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Chemical analysis of nitride bonded silicon carbide refractories

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March 2005

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ICS

English version

## Chemical analysis of nitride bonded silicon carbide refractories

Chemische Analyse von feuerfesten Erzeugnissen aus  
nitridgebundenem Siliciumcarbid

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 187.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

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COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

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## Foreword

This document (prEN 12698:2005) has been prepared by Technical Committee CEN/TC 187 “Refractories”, the secretariat of which is held by BSI.

This document is currently submitted to the CEN Enquiry.

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## 1 Scope

This part of EN 12698 describes the methods for the analysis of all refractory products containing nitride bonded silicon carbide, irrespective of the Silicon carbide level. It includes details of sample preparation, general principles of chemical analysis and detailed methods for the determination of carbon, silicon carbide, free aluminium, free silicon, total nitrogen and oxygen.

Silicon nitride, silicon oxynitride, silicon, free silica and silicon aluminium oxynitride (sialon) can be determined by XRD.

## 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.

EN ISO 21068 *Chemical analysis of silicon carbide refractories*

ISO 3310-1 *Test sieves -- Technical requirements and testing -- Part 1: Test sieves of metal wire cloth*

ISO 5022 *Sampling of shaped refractories*

ISO 8656 *Sampling of unshaped refractories*

ISO 5725 *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests* (standards.iteh.ai)

## 3 Choice of method of determination

A list of methods and the relevant European Standards is given in Table 1.

Table 1 — Methods and relevant European Standards	
Item tested	European Standard
Carbon and silicon carbide	EN ISO 21068
Free silicon	EN ISO 21068
Oxygen	EN ISO 21068
Free aluminium	EN 12698
Total nitrogen	EN 12698
Silicon nitride/oxynitride, free silica	EN 12698
XRD	EN ISO 21068 and EN 12698
Sialon	EN 12698
Free carbon	EN ISO 21068 or EN 12698
Total carbon	EN ISO 21068
Silicon carbide	EN ISO 21068 and EN 12698
Free alumina	EN 12698

Carbon and silicon carbide can be determined by evolution of carbon dioxide on combustion in a stream of oxygen at selected temperatures. The carbon dioxide evolved can be conveniently measured coulometrically, gravimetrically or by infra-red detection by absorption onto soda lime.

Free aluminium can be determined by evolution of hydrogen on treatment with hydrochloric acid and measurement of the gas volume in a nitrometer. Free silicon can be determined on the same sample by treatment with sodium hydroxide after washing by decantation.

Total nitrogen can be determined by a variety of methods.

Distinction between silicon nitride and aluminium nitride can be made by the reaction with sodium hydroxide solution, while aluminium nitride is quantitatively decomposed in this way yielding free ammonia, silicon nitride is unaffected.

A convenient commercial apparatus for the determination of total oxygen consists of an induction furnace in which the sample is heated with pure carbon. Carbon dioxide and carbon monoxide are measured by infra red absorption and the integrated signals are combined to give the total oxygen content.

Specification of many of the constituents can often be made by use of XRD techniques, e.g. free silicon, silicon nitride, silicon oxynitride, quartz and cristobalite peaks.

## 4 Determination of free aluminium

### 4.1 Principle

The volume of hydrogen generated by the action of dilute hydrochloric acid on any free aluminium in a sample is measured.

It is not a very specific method.

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

NOTE 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.

### 4.2 Reagents

Use distilled water or water which has been fully demineralized by ion exchange (de-ionized water) and reagents of analytical grade.

4.2.1 Dilute hydrochloric acid, 1+1 by volume

### 4.3 Apparatus

4.3.1 Nitrometer, as used for the determination of free silicon.

4.3.2 Balance capable of reading to the nearest 0.1 mg

### 4.4 Procedure

Weigh  $0,5000 \text{ g} \pm 0,0100 \text{ g}$  of sample into a clean, dry nitrometer tube. Place a dry ignition tube also inside the tube, and holding the nitrometer tube upright, introduce about 5 ml of dilute hydrochloric acid into the ignition tube, using a long dropping pipette, and without letting any touch the sample.

Carefully fit the bung of the apparatus making sure of a good seal. Equalise the pressure as in the free silicon determination and leave the 3-way tap in a position that connects the sample and graduated tube. Tip the acid out of the ignition tube onto the sample. Shake gently and allow to stand about 15 minutes. Read off the volume after equalising the pressure. Shake gently and read again after another 5 min to 10 min. Record the final volume reading when consecutive readings are the same. Also note the temperature and barometric pressure.

NOTE For frequent use of this method, it is recommended that a conical flask with airtight sample insert device, e.g. a side-on positioned ground-in connection and ground-in stopper with weighing bottle (special version) is used. The weighed sample is placed into the stopper-connected weighing bottle. The hydrochloric acid added to the flask. After equalising of pressure, the sample powder is added to the acid by turning the stopper.

#### 4.5 Calculation and expression of results

Correct the volume reading to the gas volume at Standard Temperature,  $V_{(STP)}$  in ml, using the equation:

$$V_{(STP)} = V_1 \cdot \frac{(P - \rho)}{760} \cdot \frac{273}{(273 + T)} \quad (1)$$

where

$V_1$  is the measured volume, in ml;

$P$  is the atmospheric pressure at time of measurement, in mPa;

$\rho$  is the partial pressure of water vapour at the measured temperature, in mPa;

$T$  is the measured temperature, in °C.

Calculate the percentage of free aluminium,  $A$ , using the equation:

$$A = V_{(STP)} \cdot 0,000804 \cdot \frac{100}{m} \quad (2)$$

where

$m$  is the mass of the sample, in g.

Report the result to the nearest 0,1 %.

## 5 Determination of total nitrogen

### 5.1 Determination of total nitrogen by carrier gas fusion (CGF)

#### 5.1.1 Principle

A sample, prepared as described in clause 5.1.4, is decomposed in a graphite crucible in a stream of carrier gas (helium) by heating to a temperature above 2 400 °C in a resistance furnace (electrode furnace).

The gases released are mainly nitrogen, carbon monoxide and hydrogen. The carbon monoxide and hydrogen are oxidized, respectively, to carbon dioxide and water and then removed by absorption. Alternatively, oxidation may be confined to the carbon monoxide and gases other than nitrogen are removed, for example, using a molecular sieve. The change in thermal conductivity due to the nitrogen component is then measured.



The details of the determination procedure may vary with the type of apparatus used and it is therefore only possible to give general instructions which can be used with any type of apparatus, whose nitrogen content has been determined by an absolute method (see 5.2 and 5.3). Using the gas calibration, the validity of the results shall be confirmed by analysing a reference material having a similar extraction behaviour.

### 5.1.2 Reagents

Use distilled water or water which has been fully demineralized by ion exchange (de-ionized water) and reagents of analytical grade.

5.1.2.1 Helium, having a minimum purity of 99,99 %.

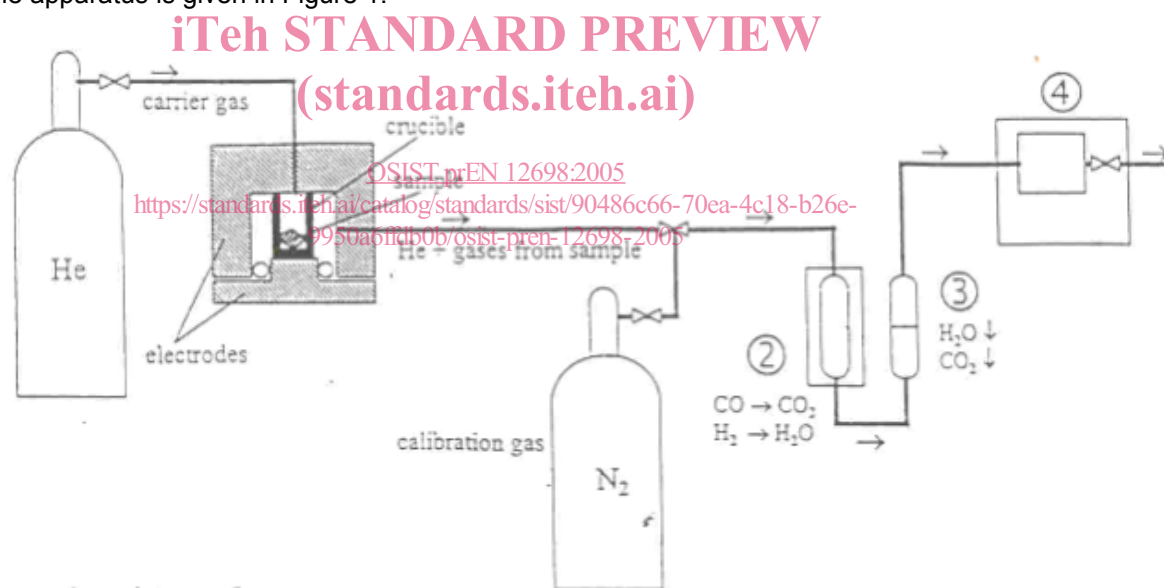
5.1.2.2 Nitrogen, having a minimum of 99,99 %.

5.1.2.3 Catalysts, such as copper oxide.

5.1.2.4 Sorption agents for removing water vapour and carbon dioxide, e.g. magnesium perchlorate, sodium hydroxide on a support, or a molecular sieve.

### 5.1.3 Apparatus

5.1.3.1 Commercially available apparatus consisting of a resistance furnace and a measuring unit for the determination of nitrogen in a stream of carrier gas using a thermal conductivity cell. An example of a suitable apparatus is given in Figure 1.



#### Key

1. Resistance furnace
2. Apparatus for oxidizing carbon monoxide and hydrogen
3. Carbon dioxide and water vapour absorption tubes
4. Thermal conductivity cell

**Figure 1 — Gas flow diagram for the determination of total nitrogen by carrier gas fusion**

5.1.3.2 Analytical balance capable of measuring to the nearest 0,01 mg.

5.1.3.3 Graphite crucibles having approximately the same electrical resistance. The crucibles shall contain only extremely small amounts of nitrogen which can be removed by degassing.

#### 5.1.4 Sampling

Sample shaped and unshaped products using the procedures given in ISO 5022 and ISO 8656 respectively.

In sampling large fragments, take care to collect samples from different points of individual pieces.

Homogenize the sample by reducing the maximum particle size to 150 µm and take the test sample from this material.

#### 5.1.5 Sample preparation

Dry the test sample to constant mass at a temperature of 105 °C ± 5 °C to 135 °C ± 5 °C. It is advisable to encase the sample in tin, nickel or platinum and compress it so that as little air as possible is included. The use of the bath metals as casing materials (capsules or foil) will ensure the formation of a homogeneous melt for the extraction.

NOTE The addition of bath metals, e.g. nickel or tin, may also be necessary to complete the extraction.

#### 5.1.6 Procedure

The mass of the sample depends on the type of apparatus used, but shall not be less than 4 mg.

The lower limit depends on the homogeneity of the sample material and the upper limit on the calibration range of the apparatus; the initial sample mass will depend on the anticipated nitrogen content.

Follow the manufacturer's operating instructions for the apparatus.

Place the crucible in the furnace and degas it at a temperature of about 100 °C above the analysis temperature. Weigh the sample and record its mass to the nearest 0,01 mg. Add the sample to the crucible and heat.

NOTE Reliable analytical results will only be obtained if adequate information relating to sample preparation, procedure, calibration, recalibration and checking, and apparatus maintenance is available from in-house experiments and experience.

#### 5.1.7 Calibration and recalibration

##### 5.1.7.1 Gas calibration

Gas calibration shall be carried out by adding a known amount of nitrogen gas. Calculate the amount of gas added,  $m$  in mg, using the equation:

$$m = \frac{\rho V_T \cdot \rho N_2}{\rho_n (1 + \gamma T)} \quad (3)$$

where

$\rho$  is the corrected barometric pressure, in mPa;

$T$  is the temperature, in °C;

$V_T$  is the gas volume added, in ml at  $T$  °C and  $\rho$  mPa;

$\rho N_2$  is the density of nitrogen gas under standard conditions, i.e. 1,2504 mg/ml;

$\gamma$  is the cubic coefficient of thermal expansion of nitrogen (0,003671 /K);

$p_n$  is the standard pressure, 1013,25 mPa.

By this procedure the linearity of the evaluation curve is fixed. This can also be done with a computer connected to the measuring equipment. The calibration, however, will not provide any information about the efficiency of the extraction process. This can only be determined by analysing suitable reference samples. The latter approach is the only one possible in the case of systems not designed for gas calibration.

#### 5.1.7.2 Calibration using solids

For calibration with solids, the reference material shall be analysed using widely varying sample masses, if possible, covering the entire calibration range of the apparatus. However, the increase in the relative analytical error has to be considered, if smaller sample masses are used.

NOTE If a linearity has been found beforehand by calibration using gas addition or a reference sample, any variation in the analytical result in connection with the initial sample mass can be unambiguously ascribed to an inefficient extraction process.

#### 5.1.8 Checking and maintaining the apparatus

Before a new apparatus is used, the manufacturer's data on the measurement range, the initial sample mass, the reproducibility and the stability shall be checked using suitable samples with known nitrogen contents. The manufacturer's instructions for regular checks and maintenance shall be carried out. The replacement of the oxidation and sorption reagents is particularly important and incorrect results are to be expected if it is not carried out in due time.

#### 5.1.9 Precision of the method

Under the conditions specified, the values of the repeatability limit  $r$  and the reproducibility limit  $R$  as conducted in ISO 5725 are:

$$r = 1 \% \quad \text{OSIST prEN 12698:2005}$$

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$$R = 2 \%$$

NOTE An improved reproducibility and accuracy may be expected if certified reference materials are used for calibration.

### 5.2 Determination of total nitrogen content by fusion decomposition

#### 5.2.1 General

The method referred to in clause 3 of this standard is used to determine nitrogen in silicon nitride,  $\text{Si}_3\text{N}_4$ , 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.

#### 5.2.2 Principle

The sample is fused with lithium hydroxide at a temperature of not more than 700 °C to convert the nitrogen into ammonia. A gentle stream of inert gas is used to transfer the ammonia to a receiving vessel containing boric acid solution and the amount of nitrogen is determined by titration with an acid of known concentration.

#### 5.2.3 Reagents

Use distilled water or water which has been fully demineralized by ion exchange (de-ionized water) and reagents of analytical grade.

**5.2.3.1** Powdered lithium hydroxide, LiOH.

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

**5.2.3.3** Standard 0,1 mol/l hydrochloric or sulfuric acid of known standardization for titration. The coefficient of variation of the standardization shall not exceed 0,001.

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

**5.2.3.5** Inert gas, argon or nitrogen, with a purity of 99,99 % as inert gas.

**5.2.3.6** Sodium carbonate,  $Na_2CO_3$ , 99,95% to 100,05 %.

**5.2.3.7** Dried calcium chloride,  $CaCl_2$ .

## **5.2.4 Apparatus**

**5.2.4.1** Analytical balance, capable of reading to the nearest 0,01 mg.

**5.2.4.2** Apparatus for releasing, carrying over and absorbing ammonia (see figure 2), comprising:

- a) flow meter;
- b) gas washing bottles;
- c) vitreous silica reaction tube with ground joints, stoppers and gas inlet;
- d) unglazed porcelain boats;
- e) tubular furnace, e.g. heated by infrared radiation, capable of being heated to, and maintained at  $(700 \pm 10)$  °C;
- f) vitreous silica wool;
- g) gas inlet tube with ground joint and capillary tip;
- h) absorption vessel.

In this apparatus, the inert gas from a pressurised gas cylinder passes through a gas washing bottle filled with sulphuric acid having a density,  $\rho = 1,84$  g/ml, preceded and followed by an empty washing bottle for safety reasons.

**NOTE 1** No gas purification is necessary if the ammonia content of the inert gas does not exceed 0,005 % by volume.

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

**NOTE 2** The reaction tube may also be a gas-tight ceramic tube with the sample inlet and borosilicate glass ground joint shown in figure 1, which are fused on or attached by means of silicone hoses.

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