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Interested committees:

Title: Draft BS EN 15991 BS 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).

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Introduction

This draft standard is based on national and international discussions. Your comments on this draft are invited and will assist in the preparation of the consequent standard.

For international standards, comments will be reviewed by the relevant UK national committee before sending the consensus UK vote and comments to the international committee, which will then decide appropriate action. If the international standard is approved, it is usual for the text to be published as a British Standard.

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Template for comments and secretariat observations

Date: xx/xx/20xx	Document: ISO/DIS xxxx
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1	2	(3)	4	5	(6)	7
MB	Clause No./ Subclause No./Annex (e.g. 3.1)	Paragraph/ Figure/Table/Note	Type of comment	Comment (justification for change) by the MB	Proposed change by the MB	Secretariat observations on each comment submitted
	3.1	Definition 1	ed	Definition is ambiguous and needs clarifying.	Amend to read '...so that the mains connector to which no connection...'	
	6.4	Paragraph 2	te	The use of the UV photometer as an alternative cannot be supported as serious problems have been encountered in its use in the UK.	Delete reference to UV photometer.	

English Version

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)

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)

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)

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

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents	Page
European foreword.....	3
1 Scope.....	4
2 Normative references.....	4
3 Terms and definitions	4
4 Principle	4
5 Spectrometry	5
6 Apparatus.....	6
7 Reagents and auxiliary material.....	7
8 Sampling and sample preparation.....	8
9 Calibration	8
10 Procedure.....	9
11 Emission lines and working range.....	10
12 Calculation of the results and evaluation.....	10
13 Reporting of results.....	10
14 Precision.....	11
14.1 Repeatability.....	11
14.2 Reproducibility	11
15 Test report.....	11
Annex A (informative) Results of interlaboratory study	12
Annex B (informative) Emission lines and working range	17
Annex C (informative) Possible interferences and their elimination	19
Annex D (informative) Information regarding the evaluation of the uncertainty of the mean value.....	22
Annex E (informative) Commercial certified reference materials.....	23
Annex F (informative) Calibration using aqueous solutions and powdered calibration samples	24
Bibliography.....	27

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.

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)

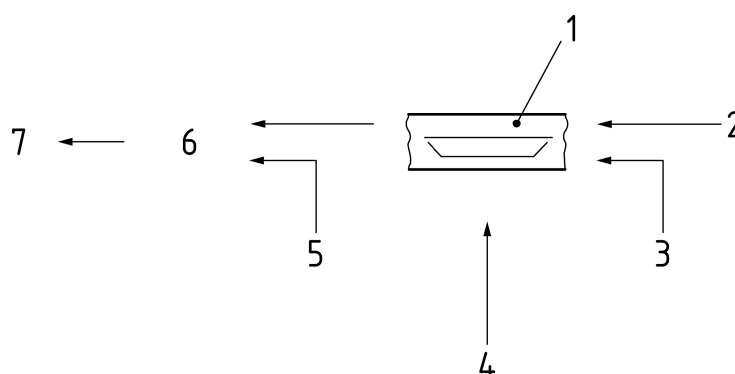
is mixed to the argon carrier-gas stream (see Figures 1 and 2) which converts the carbides into volatile halides (see [1], [3], [5] and [10].)

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.

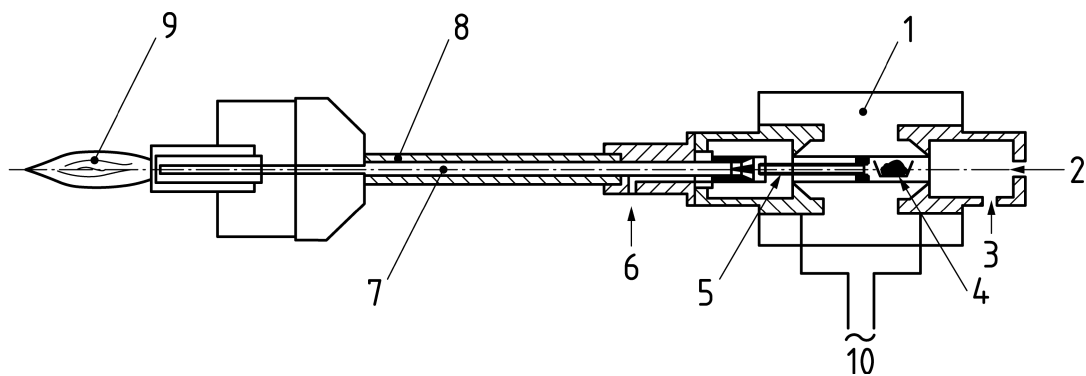
In a simultaneous emission spectrometer in, for example Paschen-Runge- or Echelle-configuration, the optical radiation is dispersed. The intensities of suited emission lines or background positions are registered with applicable detectors like photomultipliers (PMT), charge coupled devices (CCD), complementary 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 ₂ F ₂)	7	to the ICP-torch
4	shield gas (Ar)		

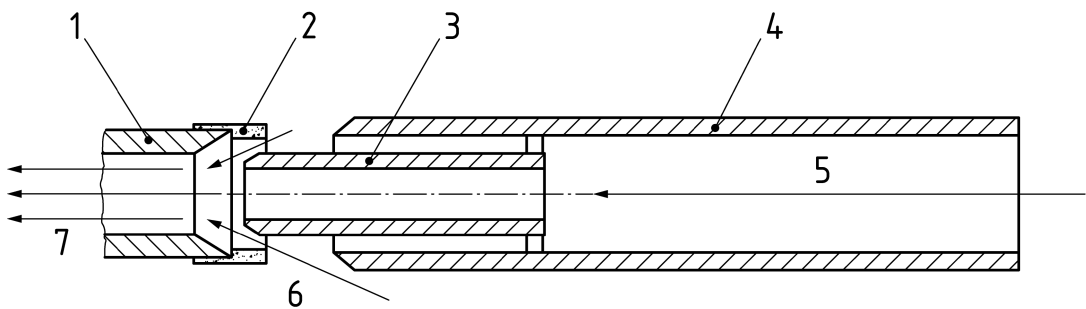
Figure 1 — Schematic representation of the ETV gas flows



Key

- | | | | |
|---|--|----|--|
| 1 | graphite tube furnace | 6 | bypass-gas (Ar) |
| 2 | pyrometer | 7 | dry aerosol to ICP-OES |
| 3 | carrier gas (Ar) + reaction gas (CCl ₂ F ₂) | 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 ₂ F ₂) 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 (Al_2O_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 (CCl_2F_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 CCl_2F_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 CCl_2F_2 is allowed for laboratory and analytical purposes. CCl_2F_2 is completely decomposed in the hot graphite furnace and in the downstream inductively coupled plasma. The use of CCl_2F_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 CCl_2F_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.