour of iodostarch disappears. Separately, as a blank test, transfer 10 ml of water, carry out the same procedures as described above, and adjust the titration value using this blank test result.

Calculate the effective chlorine of the sodium hypochlorite solution, N, in grams per litre, using Equation (7).

$$N = V_t \times F \times \frac{200}{10} \times \frac{1}{V} \times 0{,}000\,546 \times 1\,000 \quad (7)$$

where

V_t is the titration volume of 0,1 mol/l sodium thiosulfate solution, in millilitres;

F is the factor of 0,1 mol/l sodium thiosulfate solution;

V is the volume of sodium hypochlorite solution, in millilitres.

5.3.2.6 Ammonium ion standard solution, 1 mg NH^{4+}/ml.

Keep ammonium sulfate in a desiccator overnight. Weigh 3,66 g of ammonium sulfate, dissolve in water, transfer to a 1 000 ml volumetric flask, and dilute to the mark with water.

5.3.3 Apparatus

Use the same pressurization apparatus as described in 5.2.3.1.

5.3.4 Mass of test portion

Weigh 0,5 g of the sample.

5.3.5 Procedure

Carry out the procedure in 5.2.5, but adding 50 ml of sulfuric acid (0,05 mol/l) to the gathering vessel instead of 0,1 mol/l amidosulfonic acid solution.

Transfer the distillate into a 250 ml volumetric flask and dilute to the mark with water. Transfer an aliquot of this solution to a 50 ml volumetric flask and dilute to about 25 ml with water.

NOTE The volume of the aliquot portion of the stock solution depends on the content of silicon nitride (percent), as shown in Table 2.

Table 2 — Aliquot portion of stock solution

Silicon nitride content % by mass	Aliquot of stock solution ml
below 0,5	10
0,5 to 1	5
above 1	2

Add 10 ml of sodium phenolate solution to a 50 ml volumetric flask and shake it, add 5 ml of sodium hypochlorite solution (effective chlorine 10 g/l), dilute to the mark with water, allow to stand at 25 °C ± 2,5 °C for about 30 min.

Transfer a portion of the solution to a 10 mm cell and measure the absorbance at a wave-length around 630 nm against water as a reference.

5.3.6 Blank test

Carry out the procedure in accordance with 5.3.5 without the sample.

5.3.7 Plotting of calibration graph

Dilute the ammonium ion standard solution precisely 2 000 times with water, transfer a range from 0 ml to 25 ml (0,0 mg to 0,125 mg as ammonium ion) of the diluted solution to several 50 ml volumetric flasks, dilute to about 25 ml with water. Carry out the procedure described in 5.3.5 and plot the relation between the absorbance and mass of ammonium ion, and prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

5.3.8 Calculation

Calculate the mass fraction of silicon nitride, $w_{Si_3N_4}$, expressed as a percentage, in the sample using Equation (8), with the amount of ammonium ion obtained from the absorbances obtained in 5.3.5 and 5.3.6, and the calibration graph plotted in 5.3.7.

$$w_{Si_3N_4} = \frac{(A_1 - A_2)}{m} \times \frac{250}{V} \times 1{,}944 \times 100 \qquad (8)$$

where

A_1 is the ammonium ion amount in 5.3.5, in grams;

A_2 is the ammonium ion amount in 5.3.6, in grams;

V is the volume of the aliquot portion in 5.3.5, in millilitres;

m is the mass of the test portion, in grams.

5.4 Inert-gas fusion — Thermal conductivity method

5.4.1 Principle

A sample is thermally fused with a co-fusion metal in an inert-gas atmosphere by the impulse method using a graphite crucible, and the resulting nitrogen gas is extracted with other gases. After the obtained hydrogen gas and carbon monoxide are oxidized to water and carbon dioxide respectively, and after their absorption, the remaining gases are sent to a thermal conductivity analyser and the change of the thermal conductivity is measured.

5.4.2 Reagents

5.4.2.1 Inert gas, helium above 99,99 % by volume.

5.4.2.2 Capsule, made of tin or nickel and designated for each apparatus.

5.4.2.3 Co-fusion metal, granular, basket-like, or pellet tin or nickel, made from a different sort of metal from the capsule metal.

5.4.2.4 Calibration sample, comprising powdered standard materials, powdered silicon nitride with a known nitrogen percentage.

5.4.3 Apparatus

5.4.3.1 Graphite crucible, suitable for an impulse furnace. Examples are shown in Figure 2.

Dimensions in millimetres

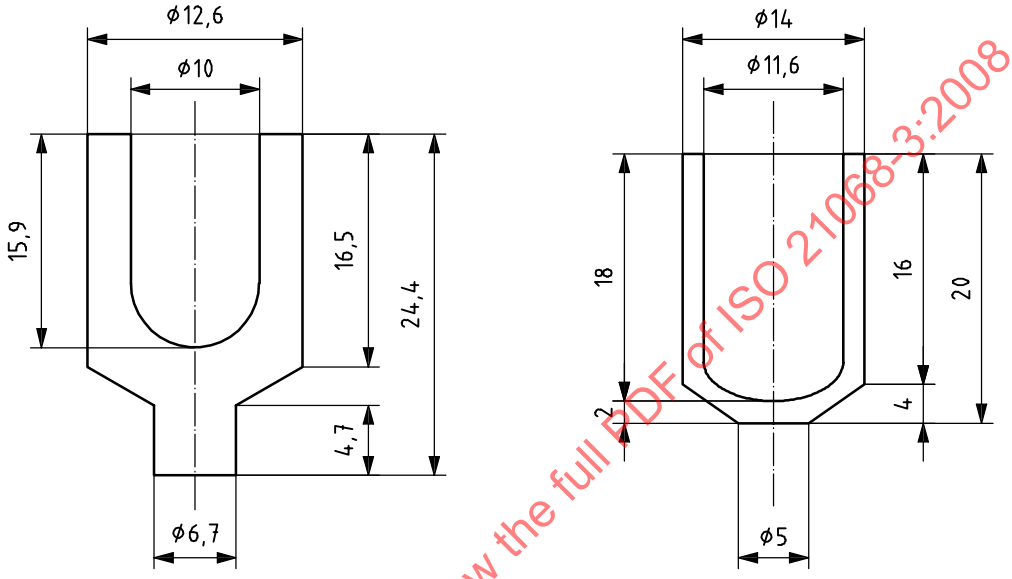
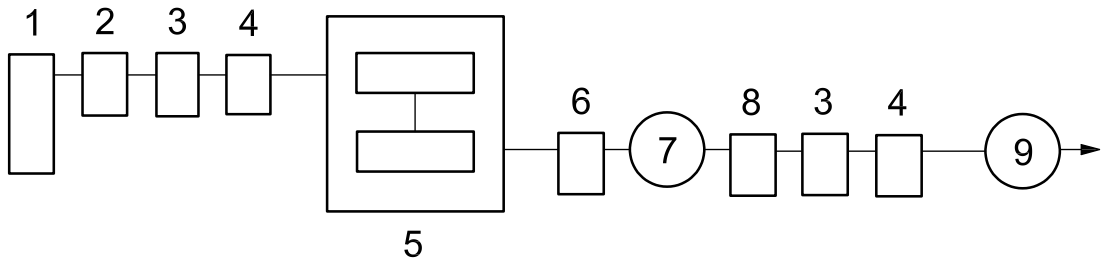
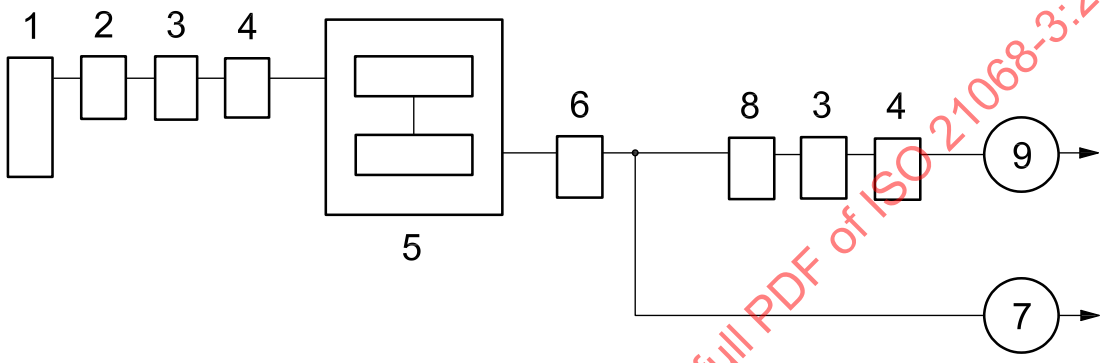


Figure 2 — Examples of graphite crucible for impulse furnace

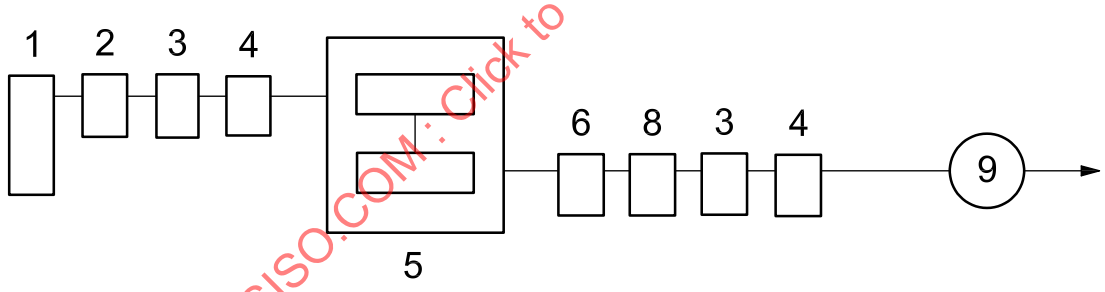
5.4.3.2 Nitrogen determination apparatus, composed of the components given in 5.4.3.2.1 to 5.4.3.2.3. A schematic diagram of the apparatus for inert-gas fusion thermal conductivity determination of nitride is shown in Figure 3.



a) Nitrogen/oxygen analyser type (1 pass type)



b) Nitrogen/oxygen analyser type (2 passes type)



c) Nitrogen analyser type

Key

1 helium
2 deoxidizing tube with electric furnace
3 carbon dioxide absorbing tube
4 dehydration tube
5 impulse furnace
6 dust tube
7 infra-red analyser
8 oxidizing tube with electric furnace
9 thermal conductivity analyser

Figure 3 — Apparatus for inert-gas fusion thermal conductivity determination of nitrogen

5.4.3.2.1 Inert-gas refining part, composed of a deoxygenating tube (for example, reducing copper) with electric furnace, a carbon dioxide absorbing tube (soda lime) and a dehydration tube (magnesium perchlorate – for dryness).

NOTE One type of apparatus has a de-nitration tube (sponge titanium).

5.4.3.2.2 Gas extracting part, consisting of a sample loading and an impulse furnace for the inert-gas fusion determination. The furnace is equipped with fixed upper and moveable lower electrodes which are cooled by running water.

The capsule containing the sample is inserted via the sample loading equipment into the graphite crucible (5.4.3.1) in the impulse furnace in an inert-gas atmosphere. The graphite crucible is positioned between the two electrodes and is heated up by the impulse furnace to 3 000 °C.

5.4.3.2.3 Gas separating part, composed of a dust tube (glass wool), an oxidizing tube with electric furnace, copper(II) oxide, a carbon dioxide absorbing tube (soda lime) and a dehydration tube (magnesium perchlorate).

The gas extracted above is transported into a thermal conductivity analyser, where the difference of electric resistances between sample and reference cells are converted into the nitrogen concentration using a previously established calibration.

5.4.4 Mass of test portion

The mass of the test portion depends on the content of silicon nitride , as shown in Table 3.

Because of the low mass of test portion required in this determination, ensure that the sample taken is representative of the bulk.

Table 3 — Mass of test portion

Silicon nitride content % by mass	Mass of test portion g
below 5	0,10 to 0,15
5 to 20	0,05 to 0,10
above 20	0,02 to 0,05

5.4.5 Procedure

Carry out the determination of blank test, calculation of calibration coefficient, and measurement of sample in accordance with the manufacturer's operating instructions and using the procedure given in 5.4.5.1 to 5.4.5.4.

NOTE It is only necessary to carry out the procedures 5.4.5.1 and 5.4.5.2 once if several samples are analysed as a batch on the same day.

5.4.5.1 Switch on the cooling water and inert gas, switch on the apparatus, and wait for the equipment to stabilize. Then carry out a leak check on the inert gas, according to the manufacturer's operating instructions.

5.4.5.2 Place a new graphite crucible in the impulse furnace and de-gas it at a temperature of more than 2 900 °C under the inert-gas flow. Perform some idling cycles at the gas extraction temperature of 2 500 °C for 3 to 4 min and measure the integrated value of thermal conductivity. Repeat this until the integrated values have stabilized to a constant value.

NOTE 1 The temperature adjustment of the graphite crucible is achieved by adjusting an electrical current or voltage. The relationship between temperature and current/voltage has to be achieved before the equipment is used for determinations. The de-gas temperature is about 100 °C higher than the gas extracting temperature.

NOTE 2 The optimum gas extracting temperature is determined beforehand by using a reference material of known nitrogen content.

5.4.5.3 Referring to the manufacturer's operating instructions, add the recommended amount of co-fusion metal to a new graphite crucible and insert the crucible into the impulse furnace. Weigh the sample into the capsule, press and bend the mouth of the capsule using a jig, and place it in the sample loading device. With the inert gas flowing, heat at the de-gas temperature for 3 to 4 min.

NOTE In an apparatus with a feeder of co-fusion metal, co-fusion metal is de-gassed after the degassing of the graphite crucible.

5.4.5.4 Insert the capsule containing the sample into the graphite crucible treated as in 5.4.5.1 and 5.4.5.3, heat at the extraction temperature and measure the integrated conductivities.

It is recommended that the optimum extraction temperature be established by trials using samples with known nitrogen contents.

NOTE Much equipment of the type used for this determination is fully automated, so many of the steps described above are carried out without the need for operator intervention.

5.4.6 Blank test

Carry out the procedure given in 5.4.5 without the sample. Calculate the mean of the integrated values obtained from 3 to 5 consecutive measurements.

5.4.7 Calculation of calibration coefficient

Carry out the procedure given in 5.4.5 using the calibration sample. Calculate the mean of the integrated values obtained from 3 to 5 consecutive measurements and calculate the calibration coefficient using Equation (9).

$$K = \frac{m_c}{A_0 - A_1} \times \frac{w_N}{100} \tag{9}$$

where

K is the calibration coefficient, in grams/integrated value;

m_c is the mass of sample for calibration, in grams;

w_N is the mass fraction of nitrogen for the calibration sample, expressed as a percentage;

A_0 is the integrated value of the calibration sample;

A_1 is the integrated value obtained in 5.4.6.

5.4.8 Calculation

Calculate the mass fraction of silicon nitride, $w_{Si_3N_4}$, expressed as a percentage, using Equation (10).

$$w_{Si_3N_4} = \frac{(A_2 - A_1) \times K}{m} \times 2{,}504 \times 100 \tag{10}$$

where

A_2 is the integrated value obtained in 5.4.5;

A_1 is the integrated value obtained in 5.4.6;

K is the calibration coefficient, in grams/integrated value;

m is the mass of test portion in grams.

5.5 Determination of total nitrogen

5.5.1 Determination of total nitrogen by fusion decomposition

Determine the total nitrogen content as described in 7.3 of EN 12698-1:2007.

NOTE The method is used to determine nitrogen in silicon nitride, Si_3N_4, by fusion decomposition. Analogous methods can be used to determine nitrogen in materials containing not less than 5 % of nitrogen as silicon and aluminium nitrides.

The sample is fused with lithium hydroxide at a temperature of not more than 700 °C ± 25 °C to convert the nitrogen into ammonia. The amount of nitrogen is determined by titration with an acid of known concentration.

5.5.2 Determination of total nitrogen by Kjeldahl distillation

Determine the total nitrogen content as described in 7.4 of EN 12698-1:2007.

The sample is dissolved in hydrofluoric acid under pressure and the nitrogen is distilled over as ammonia into a receiving vessel containing boric acid solution, using an ammonia distillation apparatus, and determined by potentiometric titration.

5.5.3 Determination of total nitrogen by microwave digestion

Determine the total nitrogen content as described in 7.5 of EN 12698-1:2007.

6 Determination of free Iron by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

6.1 General

Free iron can be introduced to materials during manufacture and into powdered samples by the use of milling apparatus that has iron-containing components in its construction. It can interfere with some methods for analysis of silicon-carbide-based materials and as a consequence adversely affects calculation of the total composition of a sample. Therefore it has to be determined to some degree of accuracy to enable allowances to be made for the effects of its presence. These include the following:

a) erroneous and variable results during the determination of total iron by X-ray fluorescence (XRF), because the free iron alloys with the platinum vessels used for fusion;

b) interference with the determination of free silicon by the silver displacement method if the sample is not acid washed, before analysis, to remove the iron;

c) errors in determination and calculations using weight-change measurements (e.g. free carbon in accordance with ISO 10060[2] or Clause 4 of ISO 21068-2:2008) being caused because the iron is oxidized on heating.

Whilst the presence of free iron can be detected by X-ray diffraction, its accurate determination should be carried out by chemical methods. Two methods are described. In the bromine/methanol method the free iron in the dried sample reacts with anhydrous bromine in methanol solution under reflux. After filtration and removal of the methanol, the iron is dissolved in dilute hydrochloric acid. In the copper sulfate method, the free iron is extracted into copper sulfate solution under reflux by displacing copper from solution. The iron content of the solutions from both methods is determined by ICP-AES.

The two methods give results on silicon-carbide-based materials that agree acceptably and have been shown to be accurate. The copper sulfate method has several advantages as it uses fewer toxic and no flammable reagents and requires no evaporation stage. It is consequently more convenient, quicker to carry out and is less expensive. The bromine/methanol method is useful where comparison of results may be required in the case of a new material or doubt.

6.2 Copper sulfate method

6.2.1 Principle

Free iron in the sample reacts under reflux with copper sulfate solution. Undissolved material is removed by filtration and the iron content of the solution determined by inductively coupled plasma optical emission spectroscopy (ICP-AES).

NOTE The procedure describes the determination of free iron in silicon-carbide-based materials up to 1 % iron by mass. Higher contents can be determined by adjusting the sample mass taken accordingly.

6.2.2 Reagents

Use only reagents of analytical grade and prepare all solutions using distilled or deionized water and store in polyethylene bottles.

WARNING — Nitric acid causes severe burns. Prevent inhalation of fumes and contact with skin or eyes. Dilute the concentrated acid in a fume cupboard and wear protective PVC gloves and a face shield.

6.2.2.1 **Nitric acid**, concentrated, density 1,5 g/ml.

6.2.2.2 **Nitric acid solution**, 20 % by volume.

Dilute 200 ml of concentrated nitric acid to 1 l with water.

6.2.2.3 **Copper sulfate**, $CuSO_4 \cdot 5H_2O$.

6.2.2.4 **Copper sulfate solution**, 10 % (mass/volume).

Dissolve 50 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 200 ml of water and dilute to 500 ml.

6.2.2.5 **Standard solution**, containing 1 000 mg/l Fe of spectroscopic grade.

Commercially available, traceable standard solutions may be used.

6.2.2.6 **Matrix solution**.

Dissolve 30 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 200 ml of water, add 100 ml of concentrated nitric acid (6.2.2.1) and dilute to 500 ml.

6.2.2.7 **Calibration solutions**.

Into a series of six 250 ml volumetric flasks add 0,0 ml, 1,00 ml, 2,00 ml, 3,00 ml, 4,00 ml and 5,00 ml of standard solution. To each flask, add 50 ml of matrix solution (6.2.2.6). Dilute to volume at room temperature.

6.2.3 Apparatus

6.2.3.1 **Conical flasks**, 100 ml with a ground-glass B24 socket.

6.2.3.2 **Air condensers**, B24 cone with 100 mm shank length.

6.2.3.3 **Filter apparatus**, preferably the dismountable Buchner type.

6.2.3.4 Inductively coupled plasma atomic emission spectrometer.

6.2.4 Instrument conditions

The measuring parameters will be instrument dependent.

NOTE The Fe 259,94 nm line is preferable.

6.2.5 Procedure

Dry about 5 g of finely powdered sample by heating for at least 2 h in an air oven at 110 °C ± 10 °C. Remove and cool in a desiccator. Weigh accurately about 0,5 g, to the nearest 0,1 mg, of dry sample and transfer to a 100 ml conical flask. Add 30 ml of 10 % (mass/volume) copper sulfate solution (6.2.2.4) and a magnetic stirrer bar and fit an air condenser to the flask. Heat to boiling on a stirrer hotplate and maintain refluxing conditions for 30 min. Allow to cool and filter through the hardened ash-less filter paper on a Buchner funnel. Wash the residue well with hot water to give a filtrate volume of about 150 ml. Transfer the filtrate quantitatively to a 250 ml volumetric flask containing 50 ml of nitric acid solution, 20 % (6.2.2.2). Dilute to volume at room temperature and mix thoroughly.

Repeat the procedure to provide duplicate analysis solutions for each sample.

Prepare a blank solution by following the above procedure omitting the sample.

Calibrate the ICP/AES spectrometer instrument using the calibration solutions. Analyse the sample and blank solutions. At the end, re-run the top and bottom calibration standards as unknowns, to allow compensation to be made to sample solution readings for any changes occurring in instrument sensitivity during the analysis.

6.2.6 Calculation

Calculate the mass fraction of iron, w_{Fe}, expressed as a percentage, using Equation (11).

$$w_{Fe} = \frac{(\rho_s - \rho_b) \times \rho}{\rho_0} \times \frac{0{,}025}{m_d} \qquad (11)$$

where

ρ_s is the observed iron concentration of the sample solution, in milligrams per litre;

ρ_b is the observed iron concentration of the blank solution, in milligrams per litre;

ρ is the iron concentration of the calibration solution, in milligrams per litre;

ρ_0 is the observed iron concentration of the calibration solution, in milligrams per litre;

m_d is the mass of dry sample, in grams.

Report individual values to three decimal places and mean values to two places.

6.3 Bromine/methanol method

6.3.1 Principle

Free iron in the dried sample reacts under reflux with 5 % bromine in methanol solution. Undissolved material is removed by filtration and the methanol removed by boiling in the presence of a little sulfuric acid. The residue is dissolved in dilute hydrochloric acid and the iron content of the solution determined by ICP/AES.

NOTE The procedure describes the determination of free iron in silicon-carbide-based materials up to 2,5 % iron by mass. Higher contents can be determined by adjusting the sample mass accordingly.

6.3.2 Reagents

Use only reagents of analytical grade unless stated to the contrary and prepare all solutions using distilled or deionized water and store in polyethylene bottles.

WARNING — Bromine is toxic and causes severe burns. Prevent inhalation and contact with skin and eyes. Wear protective clothing, gloves and eye protection, and carry out all operations in a fume cupboard.

WARNING — Sulfuric acid causes severe burns. Prevent contact with skin and eyes. Wear protective clothing, PVC gloves and face protection when diluting concentrated acid.

WARNING — Hydrochloric acid causes burns and has an irritating vapour. Prevent inhalation and contact with skin and eyes. Proceed as for sulfuric acid, carrying out the dilution in a fume cupboard.

6.3.2.1 Bromine.

6.3.2.2 Methanol GPR, specially dried.

6.3.2.3 Bromine/methanol, 5 % by volume.

Carefully add 25 ml of bromine to 475 ml of the methanol. Mix and transfer to a dry stoppered vessel. Prepare freshly as required.

6.3.2.4 Sulfuric acid, concentrated, density 1,84 g/ml.

6.3.2.5 Sulfuric acid (1+1 solution).

Carefully add 50 ml of acid to 50 ml of water to a beaker cooled in a water bath. Stir the mixture continuously. Allow to cool and store.

6.3.2.6 Hydrochloric acid, concentrated, density 1,18 g/ml.

6.3.2.7 Hydrochloric acid (1+9 solution).

Add 25 ml of acid to 225 ml of water, mix well and store.

6.3.2.8 Standard solution, containing 1 000 mg/l Fe, spectroscopic grade.

Commercially available, traceable, standard solutions may be used.

6.3.2.9 Calibration solutions.

Into a series of six 50 ml volumetric flasks, pour 0,0 ml, 1,00 ml, 2,00 ml, 3,00 ml, 4,00 ml and 5,00 ml of standard solution. To each flask, add 25 ml of (1+9) hydrochloric acid solution. Dilute to volume at room temperature.

6.3.3 Apparatus

Ordinary laboratory apparatus and the following.

6.3.3.1 Conical flasks, 100 ml with a ground-glass B24 socket.

6.3.3.2 Air condensers, B24 cone with 100 mm shank length.

6.3.3.3 **Filter apparatus**, preferably dismountable Buchner type.

6.3.3.4 **Filter paper**, (hardened ash-less grade).

6.3.3.5 **Inductively coupled plasma atomic emission spectrometer**.

6.3.4 Instrument conditions

The measuring parameters will be instrument dependent.

NOTE The Fe 259,94 nm line is preferable.

6.3.5 Procedure

Dry about 5 g of finely powdered sample by heating for at least 2 h in an air oven at 110 °C ± 10 °C. Remove and cool in a desiccator. Weigh accurately about 0,2 g, to the nearest 0,1 mg, of the dry sample and transfer to a dry 100 ml conical flask. Add 50 ml of 5 % bromine/methanol solution and a magnetic stirrer bar, and fit an air condenser to the flask. Heat to boiling on a stirrer hotplate and maintain refluxing conditions for 30 min. Allow to cool and filter through the hardened ash-less filter paper on a Buchner funnel. Wash the residue well with dry methanol to give a filtrate volume of about 150 ml. Transfer the filtrate quantitatively to a 250 ml beaker, add 5 drops of (1+1) sulfuric acid and some anti-bumping granules. Heat to boiling and evaporate to dryness.

Cool the beaker, add 25 ml of (1+9) hydrochloric acid and heat to gentle boiling to dissolve salts. Cool and transfer quantitatively to a 250 ml volumetric flask. Dilute to volume and mix thoroughly.

Repeat the procedure to provide duplicate analysis solutions for each sample. Prepare a blank solution by following the above procedure but omitting the sample. Calibrate the ICP-AE spectrometer using the calibration solutions.

Determine the iron content of the sample solutions. After reading the contents of the duplicate sample solutions for each sample, record the indicated content of one of the calibration solutions. This latter reading allows compensation to be made to sample solution readings for any changes occurring in instrument sensitivity during the analysis.

6.3.6 Calculation

Calculate the mass fraction of iron, w_{Fe}, expressed as a percentage, using Equation (12).

$$w_{Fe} = \frac{(\rho_s - \rho_b) \times \rho}{\rho_0} \times \frac{0{,}025}{m_d} \qquad (12)$$

where

ρ_s is the observed iron concentration of the sample solution, in milligrams per litre;

ρ_b is the observed iron concentration of the blank solution, in milligrams per litre;

ρ is the iron concentration of the calibration solution, in milligrams per litre;

ρ_0 is the observed iron concentration of the calibration solution, in milligrams per litre;

m_d is the mass of dry sample, in grams.

Report individual values to three decimal places and mean values to two places.

7 Determination of free aluminium and free magnesium

7.1 General

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

a) acid decomposition – ICP-AES (7.2);

b) acid decomposition – FAAS (7.3);

c) the hydrogen generating method (7.4), which can be used for free aluminium.

NOTE Methods a) and b) cannot be applied for the determination of free aluminium or free magnesium corresponding to each compound where the sample contains soluble aluminium or magnesium compounds, except metal aluminium or metal magnesium. For example, where magnesia-graphite brick contains metal aluminium and metal magnesium, the above method can be applied to the determination of free aluminium but cannot be applied to the determination of free magnesium because of the solubility of magnesia clinker as the main material in hydrochloric acid.

7.2 Acid decomposition — Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

7.2.1 Principle

Determination of free aluminium and free magnesium by acid decomposition, using acid decomposition – ICP-AES. The sample is dissolved at room temperature by addition of hydrochloric acid. The emission intensities of each element are measured by ICP-AES.

7.2.2 Reagents

Use only reagents of analytical grade and prepare all solutions using distilled or deionized water.

7.2.2.1 **Hydrochloric acid** solutions, (1+1), (1+5) and (1+50).

7.2.2.2 **Aluminium standard solution**, 1,0 mg Al/ml.

Wash the surface of aluminium (purity more than 99,9 % by mass) with hydrochloric acid solution (1+3), dissolve the oxidized layer, then wash with water, ethanol (99,5 %), and diethyl ether and dry in a desiccator. Weigh 1,000 g of aluminium on a platinum dish, cover with a watch glass, add 50 ml of hydrochloric acid solution (1+1), and heat to dissolve on a steam bath. After cooling, transfer into a 1 000 ml volumetric flask and dilute to the mark with water.

Commercially available, traceable standard solutions may be used.

7.2.2.3 **Magnesium standard solution**, 1,0 mg Mg/ml.

Wash the surface of magnesium (purity more than 99,9 % by mass) with hydrochloric acid solution (1+3), dissolve the oxidized layer, then wash with water, ethanol (99,5 %), and diethyl ether and dry in a desiccator. Weigh 1,000 g of magnesium in a beaker (200 ml), cover with a watch glass, add 30 ml of hydrochloric acid (1+1), and heat to dissolve on a steam bath. After cooling, transfer into a 1 000 ml volumetric flask and dilute to the mark with water.

Commercially available, traceable standard solutions may be used.

7.2.2.4 **Mixed standard solution**, 0,1 mg Al/ml, 0,05 mg Mg/ml.

Transfer 20 ml of aluminium standard solution and 10 ml of magnesium standard solution into a 200 ml volumetric flask precisely and dilute to the mark with water.

7.2.3 Apparatus

Ordinary laboratory apparatus and the following.

7.2.3.1 **Inductively coupled plasma atomic emission spectrometer**.

7.2.4 Mass of test portion

1,00 g of the test sample shall be weighed out for the determination.

7.2.5 Procedure

The measuring parameters will be instrument dependent.

Weigh the sample into a 100 ml beaker, add 30 ml of hydrochloric acid (1+5), cover with a watch glass, and allow to stand at room temperature.

After 16 h, filter with a filter paper (type 5 B) and wash completely with hydrochloric acid (1+50). Transfer the filtrate and washings into a 200 ml volumetric flask and dilute to the mark with water.

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

Transfer precisely an aliquot portion of stock solution into a 100 ml volumetric flask, add 2 ml of hydrochloric acid (1+1), and dilute to the mark with water.

NOTE The volume of the aliquot of the stock solution depends on the content of free aluminium and free magnesium, as shown in Table 4.

Table 4 — Aliquot portions of stock solution

Al_{free} **and** Mg_{free} % by mass	**Free aluminium**	**Free magnesium**
< 1	20	10
1 to 5	10	5
> 5	5	2

Spray a portion of the stock solution into the Ar plasma flame of an ICP-AE spectrometer, and measure the emission intensity at an appropriate wavelength, for example 369,15 nm for Al and 279,55 nm for Mg.

7.2.6 Blank test

Carry out the procedure in 7.2.5 without the sample.

7.2.7 Plotting of calibration graph

Transfer precisely a range from 0 ml to 30 ml portions of the mixed standard solution (0 mg to 3 mg as aluminium and 0 mg to 1,5 mg as magnesium) into separate 100 ml volumetric flasks. Add 2 ml of hydrochloric acid (1+1) to each flask and dilute to the mark with water. Spray these solutions in the same way as the samples (see 7.2.5) and measure the absorptions against the reference solution. Then plot the relations between the emission intensities for each element and mass of each metal component. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

The measurement of the series of calibration solutions should be carried out simultaneously as a pair of measurements of the stock and blank solutions. The calibration line is prepared newly for each measurement.

7.2.8 Calculation

Calculate the mass fractions of aluminium, w_{Al}, and magnesium, w_{Mg}, expressed as a percentage, using Equations (13) and (14), with the amounts of each metal component which are derived from emission intensities in 7.2.5 and 7.2.6, and the calibration in 7.2.7.

$$w_{Al} = \frac{m_1 - m_2}{m} \times \frac{200}{V} \times 100 \quad (13)$$

$$w_{Mg} = \frac{m_3 - m_4}{m} \times \frac{200}{V} \times 100 \quad (14)$$

where

m_1 is the mass of aluminium in 7.2.5, in grams;

m_2 is the mass of aluminium in 7.2.6, in grams;

m_3 is the mass of magnesium in 7.2.5, in grams;

m_4 is the mass of magnesium in 7.2.6, in grams;

m is the mass of the test portion, in grams;

V is the volume of the aliquot portion of the stock solution in 7.2.5, in millilitres.

7.3 Acid decomposition — Flame Atomic Absorption Spectrometry (FAAS)

7.3.1 Principle

Determination of free aluminium and free magnesium by acid decomposition using Flame Atomic Absorption Spectroscopy (FAAS).

The sample is dissolved at room temperature by adding hydrochloric acid. The intensities of each element are measured by the atomic absorption spectrometer.

7.3.2 Reagents

The reagents are as specified in 7.2.2.

7.3.3 Apparatus

Ordinary laboratory apparatus and the following.

7.3.3.1 FAAS spectrometer.

7.3.4 Procedure

NOTE The operating conditions will depend on the instrument used.

Carry out the procedures as given in 7.2.5, except for spraying a portion of the stock solution into the acetylene/dinitrogen monoxide flame of the atomic absorption spectrometer, and measure the absorbance at the wavelength of 309,3 nm for Al and 285,2 nm for Mg

7.3.5 Blank test

Carry out the procedure given in 7.2.5 without the sample.

7.3.6 Plotting of calibration graph

Transfer precisely a range from 0 ml to 30 ml portions of the mixed standard solution (0 mg to 3 mg as aluminium and 0 mg to 1,5 mg as magnesium) into separate 100 ml volumetric flasks. Add 2 ml of hydrochloric acid (1+1) to each flask and dilute to the mark with water.

Spray a portion of these solutions into the acetylene/di-nitrogen monoxide flame of an atomic absorption spectrometer, and measure the absorbance at the wavelength of 309,3 nm for Al and 285,2 nm for Mg and measure the absorbance against the reference solution.

Plot the relations between the emission intensities for each element and mass of each metal component. Prepare the calibration graph by adjusting the curve so that it passes through the point of origin.

7.3.7 Calculation

Calculate the mass fraction of aluminium, w_{Al}, and magnesium, w_{Mg}, expressed as a percentage, using Equations (15) and (16), with amounts of each metal component which are derived from emission intensities in 7.3.4 and 7.3.5, and the calibration in 7.3.6.

$$w_{Al} = \frac{m_1 - m_2}{m} \times \frac{200}{V} \times 100 \quad (15)$$

$$w_{Mg} = \frac{m_3 - m_4}{m} \times \frac{200}{V} \times 100 \quad (16)$$

where

m_1 is the mass of aluminium in 7.3.4, in grams;

m_2 is the mass of aluminium in 7.3.5, in grams;

m_3 is the mass of magnesium in 7.3.4, in grams;

m_4 is the mass of magnesium in 7.3.5, in grams;

m is the mass of the test portion, in grams;

V is the volume of the aliquot portion of the stock solution in 7.2.5, in millilitres.

7.4 Hydrogen generating method

The method described is very susceptible to failure and therefore should be handled with care.

Determine the free aluminium content as described in Clause 6 of EN 12698-1:2007, using the same apparatus as used as for the determination of free silicon described Clause 8 of ISO 21068-2:2008.

This method measures the volume of hydrogen generated by the action of dilute hydrochloric acid on any free aluminium in a sample.

In the presence of free silicon, free aluminium is not quantifiable by this method.

If the sample is known to contain carbonate, then the volume of hydrogen evolved shall be corrected for the known carbonate present.

The free aluminium content can also be determined by evolution of hydrogen using sodium hydroxide. In this case, the volume of hydrogen evolved shall be corrected for the known silicon content. Free iron will also evolve hydrogen; correction shall be made for the known iron content.

8 Analysis of oxides

8.1 General

Determine the content of oxides by the following:

a) wet chemical methods, as described in ISO 26845 and ISO 21587-1 and ISO 21587-2;

b) FAAS and ICP-AES as described in ISO 21587- 1 and ISO 21587-3 (alumino-silica products), ISO 10058-3 (basic products) and ISO 21079-3;

NOTE For products containing chrome, ISO 20565-3 can be used in place of ISO 21587-1.

c) XRF fusion method after ignition of the sample as described in ISO 12677, with modifications to the method as given;

d) determination of oxides after ignition at 850 °C (see 8.5.2).

8.2 Wet methods

Carry out the analysis of oxides as described in ISO 21587-1 and ISO 21587-2 (alumino-silica products), ISO 10058-2 (basic products) or ISO 26845. Take care that specks of infused sample do not make direct contact with platinum ware. Make a modification to the sample mass used to allow for its gain in mass on fusion.

Components such as Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, K_2O, Na_2O may be determined either on the filtrate after removal of total silica (see Clause 7 of ISO 21068-2:2008) or after complete decomposition of the material (see 8.3).

8.3 Flame atomic absorption and/or inductively coupled plasma atomic emission spectrometer

8.3.1 General

Carry out the analysis as described in ISO 21587-1 and ISO 21587-3 (alumino-silica products), ISO 10058-3 (basic products) or ISO 21079-3 but decompose the sample using one of the fusion techniques described in 8.3.2 or 8.3.3 to obtain dissolution.

8.3.2 Sodium carbonate boric acid fusion method

Take a ground sample of 0,5 g ± 0,001 g and place it in a platinum crucible. Add 1,4 g ± 0,000 1 g of fusion mixture (12 parts of anhydrous sodium carbonate and 2 parts of boric acid ground in a sling mill for 10 s), mix well and cover with a platinum lid. Place the crucible on a bench heater for approximately 20 min.

This ensures that the bulk of the silicon carbide reacts at a preliminary low temperature with adequate access of air to prevent significant attack of the platinum crucible. If the initial tests show that free silicon is present, this stage should be carried out with caution.

Remove the crucible from the heater and place in a muffle furnace at 1 200 °C ± 50 °C for 25 min. Remove the crucible from the furnace and allow to cool. Add 1,0 g of anhydrous potassium carbonate, without mixing. Cover the crucible with a platinum lid, replace in the muffle furnace at 1 200 °C ± 50 °C for 5 min. Remove again and cool, then place the crucible and lid in a 250 ml squat beaker containing 100 ml of (1+2) HCl. Heat until dissolution is complete. Pour the dissolved sample into a 250 ml volumetric flask, make up to the mark and mix.

If the melt has a glassy appearance, indicating a high silicon content, modify the dissolution stage by adding 50 ml of distilled water instead of (1+2) HCl. Cover with a watch glass and heat with continuous agitation. Pour the solution into 65 ml of (1+1) HCl and heat with continuous agitation until dissolution is complete.

8.3.3 Lithium metaborate fusion method

Weigh 2 g of lithium metaborate into a clean platinum crucible, fuse at 1 200 °C ± 50 °C, and swirl whilst cooling to coat the walls of the crucible. Weigh the required amount of sample into the crucible. For samples containing free carbon, heat gently at 400 °C ± 25 °C and then gradually to 750 °C ± 25 °C to remove free carbon.

NOTE A pre-ignited sample can be used for analysis.

Add 1 g of vanadium pentoxide and mix carefully. Heat at 820 °C ± 25 °C for 1,5 h with the crucible partially covered. Transfer to the furnace at 1 200 °C ± 50 °C for 15 min. Swirl the contents after 5 min and 10 min, and whilst cooling spread the fusion around the walls to assist extraction.

Cool to ambient temperature and extract with 150 ml of water containing 8 ml concentrated nitric acid, using a magnetic stirrer with vigorous agitation until dissolved. Pour the dissolved sample into a 250 ml volumetric flask, make up to the mark and mix.

FAAS and/or ICP-AES is used to obtain the concentration of Al, Ca, Mg and Si in this solution.

8.4 XRF fusion method after ignition of the sample

8.4.1 General

Carry out the analysis of oxides as described in ISO 12677, with modifications to the methods as given in 8.4.2 to 8.4.4

8.4.2 Loss on ignition

Determine the loss on ignition to maximum mass loss at 750 °C ± 25 °C, making successive ignitions at 15 min intervals. Samples containing carbon or other carbonaceous material will require a burning-out stage over a burner at between 400 °C ± 25 °C and 600 °C ± 25 °C, both to constant mass.

NOTE The time required will vary from a few minutes for samples containing 10 % carbon to overnight or about 16 h for samples containing more than 30 % carbon.

8.4.3 Fusion

Reduce the mass of ignited sample taken in accordance with the known or expected mass fraction of SiC. 1 g of silicon carbide (SiC) will produce 1,5 g of SiO_2 on fusion. The mass of sample required for fusion, M, is given by Equation (17).

$$M = \frac{100 \times m_f}{100 + 0{,}5 w_{SiC}} \tag{17}$$

where

w_{SiC} is the expected mass fraction of SiC in the ignited sample, expressed as a percentage;

m_f is the normal mass of the fused sample, in grams.

The sample shall be protected from the fusion vessel during the initial stages. Line the fusion vessel with a layer of lithium tetraborate or boric oxide. Sinter the sample, well mixed with either lithium carbonate, lanthanum oxide or vanadium pentoxide, on the top of this layer at a temperature that allows the sample to decompose without melting the protective layer. This is achieved by progressively increasing the heat to a point where sintering is observed to take place but no melting of the protective layer occurs. Maintain this temperature until the reaction is complete.

NOTE 1 The reaction of SiC and most of the other reduced species contained in silicon carbide materials is strongly exothermic and silicon carbide forms a eutectic with platinum. The reaction damages the platinum used.

NOTE 2 As vanadium pentoxide might attack silicon carbide, its determination can be required.

Reconstitute the normal flux into masses of sintering agent and protective layer that together have the same mass and composition as the normal flux, in order to allow samples to be analysed on the existing calibrations.

EXAMPLES

1) If the flux is 7,5 g of a 1:4 mixture of lithium tetraborate:lithium metaborate, the sintering agent would be 2,228 g of lithium carbonate, and the protective layer would be 6,60 g lithium tetraborate.

2) If the flux is 7,5 g of lithium tetraborate, then the sintering agent would 3,276 g of lithium carbonate and the protective layer would consist of 6,175 g of boric oxide;

3) If the flux is 10 g of 10 % lanthanum oxide in lithium tetraborate, the sintering agent would be 1,000 g of lanthanum oxide and the protective layer 9,000 g of boric oxide.

Once the sample is completely decomposed in the sintering agent, raise the temperature to allow all the contents to mix and fuse. Prior to casting the melt, the dish and its contents shall be weighed to allow the dilution of the sample in the melt to be calculated and hence correct the results for deviations from the normal dilution factor.

8.4.4 Blanks and slope factors

There are differences in the levels of impurities in the modified fluxes used to decompose silicon carbide materials and those in the normal flux used in calibration. Beads of pure silica and alumina shall be prepared in duplicate, measured by XRF, and the differences in blank levels recorded; these may be negative or positive. The analyses shall be corrected for these blanks. A difference in stoichiometry may lead to slight differences in slope factor both for silica and alumna. Measure any such changes and apply corrections. Differences in slope factor for minor constituents, if any, will not be significant.

8.5 Determination of silicon(IV) oxide, aluminium oxide, iron(III) oxide, titanium(IV) oxide, calcium oxide, magnesium oxide, sodium oxide, potassium oxide, chromium(III) oxide, zirconium oxide, and boron oxide

8.5.1 General

The test sample is obtained from the heat residue at 850 °C and the content of each component is determined by using analytical methods given in 8.5.3.

8.5.2 Measurement of ratio on heat residue at 850 °C

Carry out the determination as described in 4.6 of ISO 21068-2:2008 and use the residue for the determination of the components as described in 8.5.3 and 8.5.4.

8.5.3 Methods of determination of each component

Analytical methods are as follows:

a) analytical methods for refractories, as shown in Table 5;

b) ICP-AES method given in 8.3;

c) XRF analysis method given in 8.4.

Table 5 — Selection of analytical method according to materials

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