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**Preskušanje keramičnih surovin in keramičnih materialov - Neposredno določevanje masnih frakcij nečistoč v prahu in zrnih silicijevega karbida z optično emisijsko spektroskopijo in induktivno sklopljeno plazmo z elektrotermičnim uparovanjem (ETV-ICP-OES)**

Testing of ceramic raw materials and ceramic materials - Direct determination of mass fractions of impurities in powders and granules of silicon carbide by inductively coupled plasma optical emission spectrometry with electrothermal vaporisation (ETV-ICP-OES)

Prüfung keramischer Roh- und Werkstoffe - Direkte Bestimmung der Massenanteile von Spurenverunreinigungen in pulver- und kornförmigem Siliciumcarbid mittels optischer Emissionsspektroskopie mit induktiv gekoppeltem Plasma und elektrothermischer Verdampfung (ETV-ICP-OES)

Essai des matières premières céramiques et des matériaux céramiques - Détermination directe des fractions massiques d'impuretés dans les poudres et les granulés de carbure de silicium par spectroscopie d'émission optique avec plasma induit par haute fréquence avec vaporisation électrothermique (ETV-ICP-OES)

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## **European foreword**

This document (prEN 15991:2024) has been prepared by Technical Committee CEN/TC 187 “Refractory products and materials”, the secretariat of which is held by BSI.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 15991:2015.

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## 1 Scope

This document defines a method for the determination of the mass fractions of the elements Al, Ca, Cr, Cu, Fe, Mg, Ni, Ti, V and Zr in powdered and granular silicon carbide.

Dependent on element, emission lines, plasma conditions and sample mass, this test method is applicable for mass fractions of the above trace contaminations from about 0,1 mg/kg to about 1 000 mg/kg, after evaluation also from 0,001 mg/kg to about 5 000 mg/kg.

NOTE 1 Generally for optical emission spectrometry using inductively coupled plasma and electrothermal vaporization (ETV-ICP-OES) there is a linear working range of up to four orders of magnitude. This range can be expanded for the respective elements by variation of the sample mass or by choosing emission lines with different sensitivity.

After adequate verification, this document is also applicable to further metallic elements (excepting Rb and Cs) and some non-metallic contaminations (like P and S) and other allied non-metallic powdered or granular materials like carbides, nitrides, graphite, soot, coke, coal, and some other oxidic materials (see [1], [4], [5], [6], [7], [8], [9] and [10]).

NOTE 2 There is positive experience with materials like, for example, graphite, boron carbide ( $B_4C$ ), silicon nitride ( $Si_3N_4$ ), boron nitride (BN) and several metal oxides as well as with the determination of P and S in some of these materials.

## 2 Normative references

There are no normative references in this document.

## 3 Terms and definitions

No terms and definitions are listed in this document.

## 4 Principle

For the determination of impurities in silicon carbide, ICP-OES is a suited method. The classic application of ICP-OES is based on the nebulization of sample solutions. For silicon carbide, sample digestion by wet-chemical methods is required to obtain these sample solutions, for example by melt-fusion or acid/pressure-decomposition. These sample digestion procedures are time-consuming, require the use of hazardous chemicals, deteriorate the detection limits due to the dilution of the sample and the possibility of introduction of impurities as well as analyte losses represents a source of systematic errors.

With ETV-ICP-OES, the impurities are measured directly from the powdered silicon carbide sample, thus avoiding sample digestion and the associated disadvantages. Compared to wet-chemical ICP-OES methods, ETV-ICP-OES requires more effort for method development and is therefore particularly suitable when many samples of one matrix are to be measured with high sample throughput and with high detection sensitivity.

In ETV-ICP-OES, sample introduction by nebulization of liquids is replaced by the electrothermal vaporization of solid samples at high temperatures in the graphite tube furnace of the ETV-system.

The sample material, crushed if necessary, is evaporated in an argon carrier-gas stream in a graphite boat in the graphite tube furnace of the ETV-system. A suitable design of the furnace (see Figures 1 and 2) and an optimized gas flow in the transition area between graphite tube and transport tube (see Figure 3) ensure that the sample vapour is transferred into a form that is transported to the ICP-OES with almost no losses (see [5], [6], [7], [8], [10]). Elements, for example titanium or zirconium, forming refractory carbides that are incompletely or not evaporating need to be converted in the graphite tube furnace into a chemical form which easily evaporates. For this purpose, a suitable reaction gas (halogenating agent)

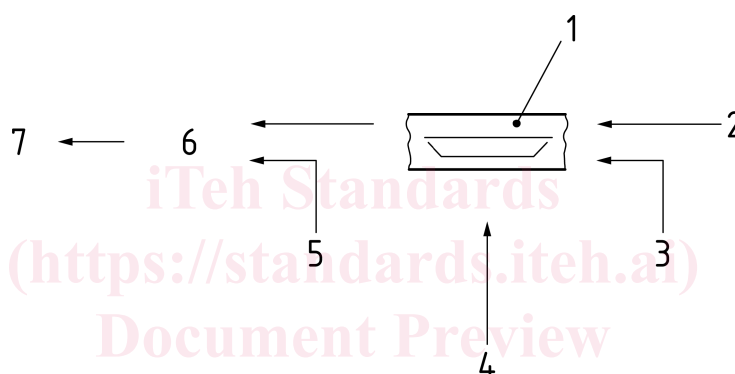
is mixed to the argon carrier-gas stream (see Figures 1 and 2) which converts the carbides into volatile halides (see [1], [3], [5] and [10].)

The evaporation products containing the element traces are transported by the transport tube as dry aerosol to the ICP-torch, injected into the plasma and there excited for the emission of optical radiation (see Figure 2).

## 5 Spectrometry

Optical emission spectrometry is based on the generation of line spectra of excited atoms or ions, where each emission line is associated with an element and the line intensities are proportional to the mass fractions of the elements in the analysed sample.

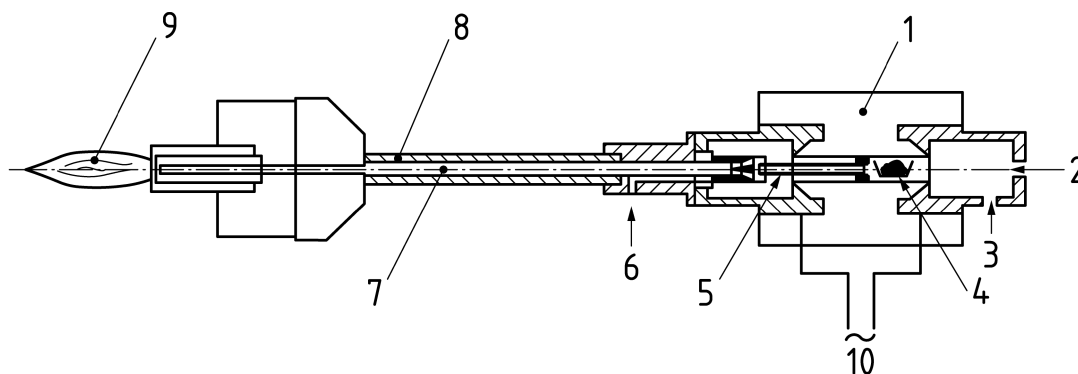
In a simultaneous emission spectrometer in, for example Paschen-Runge- or Echelle-configuration, the optical radiation is dispersed. The intensities of suited emission lines or background positions are registered with applicable detectors like photomultipliers (PMT), charge coupled devices (CCD), complementary metal-oxide semiconductor (CMOS), charge injection devices (CID), and serial coupled devices (SCD). By comparison of the intensities of the element-specific emission lines of the sample with calibration samples of known composition, the mass fractions of the trace elements in the sample are determined.



### Key

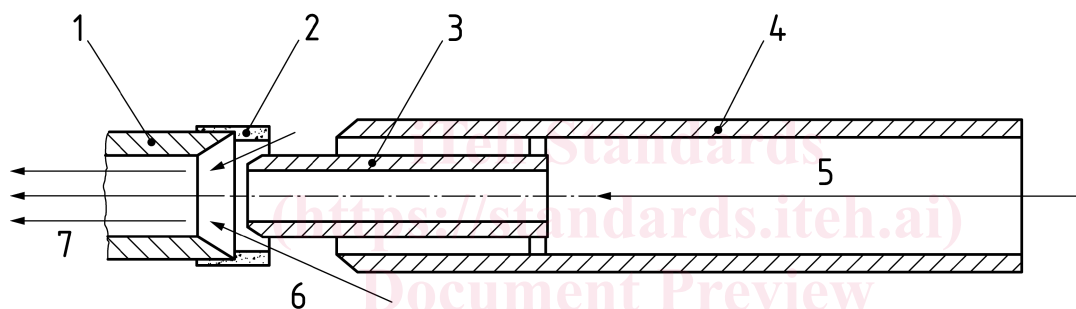
1	graphite tube with graphite boat and sample	5	bypass gas (Ar)
2	carrier gas (Ar)	6	dry aerosol
3	reaction gas (CCl <sub>2</sub> F <sub>2</sub> )	7	to the ICP-torch
4	shield gas (Ar)		

**Figure 1 — Schematic representation of the ETV gas flows**

**Key**

- |   |  |    |  |
|---|--|----|--|
| 1 | graphite tube furnace  | 6  | bypass-gas (Ar)                        |
| 2 | pyrometer  | 7  | dry aerosol to ICP-OES                 |
| 3 | carrier gas (Ar) + reaction gas (CCl <sub>2</sub> F <sub>2</sub> ) | 8  | transport tube                         |
| 4 | solid sample in graphite boat                                      | 9  | inductively coupled plasma of the OES  |
| 5 | evaporation products   | 10 | power supply for graphite tube furnace |

**Figure 2 — Schematic design of the ETV-system/ICP-OES coupling (example)**

**Key**

- |   |                         |   |  |
|---|-------------------------|---|--|
| 1 | alumina transport tube  | 5 | carrier gas (Ar + CCl <sub>2</sub> F <sub>2</sub> ) and evaporation products of the sample |
| 2 | alumina transition ring | 6 | bypass gas (Ar)  |
| 3 | nozzle of graphite tube | 7 | dry aerosol in laminar flow to ICP-OES   |
| 4 | graphite tube           |   |  |

**Figure 3 — Schematic design of the transition area between graphite-tube and transport-tube (example)**

NOTE Figure 1, Figure 2 and Figure 3 show a commercially available ETV-system.

## 6 Apparatus

**6.1 Common laboratory instruments** and laboratory instruments according to 6.2 to 6.7.

**6.2 Inductively coupled plasma optical emission spectrometer (ICP-OES)**, simultaneous, with the possibility to register transient emission signals with a sampling rate of minimum 5 Hz and suited for the synchronised start of ETV vaporization cycle and registration of emission signals.

NOTE Especially for changing matrices the measurement of the spectral background near the emission lines is beneficial, because by this the systematic and stochastic contributions of the measurement uncertainty can be



decreased, the latter only by simultaneous measurement of the background. The use of spectrometers equipped with area- or array-detectors is an advantage in such cases as they allow simultaneous background measurement.

**6.3 Electrothermal vaporization (ETV) system**, with graphite tube furnace with suited transition zone between graphite tube and transport tube for optimized aerosol formation, to be connected to the injector tube of the ICP-torch by a transport tube for example made of alumina ( $\text{Al}_2\text{O}_3$ ), polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA) or polyvinyl chloride (PVC), with controlled gas flows (preferably with mass flow control) and furnace control (preferably with continuous temperature control of the graphite boat by a pyrometer) for a reproducible control of the ETV-system.

NOTE The use of an automatic sample changer improves the reproducibility of measurements.

**6.4 Tweezers**, self-closing, made of a material preventing contamination.

**6.5 Micro spatula**, made of a material preventing contamination.

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

NOTE An analytical balance with a resolution of 0,001 mg can improve the reproducibility of the measurements.

**6.7 Mill or crusher**, made of a material that does not contaminate the sample with any of the analytes to be determined, for example a mortar.

## 7 Reagents and auxiliary material

Only analytical grade reagents shall be used unless stated otherwise.

**7.1 Sample boats**, high-purity graphite (spectral grade) with low porosity, the size adapted to the graphite tube of the ETV-system.

**7.2 Calibration samples** with well-defined mass fractions of trace-impurities, preferably certified reference materials (CRM).

NOTE Certified reference materials are available for main-, minor- and trace-components. (see Annex E.)

**7.3 Calibration solutions**, aqueous single- or multi-element calibration solutions, prepared by dilution of commercially available standard-stock solutions with water to the required concentration.

**7.4 Reaction gas**, Dichlorodifluoromethane ( $\text{CCl}_2\text{F}_2$ ) shall be used as reaction gas for simultaneous determination of the elements listed in Clause 1.

NOTE 1 The results of the interlaboratory study (see Annex A) were obtained using  $\text{CCl}_2\text{F}_2$  as reaction gas.

NOTE 2 Inside the EU, according to the "EC-regulation on substances that deplete the ozone layer" (see [12]), the use of  $\text{CCl}_2\text{F}_2$  is allowed for laboratory and analytical purposes.  $\text{CCl}_2\text{F}_2$  is completely decomposed in the hot graphite furnace and in the downstream inductively coupled plasma. The use of  $\text{CCl}_2\text{F}_2$  for laboratory and analysis purposes is, however, subject to registration at the European Commission (registration on the website of the European Commission, search for "labODS registry").

Alternative reaction gases:

In general, compared to  $\text{CCl}_2\text{F}_2$  the use of alternative reaction gases (halogenating agents) for analysis of silicon carbide can lead for some elements to a deterioration of release behaviour and transport efficiency. The suitability of an alternative reaction gas shall therefore be checked in advance.

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The following alternative reaction gases have been used in practice for ETV-ICP-OES: trifluoromethane ( $\text{CHF}_3$ ), tetrafluoromethane ( $\text{CF}_4$ ), trichloromethane ( $\text{CHCl}_3$ ), chlorodifluoromethane ( $\text{CHClF}_2$ ), 1,1,1,2-tetrafluoroethane ( $\text{C}_2\text{H}_2\text{F}_4$ ), sulphur hexafluoride ( $\text{SF}_6$ ) and nitrogen trifluoride ( $\text{NF}_3$ ). In practice, for  $\text{CF}_4$  a comparable performance to  $\text{CCl}_2\text{F}_2$  could be confirmed.

**7.5 Carrier, bypass and shield gases**, argon (Ar), purity  $\geq 99,996\%$  (volume fraction).

## 8 Sampling and sample preparation

Sampling shall be performed in a way that the sample to be analysed is representative for the total amount of material, for example according to ISO 5022 [13], ISO 8656-1 [14] and EN ISO 21068-1 [15].

If the sample is not received in a dry state, it shall be dried at  $(110 \pm 10)^\circ\text{C}$  until constant mass is achieved ( $<0,5\%$  variation). The sample is then cooled down to room temperature and stored in a desiccator.

NOTE Drying for 2 h is normally sufficient.

The sample material shall have a particle size of  $\leq 50\ \mu\text{m}$ . If necessary, the sample shall be crushed, milled and homogenized. For this, devices suited for the analytical task shall be applied. For porous materials, it shall be checked whether crushing is required.

Crushing is necessary if the transient analysis signals show an unusual long decay (tailing).

## 9 Calibration

The calibration shall be performed for each measuring cycle with calibration samples with defined mass fractions of the elements to be determined. The procedure shall be carried out in accordance with Clause 10. The calibration shall be carried out over a range adapted to the analytical task.

NOTE 1 This can be achieved by different masses of the same calibration sample or same masses of different calibration samples with different mass fractions of the analytes or by a combination of both possibilities.

Calibration samples and the sample to be analysed shall be measured under identical conditions.

Because of the low sample mass used and therefore the resulting scattering of the measurements, the number of calibration samples shall be adapted to the desired accuracy. Practically about 10 to 15 calibration samples have proved to be successful. For example, for 10 calibration samples, five different masses of two different calibration samples with different mass fractions of the analytes are required.

Preferably calibration samples of the same or similar material should be used, if possible certified reference materials (CRM) or matrix-adapted synthetic calibration samples.

The mass fractions of trace-impurities in the calibration samples should be in the same range as of the sample material.

Dependent on the grain size distribution of the sample, the material properties of the material to be analysed and the analytical performance of the used ETV-system for certain analytes and matrices also dried aqueous calibration solutions with or without matrix adaptation may be used for calibration (see [1], [6] to [9] and Annex F). The use of dried aqueous calibration solutions shall be validated by calibration samples or certified reference materials. If such materials are not available the results of alternative analysis methods can be used for comparison.

NOTE 2 For aqueous calibration with matrix adaptation, so-called blank samples are suitable, these are materials with the same matrix as the sample and with mass fractions of trace-impurities negligible to those expected in the sample. The blank sample is weighed into the graphite boat with the same mass as the sample to be analysed, the aqueous calibration solution is added and then dried.

The calibration function for each emission line shall be calculated using the analyte masses of the calibration samples used and the net-intensities of the emission line measured for these analyte masses. A monotonically increasing slope of the calibration functions with a sufficiently high gradient is essential.

NOTE 3 The calculation of the calibration functions is usually carried out as linear regression whereby for the graphical representation of the calibration functions the analyte masses are plotted on the x-axis and the measured net-intensities of the emission lines on the y-axis. A quadratic regression can also be used.

## 10 Procedure

The ICP-OES (6.2) shall be set up in accordance with its operations manual. After an adequate waiting time (20 min is recommended) measurements can be started.

The temperature programme of the ETV-system shall be adjusted to the trace elements to be determined. For this, suited calibration samples shall be used. They also shall be used to select suitable emission lines.

The time interval for the integration of the signal intensity of the emission lines shall be adjusted to the release behaviour of the analytes using the recorded transient emission signals.

Use the sample prepared according to Clause 8 and weigh between 1 mg and 5 mg with a precision of 0,01 mg into the sample boats. Before use, the sample boats shall be cleaned by thermo-halogenation in the graphite tube furnace of the ETV-system at a temperature not lower than the vaporization temperature used for sample analysis.

Dependent on the material, the analytes, the mass fractions of the analytes, the selected emission lines and the ETV-system higher sample masses may be used. The sample masses shall be documented.

Before the analysis run is started, the blank value shall be determined with an empty and cleaned sample boat. A sample boat containing a few milligrams of a calibration sample or a dried calibration solution shall be used to verify that the measuring position for the selected emission lines and background is at optimum position.

The sample boats shall be measured in the following order: dried aqueous calibration solutions (if available) in ascending analyte mass – calibration samples in ascending analyte mass – silicon carbide samples.

The first sample boat is inserted into the furnace of the ETV-system by tweezers (6.4) or by an automated sampler changer. The analysis programme is started, while the vaporization cycle of the ETV-system and the registration of the emission signals by the spectrometer shall be triggered simultaneously.

After the end of the analysis programme the sample boat is removed from the furnace of the ETV-system by tweezers or by an automated sample changer and the next sample boat is inserted into the furnace.

The predefined ETV program for the determination of all the elements indicated in Clause 1 in silicon carbide is to be as follows:

- a) gas flows: carrier gas (7.5) 170 ml/min, bypass gas (7.5) 370 ml/min, reaction gas (7.4) 2,3 ml/min;
- b) conditioning step: 3 s heating from room temperature to 450 °C, 27 s holding time at 450 °C;
- c) vaporization step: 3 s heating to 2 300 °C, 27 s holding time at 2 300 °C;
- d) cooling;
- e) integration interval: 30 s to 60 s after starting the furnace program;
- f) integration time: 30 s. Same integration time for all emission lines or, preferably, individually for each emission line depending of the release behaviour of the analytes.